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**„Structural and elemental analysis of individual
nanocrystals embedded in an amorphous matrix by
transmission electron microscopy “**

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Zusammenfassung

Diese Arbeit untersucht Nanometer große Kristallite, eingebettet in einer amorphen Cobalt-Titan Legierung, mit verschiedenen Methoden der Transmissionselektronenmikroskopie (TEM). Im Zuge dessen wird auch ein Ablauf entwickelt, um chemische Daten aus Elektronenenergieverlustspektroskopie (EELS) ohne der Verwendung des EELS Software Paketes der Firma Gatan auszuwerten.

Das amorphe und nanokristalline Kompositmaterial entsteht in plastisch hoch verformten Proben einer Co_3Ti Legierung mit L1_2 langreichweitiger Ordnung. Die scheibenförmigen Proben haben einen Durchmesser von 8 mm und eine Dicke von circa 0.5 mm. Sie wurden in einer, dieser Arbeit vorausgehenden Behandlung, mittels Hochdruck-Torsion unter einem Druck von 4 GPa und durch 80 Umdrehungen eines Stempels verformt.

Im Rasterelektronenmikroskop weisen die Proben hoch verformte kristalline Bereiche und amorphe Bereiche mit gleicher chemischen Zusammensetzung auf. Eine TEM Untersuchung zeigt die homoge Verteilung von Nanokristalliten, mit Durchmessern von circa 5 nm bis 20 nm in den amorphen Probenbereichen. Die Nanokristallite haben eine näherungsweise runde Form und beanspruchen $\lesssim 3\%$ des Volumens der amorphen Bereiche. Für die Volumenanalyse wurden TEM Proben in Ebenen der HPT verformten Scheiben präpariert, welche senkrecht aufeinander stehen. Da die eingebetteten Nanokristallite sowohl in TEM Proben auftreten, die ausschließlich elektrolytisch gedünnt wurden, als auch in TEM Proben, die mechanisch poliert und anschließend ionengedünnt wurden, kann man ausschließen, dass sie Artefakte der Probenpräparation darstellen. Die Nanokristallite müssen während der extremen plastischen Verformung entstanden sein.

Ein Rastertransmissionselektronenmikroskop wird verwendet um mittels EELS die chemische Zusammensetzung der Nanokristallite und ihrer umgebenden amorphen Matrix entlang Line-Scans zu bestimmen. Die niederenergetischen Spektren der TEM Proben zeichnen sich durch breite Plasmon Peaks mit schwachen Maxima aus. Es wurde ein Vorgang entwickelt, um auch für Spektren mit stärkerem Hintergrundrauschen und breiten Plasmon Peaks, einen elastischen „zero-loss peak“ von dem restlichen Spektrum zu trennen. Die resultierenden „zero-loss peaks“, oder die resultierenden niederenergetischen Spektren werden verwendet, um die Dicke der TEM Probe zu bestimmen oder um den Effekt der Doppelstreuung in hochenergetischen Spektren abzuschätzen. Die amorphe Matrix umgibt die Nanokristallite auch in Richtung des einfallenden Elektronenstrahls. Ein Einfluss der amorphen Matrix, auf die erhaltene chemische Zusammensetzung an Line-Scan Positionen von Nanokristalliten, kann über die Probendicke abgeschätzt und korrigiert werden. Die Resultate der chemischen Auswertung deuten darauf hin, dass Nanokristallite in L1_2 langreichweitig geordneter Co_3Ti Phase, in der C36 Laves Phase $\text{Co}_{2.1}\text{Ti}_{0.9}$ und in der C15 Laves Phase Co_2Ti innerhalb amorpher Regionen durch polymorphe dynamische Kristallisation gebildet werden.

Hochauflösende Transmissionselektronenmikroskopie (HRTEM), unterstützt durch HRTEM Simulationen der drei diskutierten Phasen, kann das Auftreten aller drei Phasen in den betrachteten amorphen Bereichen bestätigen

Die EELS und HRTEM Untersuchungen von Randregionen der elektrolytisch gedünnten und anschließend ionengedünnten TEM Probe zeigen das Vorhandensein einer Co_3O_4 Oberflächenschicht. Diese Schicht ist ebenfalls nanostrukturiert über amorphen Probenbereichen vorhanden und führt in HRTEM Bildern von amorphen Bereichen zu einem Linienkontrast.

Abstract

In the presented work various methods of transmission electron microscopy (TEM) are used to study nanometer sized crystals that are embedded in an amorphous cobalt-titanium alloy. As a consequence a procedure is generated to analyze data from electron energy loss spectroscopy (EELS) without the EELS software package of the Gatan company.

The composite material of interest is present in severely plastically deformed samples of a $L1_2$ long range ordered Co_3Ti alloy. The samples of 8 mm in diameter and approximately 0.5 mm in height were deformed by high pressure torsion (HPT) using a pressure of 4 GPa and 80 rotations in a pre-treatment to the presented work.

Regions of severely deformed crystalline material and regions of amorphous material revealing both the same chemical composition are recognized by scanning electron microscopy. A TEM analysis shows that nanocrystals of about 5 nm to 20 nm in diameter are distributed homogeneously mainly inside band shaped amorphous regions. The shape of the nanocrystals is roughly spherical and they reveal a volume fraction of $\lesssim 3\%$. TEM specimens are prepared from 2 perpendicular planes in a HPT deformed sample to obtain these results. The embedded nanocrystals occur in TEM specimens that are prepared by electrolytic polishing or by mechanical polishing followed by ion milling. Thus, the nanocrystals are not artifacts of the TEM specimen preparation, but they are formed during the severe plastic deformation process.

The chemical composition of nanocrystals and surrounding amorphous matrix is studied by EELS line scans in a scanning transmission electron microscope. Broad plasmon peaks with weak maxima are present in electron low energy loss spectra. Here a procedure is developed to separate a zero-loss peak from the remaining electron low energy loss spectrum even for noisy spectra and broad plasmon peaks. The obtained zero-loss peaks and zero-loss peak separated electron low energy loss spectra are used to calculate the specimen thickness and to compensate the effect of plural inelastic scattering in electron high energy loss spectra. Nanocrystals are surrounded by the amorphous matrix also in the direction of the incident electron beam. Since the specimen thickness is known, the influence of the amorphous matrix on the derived chemical composition at line scan positions of embedded nanocrystals can be estimated and corrected. The resulting chemical compositions indicate that nanocrystals of $L1_2$ long range ordered Co_3Ti , of C36 Laves phase $\text{Co}_{2.1}\text{Ti}_{0.9}$ and of C15 Laves phase Co_2Ti are formed in the amorphous matrix by polymorphous dynamic crystallization.

The presence of these structural phases is confirmed by high resolution transmission electron microscopy (HRTEM) of the embedded nanocrystals. The HRTEM analysis is supported by HRTEM simulations for the three considered phases.

A study of the edge region between the specimen and the specimen hole by EELS and HRTEM reveals that a Co_3O_4 surface layer covers an electrolytically polished and ion milled TEM specimen. This layer is also nanostructured above amorphous regions and shows lattice fringe contrast in HRTEM images even at the amorphous matrix.

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I. Introduction

1. Deformation and structure

Plastic deformation of a crystalline material introduces lattice defects in the crystalline lattice of the material. An accumulation of defects rises the free enthalpy of the material. The accessible defect density is limited by dynamic recovery through a rearrangement and annihilation of dislocations, for instance.

Methods of severe plastic deformation (SPD) use geometric restrains to apply large shear strains at high amounts of hydrostatic pressure without fracturing the material. An application of SPD is the modulation of material properties by grain refinement. The hydrostatic pressure affects dislocation glide and climb and enables high defect densities. Then delayed dynamic recovery processes lead to a grain refinement resulting in very small grain sizes for bulk materials. Therefore, bulk materials of metals and alloys with ultra-fine grain structure or nanocrystalline structure can be realized by SPD. Studies of SPD applied on intermetallic compounds can be found in literature [1]. SPD can also lead to crystalline to amorphous solid-state transitions for specific compounds like reported in [2], [3] and [4], for instance.

High pressure torsion (HPT) is one method for severe plastic deformation [5]. This method places a sample of cylindric shape between two anvils. The anvils have cylindrical hollows themselves in which the sample fits in sharply. When the sample is then pressed between the anvils using a high pressure, the hollows act as a geometric restrain resulting in the hydrostatic nature of the applied pressure. The sample is strained by the rotation of one anvil which also rotates one surface disc of the sample at the applied pressure. Thus, torsional deformation of the sample can be obtained for an arbitrary strain.

Amorphous alloys are metastable materials revealing free enthalpies that are higher than the free enthalpies of their crystalline counterparts. Therefore, primary recrystallization can be triggered by overcoming the enthalpy barrier thermally due to heating or dynamically due to deformation of the amorphous alloy.

A cyclic crystalline-amorphous phase transformation is reported in literature for the cobalt-titanium alloy revealing 25 atomic % titanium when mechanically alloyed by ball milling [6]. The work presented here focuses on HPT deformed samples of this composition in the cobalt-titanium binary alloy system. The severe plastic deformation leads to a partially amorphization of the samples.

2. Motivation

Amorphous alloys reveal similar fracture strength and a high yield strength compared to their crystalline counterparts in general. But in contrast to the crystalline material they are brittle. Deformation mechanisms of amorphous alloys differ from crystalline alloys. Dislocations carrying deformation in crystalline materials can not form in amorphous alloys due to the lack of a structural long range order. Instead, strain is localized in shear bands with band width as small as 10 nm. An improvement of ductility can be obtained by a composite structure composed of nanocrystals embedded in the amorphous matrix since nanocrystals can act as obstacles for shear band propagation.

The structural study of separated nanocrystals embedded in an amorphous matrix is limited in conventional transmission electron microscopy (TEM). Selected area apertures are some magnitudes larger than the size of the nanocrystals. Thus, selected area diffraction pattern (SADP) can only be acquired from areas which reveal many embedded nanocrystals. The occurrence of multiple diffraction spots in SADP prevents the recognition of diffraction patterns for a single nanocrystal. Diffraction spots in selected area diffraction patterns are broadened due to the small size of the crystals and intensities at reciprocal distances corresponding to real space lattice spacings are dominated by the diffuse ring of the amorphous matrix.

Measurements of the chemical composition of embedded nanocrystals are also important but difficult to perform. A high spatial resolution is required to obtain chemical information of nanocrystals. In the present case small chemical variations between an amorphous matrix and embedded nanocrystals with diameters below approximately 20 nm must be resolved.

In this work chemical analysis by electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope is combined with a structural analysis by high resolution transmission electron microscopy (HRTEM) in a conventional TEM to identify the phases of nanocrystals that are embedded in an amorphous matrix. The structure of the nanocrystal including its composition can give an indication of the crystallization process forming the nanocrystals.

In the case of TEM, information of a specimen is obtained in projection on two spatial dimensions. An aim of this study is to separate the influence of an amorphous matrix on embedded nanocrystals for acquired chemical data by analyzing the specimen thickness and the shape and size of nanocrystals.

3. Phase structures in the cobalt-titanium system

A cobalt-titanium alloy is the material of interest for this work. The focus of the study is set at a composition range around 25 at.% titanium. In fig.I-3 three phases (purple area) near this composition are indicated in an equilibrium phase diagram: the intermetallic, $L1_2$ long range ordered phase Co_3Ti , the hexagonal C36 Laves phase $Co_{2.1}Ti_{0.9}$ and the cubic C15 Laves phase Co_2Ti .

- $L1_2$ long range ordered Co_3Ti has a maximum homogeneity range of about 19.5 at.% titanium to 24.5 at.% titanium in the equilibrium phase diagram of fig.I-1. The structure displayed in fig.I-3.a reveals an ABC stacking order of mixed atomic planes in an $[111]$ direction.

A detailed discussion on the structure of Laves phases can be found in Daniel Grüner's thesis [7]. The stacking of atomic planes in layer packages is specified by Frank and Kasper in [8]. Laves phases of the cobalt-titanium alloy can be characterized by the stacking of fundamental layer packages which combine four atomic layers: a triangular, or close packed net of titanium atoms followed by a Kagomé layer of cobalt atoms, a triangular net of titanium atoms again and a triangular net of cobalt atoms. These layers are displayed in fig.I-2. The triangular cobalt net has two possible stacking positions above the second triangular titanium net. The Kagomé layers and triangular titanium nets reveal together three different stacking positions relative to each layer package. This leads to a total number of six different fundamental layer packages denoted with A, B, C, A', B', C' . The Kagomé lattice itself is named after a Japanese woven bamboo pattern and was introduced by Ichirō Shōji [9].

- The C36 Laves phase $Co_{2.1}Ti_{0.9}$ has a maximum homogeneity range of about 28 at.% titanium to 31.5 at.% titanium (see fig.I-1). A symmetric unit cell is displayed in fig.I-3.d. $Co_{2.1}Ti_{0.9}$ has a hexagonal lattice system. The structure reveals an $ABA'C$ stacking order of the fundamental layer packages in $[001]$ direction.

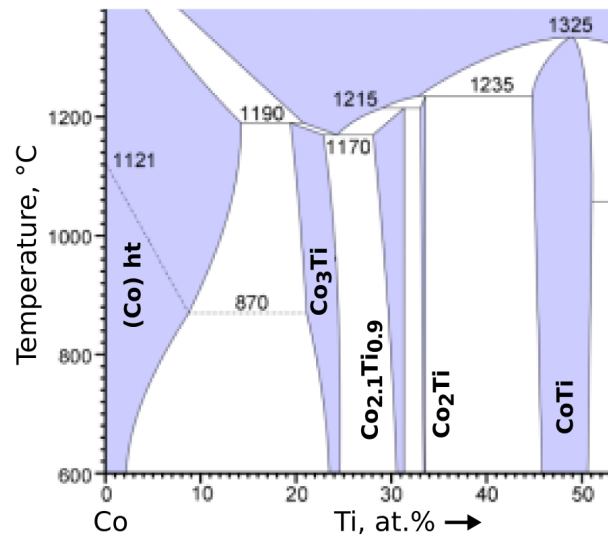


Figure I-1.: Detail of a cobalt-titanium binary alloy equilibrium phase diagram taken from literature [10]. The phases Co_3Ti , $Co_{2.1}Ti_{0.9}$ and Co_2Ti are indicated in the phase diagram.

The stacking position of the triangular cobalt net in the A' layer package is different to that of the A layer package. Thus, an exact ABAC stacking order of a double hexagonal close packed (dhcp) crystal structure is only valid for Kagomé layers and the triangular titanium nets in $\text{Co}_{2.1}\text{Ti}_{0.9}$.

- The C15 Laves phase Co_2Ti has a narrow homogeneity range of about 33 at.% titanium to 33.5 at.% titanium. Fig.I-3.b displays a symmetric unit cell. The structure reveals ABC stacking order of the fundamental layer packages in $\langle 111 \rangle$ directions. Co_2Ti has a face centered cubic (fcc) Bravais lattices. Lattice plane distances and stacking order are equivalent for fundamental layer packages and Kagomé layers in Co_2Ti .

Lattice parameters and atomic positions are given in tab.II-4 of section II-4 for the three phases discussed above.

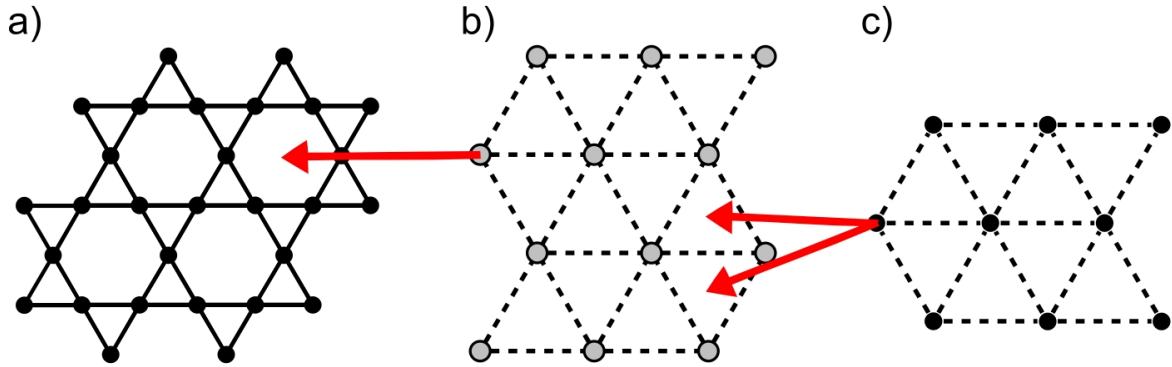


Figure I-2.: Sketches of the Kagomé layer of cobalt atoms (a), one of the two equal triangular titanium nets (b) and the triangular cobalt net (c) which form the fundamental layer package in the considered Laves phases. Red arrows indicate the relative stacking positions of the layers. Two different stacking positions are possible for (c). The image is taken from literature [7].

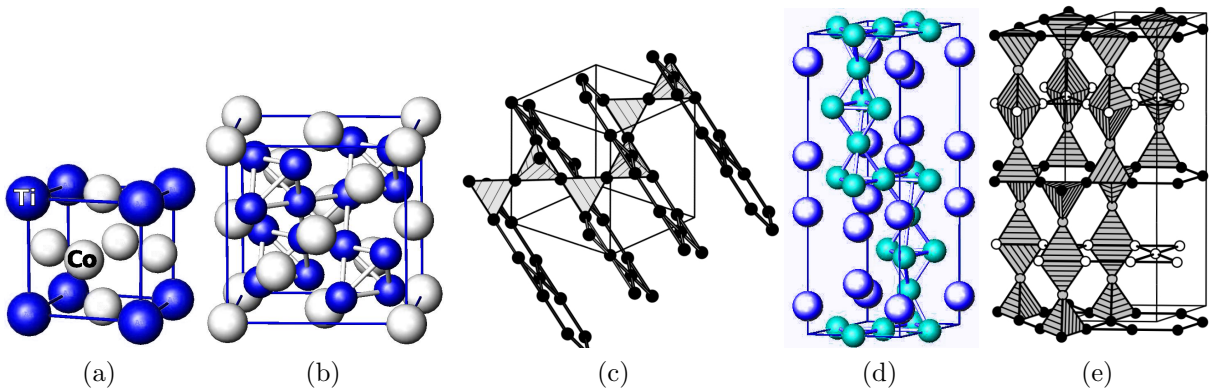


Figure I-3.: Unit cells of phase structures in the binary alloy Co-Ti system. The images for Co_3Ti (a), Co_2Ti (b) and $\text{Co}_{2.1}\text{Ti}_{0.9}$ (d) shown here are released at the homepage of OHAB's Laboratory [11]. Titanium atoms are colored in blue. The Kagomé layers and stacking positions of triangular nets of cobalt atoms are indicated in (c) for Co_2Ti and in (e) for $\text{Co}_{2.1}\text{Ti}_{0.9}$. Images (c) and (e) are taken from literature [7].

II. Methods

1. Characterization of the initial material

This section is devoted to introduce the material of interest and the preceding treatments and analyses on the material that led to the study presented here.

The studied Co-Ti alloy was bought from the company Hauner metallische Werkstoffe in form of a 50 mm long rod with a diameter of 8 mm and a nominal composition of 23 at.% titanium and 77 at.% cobalt. The alloy is made from 99.99 % pure cobalt and 99.995 % pure titanium by vacuum arc melting. Disc shaped samples of 8 mm in diameter are cut from the rod by spark erosion machining.

The as-bought material reveals two areas of different titanium to cobalt atomic concentration ratios. They are recognized by energy dispersive X-ray (EDX) measurements in the scanning electron microscope (SEM). Areas exhibiting about 21 at.% titanium and areas exhibiting about 28 at.% titanium are shown in fig.II–1. An average value of about 24.3 at.% titanium is measured at a larger area of $400 \times 300 \mu\text{m}^2$. The presence of the element oxygen is neglected for these measurements at the sample.

To homogenize the material a pre-annealing of the disc shaped samples is done at 950°C for 120 hours. After this treatment just a single L1_2 long range ordered Co_3Ti phase can be found in the material as confirmed by SEM and transmission electron microscope (TEM) analyses. A final sample thickness of $0.54 \text{ mm} \pm 0.02 \text{ mm}$ (depending on the considered sample) is obtained by mechanically wet polishing of the sample discs.

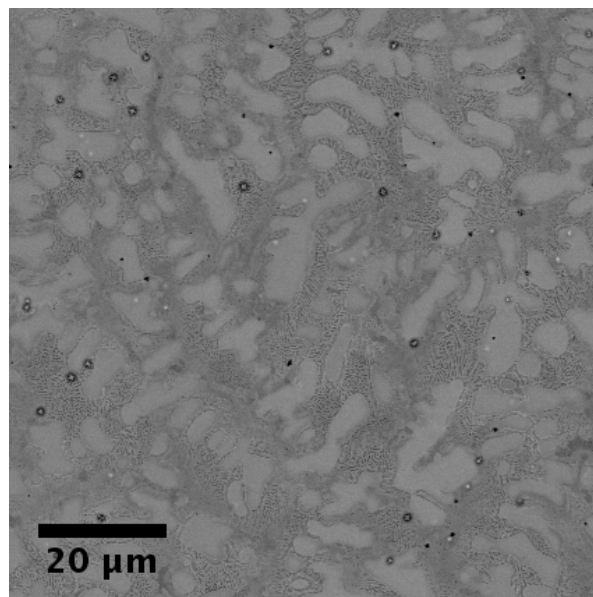


Figure II–1.: SEM image of the as-bought material using the backscattered electron (BSE) detector and a high tension of 20 kV. Bright areas reveal about 28 at.% Ti and dark areas reveal about 21 at.% Ti as measured by EDX.

II. Methods

The samples are deformed by the severe plastic deformation method of high pressure torsion. At a HPT deformation the sample is put between two anvils made from hardened steel. A high pressure is applied and one anvil is rotated. The anvils themselves have cylindric shaped dents in whom the sample fits in sharply. The dents for sample Co₃Ti-I are 0.12 mm in depth for instance. Thus, the edge of the sample is constrained and a hydrostatic pressure is established. The sample surfaces are sandblasted to have a good mechanical contact to the anvils. When one anvil rotates, the corresponding sample surface attached to the anvil rotates as well leading to a torsion of the sample. The constraints on the sample and the high pressure allow high degrees of deformation.

- Sample Co₃Ti-I was HPT deformed using a pressure of 4 GPa and 80 turns of one anvil on 8.2.2012. The sample was 0.35 mm thick after HPT deformation. The severe plastic deformation corresponds to a maximum shear strain of about 550000 % in magnitude at the outer edge of the sample. The value is rounded roughly using the as-deformed sample height. A fast enough decrease of the sample height with the number of rotations of one anvil can be assumed by comparing the as-deformed sample heights of different revolution counts. 20 rotations and 80 rotations of one anvil lead to a similar final thickness of samples for a similar sample thickness before deformation. Just one revolution also led to a thickness reduction of already about 17 % for one sample although this result could not be reproduced by a second sample. Therefore, it is reasonable to use the as-deformed thickness for estimating the maximum shear strain. The sample Co₃Ti-I is cut in three parts like shown in fig.II-2. One cut edge was mechanically polished and used as a cross section for SEM imaging.
- Sample Co₃Ti-J was HPT deformed using a pressure of 8 GPa and 20 turns of one anvil on 20.11.2012. The sample was also 0.35 mm thick after HPT deformation. The severe plastic deformation corresponds to a maximum shear strain of about 150000 % in magnitude at the outer edge of the sample.

In the as-deformed samples two different areas can be recognized in SEM images using the BSE detector. An EDX analysis in the SEM shows that the chemical composition does not change between the two areas. Measurements at 8 different positions on a cross section of the HPT deformed disc of sample Co₃Ti-J give a mean value for the chemical composition of 24.08 at.% titanium at a standard deviation (SD) of 0.12 at.%. This result is in good agreement with the measured average value of 24.3 at.% titanium for the as-bought material.

A TEM analysis reveals that the two regions correspond to an amorphous region and to a highly deformed but still crystalline region. In the amorphous regions nanocrystals are embedded homogeneously. Their sizes range from about 5 nm to 20 nm in diameter and their volume fraction is under 2% in the amorphous regions. The disc shaped TEM specimens that are analyzed to obtain these results are punched from the HPT deformed sample discs by spark erosion machining. Thus, the results only consider specimen planes that are parallel to the surface of the HPT deformed disc and therefore also parallel to the sample planes that are sheared by the torsion deformation.

2. TEM specimen preparation

TEM specimens are prepared from sample Co_3Ti_1 . The initial form of the sample Co_3Ti_1 used for TEM preparation is given as slightly more than about a quarter of a disc deformed by high pressure torsion (HPT). The disc has a diameter of 8 mm and a thickness of 0.35 mm in the as-deformed state. Fig.II-2 shows a sketch of the sample. SEM images of a cross section of the disc shaped sample Co_3Ti_1 reveal that larger amorphous regions are concentrated on one half of the sample, from one surface area to its center circle like shown in fig.III-1. This surface is named the amorphous surface and the opposite surface is named the crystalline surface.

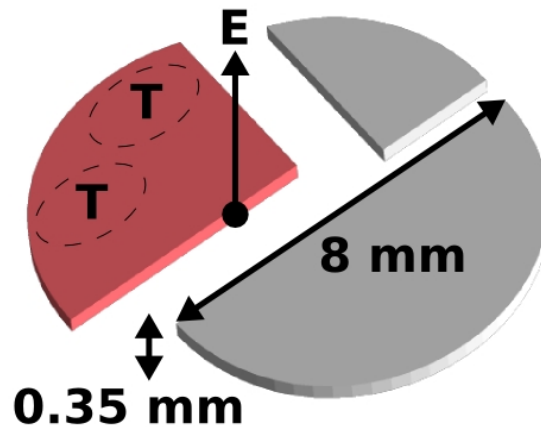


Figure II-2.: Sketch of the HPT deformed disc of sample Co_3Ti_1 . The sample part considered in this study is marked in red. (E) indicates the mechanical polished sample edge used as cross section for SEM imaging. The letters (T) mark roughly the TEM specimen positions, punched out of the sample.

2.1. Spark erosion

An advantage of spark erosion punching and cutting is the reduced injection of defects in the material during processing when compared to mechanical punching and cutting especially for ductile materials. A flowing dielectric provides a fast heat exchange and for thermal conductive metals the material is only melted local.

The spark erosion machine Charmilles Isopulse Type P25 is used to punch two TEM specimen from sample Co_3Ti_1 on 25.11.2013. Petroleum is used as a dielectric and the punch devices are made of copper. The sample is glued on a holder using a conductive glue composed of UHU-Alleskleber mixed with silver. The glue is dissolved by putting the sample in acetone after punching. The punch tube is flushed with the dielectric during processing to keep the eroded surface clean. The parameters of the spark erosion machine are adjusted in a way so that a fine punch surface is produced. The "Microfin" modulation of the current is used for punching and the parameters "A2" and "B8" are set to control the feedback of the punching head. The feed rate is set to about a third of the maximum feed rate. No additional capacitors are activated. They would increase the current used for spark erosion punching.

To be able to distinguish between the amorphous surface and the crystalline surface a marking is punched on the crystalline surface of the sample Co_3Ti_1 . Then the amorphous

surface was wet polished using abrasive paper of silicon carbide with a final graining of 600 to obtain a smooth surface. In the next step two discs of 2.3 mm diameter respectively are punched from sample Co₃Ti.I with a copper tube. The punching areas are chosen to border the outer edge (the circumference) of the sample Co₃Ti.I. In sample Co₃Ti.I the amorphous regions are increasing in radial direction towards the disc diameter according to the SEM analysis of the cross section.

2.2. Mechanical polishing

The two 2.3 mm discs are glued with their amorphous surface on a polishing specimen holder. UHU-Alleskleber and acetone are used again to glue or to dissolve the glue. The discs are mainly polished on the crystalline surfaces to preserve amorphous regions in the specimens. They are wet polished to 0.16 mm thickness using an abrasive paper of silicon carbide with a final graining of 800. Then the amorphous surfaces are polished with the 800 graining again so that a final thickness of $0.150 \text{ mm} \pm 0.005 \text{ mm}$ is obtained for both discs. The thickness is measured by a micrometer screw with 0.01 mm markings.

The two specimen are named Co₃Ti.I3 and Co₃Ti.I4. To summarize: they are 2.3 mm in diameter and yield a thickness of 0.15 mm.

2.3. Electrolytic polishing

The method of electrolytic polishing is chosen to thin the two TEM specimens to electron transparency. Height differences at the specimen surface are removed at good electrolytic polishing conditions. For the basic process the specimen is deployed as anode and immersed in an acidic electrolyte between cathodes. Then a voltage is applied. During the polishing process atoms at the metal's surface are oxidized by the acidic electrolyte, dissolved from the surface and led away by convection due to the applied voltage. The balancing of height differences at the specimen surface and the polishing effect are connected to the formation of a polishing layer at the specimen surface. The occurrence of the polishing layer can be observed by a plateau in the electric current - voltage curve of the polishing process. Especially the higher voltage end of the plateau should correspond to good polishing conditions.

The two specimen are thinned by electrolytic polishing with a Struers Tenupol 3. In this device the disc shaped specimen is put between two holder parts that have a hole at the center of the disc respectively. An electrical contact to one specimen surface is established by a platinum circular ring on one holder part. The electrolyte is flushed in jets to the center of both specimen surfaces by a pump and the flow rate can be controlled by the device. Different nozzle sizes are available for the holder parts. Here nozzles with 1 mm in diameter are selected. The electrolyte is cooled by cooling coils inside the reservoir for the electrolyte. A cooling liquid flows through the coils. It is cooled by an independent cooling unit. The cooling liquid used becomes viscose at about -30 °C. The temperature of the electrolyte is measured inside the thermal insulated reservoir of the polishing device. That temperature measurement is connected to the cooling unit and thus a target temperature can be set. This temperature is called external temperature whereas the temperature of the cooling liquid inside the cooling unit's reservoir is called the internal temperature. The influence of the external and internal temperature on the targeted temperature can be adjusted. Two voltage ranges can be selected for polishing. One voltage range provides a maximum voltage of 40 V and a maximum electric current of 5 A. The other voltage range provides a maximum voltage of 120 V at a maximum electric current of 1.6 A. The polishing voltage is set by the voltage adjustment knob. When the polishing process is

started the voltage is applied and the electrolyte is pumped to the specimen surfaces. The polishing stops after a time set or after hole formation ideally at the specimen center. The latter is facilitated by the light sensor of the Struers Tenupol 3 electrolytic polisher. The sensitivity of the sensor can also be adjusted by the "photo sensitivity" parameter.

During the electrolytic polishing the voltage is measured by a multimeter between the current connection spring at the holder (anode) and a cable that sets the potential of the cathodes. A target value of 5 V is set by turning the voltage adjustment knob. It should be noted that the voltage fluctuates during at least the first 10 seconds of polishing and that it increases slightly during the measurement. An error of the measurement of about 0.1 V has to be assumed. The measured 5 V at the multimeter corresponds well to a value of about 5 V at the voltage adjustment knob. The polishing time is measured by a clock in units of 1 seconds.

After the electrolytic polishing process stops the specimen has to be quickly cleaned from the remaining electrolyte to avoid any etching of the polished surfaces specially near the formed hole. The cleaning of the specimen is done in 4 steps and the specimen should be handled fast from one step to another:

- The complete specimen holder is dipped in a first vessel filled with methanol.
- The second vessel is also filled with methanol and a net is put on the ground inside the vessel. The specimen holder is opened inside the second vessel and disjoint into the two parts so that the specimen sinks inside the methanol on the net.
- The specimen is transported on the net to the third vessel filled with methanol. There the net is turned inside the methanol so that the specimen sinks to the vessel's ground.
- The fourth vessel is filled with pure methanol. The specimen is transported with tweezers from the third to the fourth vessel. It should be immersed into the pure methanol at an higher angle between the liquid surface and the disc surface. Immersing under a low angle and at higher velocities could lead to damage at very thin (electron transparent) regions around the specimen hole.

The electrolyte is composed of 2/3 pure methanol and 1/3 nitric acid. A target temperature of -25 °C is set at the cooling unit based to 90 % on the external temperature. The photo sensitivity and the polishing time is set to their maxima. The flow rate is set to 4.5, the ampere range to 0.5 A and the voltage to 5 V. The ampere range parameter selects the sensitive ampere range for the electrical current display of the polishing device. A electrical current of about 50 mA is measured during the polishing process by the Struers Tenupol 3 electrolytic polisher.

- Specimen Co₃Ti.I3 was electrolytically polished for 2 minutes and 32 seconds. Then the specimen was thinned to hole formation and the light sensor responded. The target voltage of 5 V $\pm$ 0.1 V measured at the multimeter could be maintained during most of the polishing process.
- Specimen Co₃Ti.I4 was electrolytically polished for 2 minutes and 49 seconds. The specimen was thinned to hole formation. The target voltage of 5 V $\pm$ 0.1 V could be maintained during most of the polishing process.

2.4. Ion milling

During ion milling atoms at the specimen surface are sputtered under vacuum by ions of an inert gas that are accelerated by the ion gun of the milling device in form of a wide beam. This process can be viewed as atomic scaled sandblasting. Ion milling could be used for thinning to electron transparency. It is a thinning method for conventional (not prepared by a focused ion beam) cross section specimens. Ion milling can also be used for polishing and cleaning specimen surfaces. A comparison of a TEM specimen edge before and after ion milling is given in fig.II-3. Note that the comparison is made for a bulk metallic glass specimen. This specimen is prepared by the same punching, grinding and electrolytic polishing method as for the specimens studied in this work.

The electrolytically polished specimen Co3Ti.I3 is ion milled for cleaning the electron transparent regions that are located around the specimen hole and for a further thinning of the specimen. The specimen is milled by the Precision Ion Polishing System (PIPS) II from the Gatan company on 10.3.2014. Argon ions are used for the milling process. The specimen is mounted on a clamp holder and rotates during the milling process. The PIPS II ion mill has two ion sources. Here the upper and lower surface of the specimen are milled at the same time. A cooling of the specimen during the milling process was omitted. The milling parameters are listed in tab.II-1.

2.5. Cross-sectional TEM specimen

After spark erosion punching of the two TEM specimen Co3Ti.I3 and Co3Ti.I4 a cross-sectional TEM specimen is prepared from the remaining sample part that is considered in this study (see fig.II-2) by Andreas Berger, the technician at the Physics of Nanostructured Materials research group at the University of Vienna. A stripe is cut from the remaining sample part by spark erosion cutting. The stripe is thinned and polished by mechanically wet grinding and wet polishing on one surface that is perpendicular to the surface of the original HPT deformed disc. Final wet polishing of one surface is done by mechanically wet polishing using abrasive paper of diamond with grain sizes down to 0.1 μm . The obtained platelet is glued at its polished surface on a disc shaped molybdenum aperture which has a hole in its center using an epoxy resin adhesive. Now the second surface of the platelet can be mechanically wet polished. Thin areas are obtained by wedge polishing. Final thinning to electron transparency is then accomplished by ion milling. The TEM specimen is named Co3Ti_cross.

acceleration voltage	milling angle	sector angle	modulation	radian frequency	milling time
0.5 kV	4 degree	60 degree	DM	0.6 RPM	2 minutes
0.5 kV	4 degree	60 degree	DM	0.6 RPM	5 minutes
0.2 kV	7 degree	60 degree	DM	0.6 RPM	5 minutes

Table II-1.: Ion milling steps for specimen Co3Ti.I3. In dual modulation (DM) the specimen is milled at opposite directions after every half turn of the specimen. The sector angle represents the sample rotation angle for which the ion beam stays activated during a single milling process. The milling angle is the angle between the ion beam and the specimen surface. The radian frequency of the specimen is given in rotations per minute (RPM).

3. Electron microscopy

3.1. SEM imaging

A mechanical polished cross section prepared from the HPT deformed sample Co3Ti.I is studied by SEM on 20.11.2013. The Zeiss Supra 55 VP SEM of the Faculty Center for Nano Structure Research at the University of Vienna is used for the study. A conductive tape is used to mount the sample on a holder. The microscope is operated at a high tension of 20 kV. Images are acquired with the BSE detector at a working distance of 8.7 mm and a magnification of 106 x. The whole cross section is imaged by recording images with slightly overlapping fields of view.

3.2. TEM imaging

The prepared TEM specimen are studied first at a PHILIPS CM200 to get an overall view of their structural features. The electron microscope is operated at a high tension of 200 kV. Bright field images of specimen areas of interest are acquired. After electrolytic polishing the TEM specimen Co3Ti.I3 and Co3Ti.I4 are studied in a TEM session on 3.12.2013. The specimen Co3Ti_cross is studied in a TEM session on 24.4.2014.

3.3. HRTEM imaging of nanocrystals at a PHILIPS CM30 ST electron microscope

The specimen Co3Ti.I3 is used for imaging. Unbounded impurities are removed from the specimen surfaces by plasma-cleaning. For this the TEM holder including the specimen is inserted in the plasma-cleaner on 1.10.2015. The specimen was cleaned twice for about 1.5 minutes, respectively.

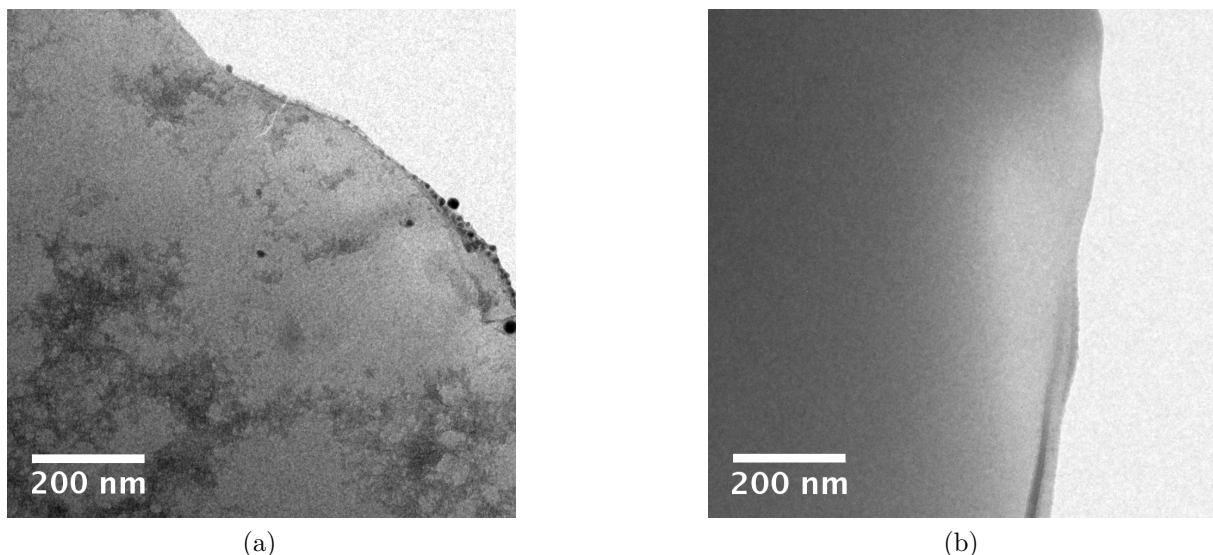


Figure II-3.: TEM bright field images of a bulk metallic glass specimen before (a) and after (b) ion milling. The specimen was thinned by electrolytic polishing until hole formation. In image (a) the remains of a polishing layer on the specimen surface can be recognized as well as particles along the edge of the specimen. These preparation artifacts are not visible anymore after ion milling like shown in image (b).

The PHILIPS CM30 ST has a point resolution of 2 Å. Images were acquired in two sessions, on 8.10.2015 and on 5.11.2015. The high tensions used were 280 kV on 8.10.2015 and 295 kV on 5.11.2015. A sketch of the specimen hole is given in fig.II-4. The selected large and thin amorphous area in the specimen is marked in the figure. Because of the small size of the nanocrystals it is not possible to obtain a selected area diffraction pattern of a single nanocrystal at the PHILIPS CM30 ST. Thus also no Kikuchi pattern could be observed which would allow to tilt the electron beam till the nanocrystal is in a good orientation for HRTEM. So the selected amorphous area is searched for nanocrystals having a strong dark contrast compared to the contrast of the amorphous phase on the fluorescence screen in bright field mode at a relative high magnification. Therefore, the specimen itself is shifted by moving the specimen holder. If a nanocrystal reveals a dark contrast in bright field mode, the intensity is focused in the diffracted beams. Then it is possible that the nanocrystal has an orientation near a pole where some lattice planes are in projection. That would be a suitable orientation for HRTEM imaging. After selecting a suitable nanocrystal the objective lens is taken out for HRTEM imaging. The defocus value is adjusted by projecting the image on a TV camera. A fine adjustment of the position of the nanocrystal in the image is done by an image shift. The images are then acquired with a CCD camera at indicated magnifications of 390 kx to 450 kx.

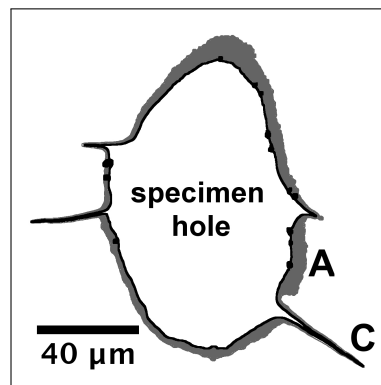


Figure II-4.: Overview of the specimen hole for specimen Co₃Ti-I3. Thin areas are marked in gray and a large amorphous area is indicated with A. At position C a thin area is located at the end of the crack that is visible in the figure.

3.4. STEM and EELS of nanocrystals at the Austrian Scanning Transmission Electron Microscope

The Austrian Scanning Transmission Electron Microscope (ASTEM) is located at the Austrian Centre for Electron Microscopy and Nanoanalysis in Graz (FELMI-ZFE). It is a Cs probe corrected FEI Titan³ G2 60-300 electron microscope featuring an energy dispersive X-ray spectrometer and a post-column electron energy filter capable of "Dual EELS" [12]. This means that electron high- and low energy loss spectra can be acquired simultaneously. The ASTEM was operated by a staff member of the FELMI-ZFE.

The specimens Co₃Ti-I4 was studied at the ASTEM on 28.01.2014 and Co₃Ti-I3 was studied on 11.03.2014. Before the specimen holder including the specimen was inserted in the electron microscope unbounded impurities were removed from the specimen surfaces by plasma cleaning. High angle annular dark field (HAADF) images and annular dark field (ADF) images were acquired simultaneously in STEM mode at an acceleration voltage

of 300 kV. The incident magnification for imaging nanocrystals was set in an range of 450 kx to 1300 kx at a probe size of 1 nm and a probe current of 1 nA.

ADF images reveal a diffraction contrast. On the contrary, electrons scattered at high angles are scattered incoherently by Rutherford scattering. The intensity measured by a HAADF detector (angles > 50 mrad) is proportional to $t Z^\alpha$, where t is the specimen thickness, Z the atomic number of the atom the electron was scattered at and $\alpha \lesssim 2$. The contrast revealed by HAADF images is therefore called a Z contrast.

Initially EDX measurements were acquired for the specimen Co3Ti.I4, but the measurements appeared to be insensitive to a possible change in the chemical composition of the nanocrystals. EDX yields a higher signal to noise ratio for thicker specimen regions. However, at thicker areas the elemental contingent of the amorphous phase dominates over that of the embedded nanocrystals. The nanocrystals themselves reveal a weaker contrast to the amorphous phase in the images due to the absorbed intensity and thus they are harder to recognize. Therefore, EELS measurements of the nanocrystal and the surrounding amorphous phase are acquired in the form of line scans. Contrary to EDX, EELS measurements are more sensitive for thinner specimen regions because the information is gathered from transmitted electrons instead from emitted x-ray radiation due to excited states in the specimen. A nanocrystal of interest is selected in the HAADF and ADF images. Then a line scans is set across the nanocrystal. Both ends of the scan line are continued into the amorphous phase surrounding the nanocrystal. The line scans cover a distance of about 20 nm to 50 nm. The parameters of the line scans are displayed in tab.II-2 for the two specimen. For specimen Co3Ti.I4 only electron energy low loss spectra are acquired. EELS line scans that are acquired at specimen Co3Ti.I3 are labeled alphabetically whereas line scans acquired at specimen Co3Ti.I4 are labeled in Roman numerals. Line scans A to D and line scans I to VIII are acquired across nanocrystals and their surrounding amorphous phase.

Two parameters that should be considered in EELS are the convergence semi-angle α of the focused incident electron beam and the EELS collection semi-angle β . The semi-angle β is defined by the position and the size of the EELS entrance aperture and limits the angle range of the inelastic electrons that can enter the spectrometer. Both values are given in tab.II-3.

specimen & spectrum type	set acquisition time per spectrum [s] & scan speeds $\left[\frac{\text{nm}}{\text{s}}\right]$	approx. spacial distance per spectrum $\left[\frac{\text{eV}}{\text{pixel}}\right]$	energy loss per pixel $\left[\frac{\text{eV}}{\text{pixel}}\right]$	approx. energy loss range [eV]
Co3Ti.I4 high loss	4 0.14 - 0.22	0.58 - 0.93	0.5	400 - 1400
Co3Ti.I3 high loss	5 - 3 0.13 - 0.52	0.71 - 1.81	0.25	370 - 880
Co3Ti.I3 low loss	5 - 3 0.13 - 0.52	0.71 - 1.81	0.25	-50 - 460

Table II-2.: EELS line scan parameters of the studies of specimen Co3Ti.I4 and Co3Ti.I3 at ASTEM. The given values represent the value range of all line scans across nanocrystallites for the considered specimen. Note that the time between the acquisition of two spectra is (slightly) longer than the acquisition time of one spectrum. This fact has been considered for the given scan speed values.

acceleration voltage	convergence semi-angle α	collection semi-angle β
300 kV	20 mrad	20.5 mrad

Table II-3.: Parameters of the electron beam.

4. Simulations of HRTEM images

To emphasize the importance of simulated HRTEM images one should be mindful to the imaging theory of HRTEM for an aberration uncorrected electron microscope. HRTEM images are phase contrast images. The atomic potential in a specimen can be imaged due to the influence of the imaging system on the electrons represented by wave functions. Thus, the patterns seen in the obtained images depend on the parameters of the imaging system. It is not straightforward to identify these patterns as the atomic lattice of the specimen. The influence of the imaging system can be described by the phase contrast transfer function where the defocus is a crucial parameter for instance. So the patterns seen in HRTEM images can also vary strongly with the defocus value. The Scherzer defocus is an optimized defocus value depending on the spherical aberration C_s and the applied high tension at the transmission electron microscope. In the weak phase approximation the observed patterns should reflect the atomic lattice at the Scherzer defocus.

By comparing the observed patterns in acquired HRTEM images with calculated patterns of an assumed crystal structure and crystal orientation this assumed structure and orientation can be approved.

HRTEM images are simulated in the software JEMS [13] for the $L1_2$ long range ordered Co_3Ti structure, and the two Laves phases Co_2Ti and $\text{Co}_{2.1}\text{Ti}_{0.9}$. The calculation is based on the Bloch wave method. Bloch waves are wave functions of the form $u(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}$ with a periodic Bloch function $u(\mathbf{r})$. They solve the time-independent Schrödinger equation for a periodic potential and thus yield a basis for the electron wave functions in a crystal.

4.1. Crystal parameters

The crystal structure data for the three considered phases is obtained from the Inorganic Material Database (AtomWork) [14], [15]. The data is based on the lattice parameters derived in [16], [17] and [18]. A lattice is defined by its space group, the atoms coordinates in the unit cell, the chemical element of the atoms and the occupation probability of the atom for the considered coordinates. The lattice positions that have to be defined in the unit cell are given by Wyckoff positions which make use of the symmetry operations allowed for the considered space group. In tab.II-4 the crystal structure data is shown. The atoms are assumed to have a neutral charge. The atomic form factors used for the calculations are taken from literature values published by L. Peng [19], [20].

4.2. Crystal orientations

The same crystal orientations are considered for the simulations as the orientations seen in the HRTEM images obtained at the FEI Titan electron microscope that are discussed in section III-4. Co_3Ti and Co_2Ti crystals are oriented in $[110]$ and $[112]$ zone axis directions and $\text{Co}_{2.1}\text{Ti}_{0.9}$ is oriented in $[100]$ and $[120]$ zone axis directions in the simulations. Also

slight deviations from the zone axes are tested in the simulations. In section II-4.2 fig.III-21 shows simulated HRTEM images of Co_2Ti in $[112]$ orientation with slight deviations along the $(2-20)$ and $(-1-11)$ plane for instance. (The deviations are selected in a simulated zone axis diffraction pattern in JEMS.)

In addition HRTEM maps for a $[100]$ orientation of Co_3Ti and Co_2Ti and a $[001]$ orientation of $\text{Co}_{2.1}\text{Ti}_{0.9}$ are calculated.

structure				structure type		space group	
Co_3Ti				Cu_3Au		Pm-3m	
lattice parameters:				$a = b = c = 0.3628 \text{ nm}$		$\alpha = \beta = \gamma = 90 \text{ degree}$	
element	coordinates			Wyckoff letter	multi-plicity	site symmetry	occupancy
	x	y	z				
Co	0	1/2	1/2	c	3	4/mm.m	1.0
Ti	0	0	0	a	1	m-3m	1.0

structure				structure type		space group	
Co_2Ti				MgCu_2		Fd-3m	
lattice parameters:				$a = b = c = 0.669 \text{ nm}$		$\alpha = \beta = \gamma = 90 \text{ degree}$	
element	coordinates			Wyckoff letter	multi-plicity	site symmetry	occupancy
	x	y	z				
Co	0	0	0	c	16	.-3m	1.0
Ti	3/8	3/8	3/8	b	8	-43m	1.0

structure				structure type		space group	
$\text{Co}_{2.1}\text{Ti}_{0.9}$				MgNi_2		$\text{P6}_3/\text{mmc}$	
lattice parameters:				$a = b = 0.4732 \text{ nm}$		$\alpha = \beta = 90 \text{ degree}$	
				$c = 1.5427 \text{ nm}$		$\gamma = 120 \text{ degree}$	
element	coordinates			Wyckoff letter	multi-plicity	site symmetry	occupancy
	x	y	z				
Co	0.16429	0.32858	1/4	h	6	mm2	1.0
Co	1/2	0	0	g	6	.2/m.	1.0
Co	1/3	2/3	0.12514	f	4	3m.	1.0
Ti	1/3	2/3	0.65583	f	4	3m.	0.9
Co	1/3	2/3	0.65583	f	4	3m.	0.1
Ti	0	0	0.09400	e	4	3m.	0.9
Co	0	0	0.09400	e	4	3m.	0.1

Table II-4.: Crystal structure data for L_{12} long range ordered Co_3Ti , the C15 Laves phases Co_2Ti and the C36 Laves phase $\text{Co}_{2.1}\text{Ti}_{0.9}$ obtained from AtomWork [14], [15]. The lattice parameters are taken from literature [16], [17] and [18]. The atom coordinates are given in units of lattice vectors. A cubic unit cell is considered for Co_3Ti and Co_2Ti . $\text{Co}_{2.1}\text{Ti}_{0.9}$ yields a hexagonal unit cell with long axis c . The Wyckoff letters define the the Wyckoff positions for the given space group. The corresponding multiplicity (number of points of the same Wyckoff position in an unit cell) and site symmetry (point symmetry for the specific position) are listed.

4.3. Electron microscope parameters

The predefined parameters for a CM30 ST electron microscope are used as template for a non-aberration corrected FEI Titan electron microscope. The spherical aberration C_s is set to $C_s = 1.2$ mm and the chromatic aberration C_c is set to $C_c = 1.2$ mm. A maximum acceleration voltage of 300 kV is chosen.

4.4. HRTEM maps

The envelope model is chosen as an illumination model for the HRTEM image simulation. In the envelope model a damping of the phase contrast transfer function is applied for high spatial frequencies.

The number of Bloch waves used in the calculation is related to the number of reflections that are assumed to contribute to the image. About 40 reflections and 20 strong reflections are used for the calculations. The exact number of reflections that can be set depends on the crystalline structure and orientation.

HRTEM maps can be calculated consisting of individual images with different defocus and specimen thickness values. The specimen thickness value is set in multiples of unit cells for a given structure. One image in a HRTEM map can show several unit cells in horizontal and vertical direction. Initial HRTEM maps of the three considered phases are acquired using a large defocus step between the specific images of a map to see which defocus region yield a reasonable pattern in the images. Then a finer defocus step between 1 and 5 nm is used.

4.4.1. Defocus and specimen thickness values

For simulating Co_3Ti in $[110]$ orientation a defocus start value of -128 nm is chosen at a specimen thickness of 12.8 nm. The defocus start value for the $[112]$ orientation is -130 nm. 10 image with varying defocus values are obtained for the two HRTEM maps respectively.

The simulation for Co_2Ti in $[110]$ orientation is realized for defocus values between -70 nm and -61 nm using a defocus step of 1 nm at a specimen thickness of 15.5 nm. Defocus values of -115 nm to -107 nm are used for HRTEM maps in $[112]$ orientation at a defocus step of 2 nm between the images. 36 reflections are selected for the calculation.

$\text{Co}_{2.1}\text{Ti}_{0.9}$ HRTEM maps are simulated in $[100]$ orientation varying the defocus from -130 nm to -60 nm in 5 nm steps at a specimen thickness of 17.5 nm. For this hexagonal C36 Laves phase and orientation there are some reflections close to the $[010]$ reflection and parallel to the $[001]$ direction. This leads to a higher number of reflections at the same reciprocal area compared to the other two phases. Thus, a higher number of 46 reflections are used for the calculations. The $[120]$ orientation is also realized at defocus values from -130 nm to -60 nm applying 5 nm steps in between the individual images. Here 44 reflections are used for the calculation.

5. Calculation of chemical composition by EELS

This section gives an introduction to the deduction of chemical data from electron high energy loss spectra and is primary based on Williams Carter's book Transmission Electron Microscopy [21]. In EELS the high energy loss spectrum starts at about 50-100 eV energy loss [21], [22]. An incident electron of the electron beam can ionize a core shell electron of an atom in the sample provided that at least the ionization energy is transferred. This leads to core loss edges in the high energy loss spectrum which can be assigned to the specific K, L, M, etc., shells of an element by the energy loss value and shape of the edge.

The energy loss integrated core loss intensity I_k is a measure for the current of the beam electrons that scatter inelastically with the electrons of the considered shell. Likewise the total transmitted intensity I represents the current of the incident electrons. Assuming single scattering the partial inelastic cross section σ_k of a core loss event can be expressed by I_k , I and the number of atoms per unit area in the sample n_a .

$$\sigma_k = \frac{1}{n_a} \frac{I_k}{I} \quad (\text{II-1})$$

If there are at least 2 elements (denoted as A and B) present in the sample, then the ratio n_a^A/n_a^B is equal to the atomic concentration ratio (c_A/c_B). The ratio σ_k^A/σ_k^B must be known for a direct calculation of the chemical composition. If the elemental concentration ratio is already obtained at another sample position by another method (EDX,...) the ratio at a position of interest can be calculated. Let (1) denote the sample position with unknown chemical composition and (2) denote the sample position with known chemical composition and atomic concentration ratio c_A^2/c_B^2 , then:

$$\frac{c_A^1}{c_B^1} = R_B^A \frac{c_A^2}{c_B^2} \quad \text{where} \quad R_B^A = \frac{I_k^{1A} I_k^{2B}}{I_k^{1B} I_k^{2A}} \quad (\text{II-2})$$

For eq.II-2 to be valid a condition is that the integration intervals for the energy loss integrated intensities are the same at position 1 and 2 for each element, respectively. The thickness of the sample may differ between position 1 and 2.

Like shown in fig.II-5 a strong background is present in the high loss spectrum. Therefore, a background subtraction is necessary before integrating a core loss edge. So there are two energy loss intervals to be considered for a core loss edge. The energy loss interval δ for the background fit in front of the edge (that is at lower energy loss values) and the energy loss interval Δ for the edge integration. This intervals are shown in fig.II-5. The background intensities can be characterized by a power law dependence on the energy loss. The determined variables of the power law function have an energy loss dependence themselves and thus a fitted power law function is only valid for a limited energy loss region [21].

The energy loss integration interval Δ should be as wide as possible to reduce statistical errors on the one hand but it is limited by systematic errors due to the background fit on the other hand. The lower energy loss limit of Δ is set at the edge threshold energy E_K which can be defined as the point of steepest rise at the edge onset. The width of Δ should be about 10% of E_K . The width of the fitting interval δ can be set between 10% and 30% of E_K and is sometimes limited by another core loss edge in front of the considered edge. To avoid chemical shifts and broadening tails of the edge, the upper energy loss limit of δ should be at least 5 eV lower than E_K .

5.1. Plural scattering and deconvolution

Electrons that are inelastically scattered by a low energy loss event like plasmon scattering in addition to a core loss scattering can influence the core loss edge in the high energy loss spectrum because of the small energy loss shift due to the plasmon scattering.

In the Fourier-Ratio method the measured (high loss) spectrum $\hat{S}(E)$ is seen as a convolution of the single scattering spectrum $S(E)$ with the measured low loss spectrum $\hat{L}(E)$ consisting of the zero-loss peak and the plasmon peaks. The energy loss is here denoted as E .

$$\hat{S}(E) = \frac{1}{I_0} S(E) * \hat{L}(E) \quad (\text{II-3})$$

I_0 represents the integrated intensity of the zero-loss peak. It enters the equation through the assumption that the proportion of plasmon intensities at the core loss edges is the same as in the low loss spectrum [22]. The Fourier transform of the single scattering high loss spectrum yields

$$\mathcal{F}\{S(E)\} = \frac{\mathcal{F}\{\hat{S}(E)\}}{\mathcal{F}\{\hat{L}(E)\}} \mathcal{F}\{ZLP(E)\} \quad (\text{II-4})$$

where $\mathcal{F}\{ZLP(E)\}$ is the Fourier transform of the zero-loss peak. Using $\mathcal{F}\{ZLP(E)\}$ instead of I_0 reduces the noise in $\mathcal{F}\{S(E)\}$ that arises from the division. A reason for this replacement is that I_0 can be seen as the Fourier transform of a zero-loss peak idealized as delta distribution. Then the idealized zero-loss peak function $I_0 \delta(0)$ is replaced by the measured $ZLP(E)$.

The deconvolved core loss edges in the single scattering high loss spectrum are now obtained by the inverse Fourier transformation of eq.II-4. In this method the measured spectrum $\hat{S}(E)$ need to be background subtracted before the deconvolution is applied. Viewing the background subtracted $\hat{S}(E)$ and $S(E)$ as a sum of single core loss edges that are present in the spectrum, eq.II-4 can be applied on each single core loss edge.

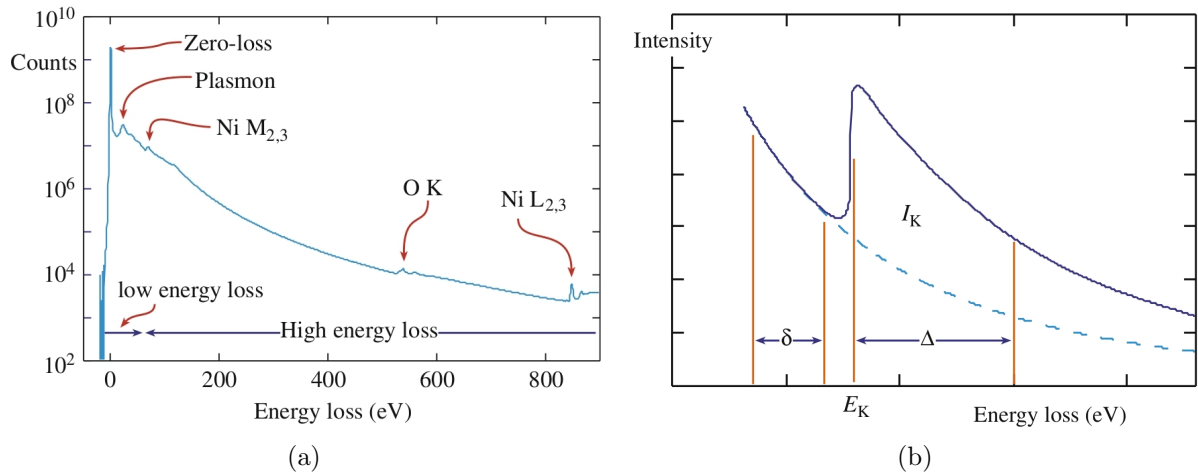


Figure II-5.: Image (a) shows an electron energy loss spectra displaying the low energy loss region and the high energy loss region. The zero-loss peak intensity is much higher than the intensities in the low loss region which are themselves some order of magnitude higher than the intensities of the ionization edges in the high loss region. In image (b) the energy loss interval δ for background fitting and an interval Δ for integrating a core loss edge in a high energy loss spectrum. The energy loss value E_K represents the steepest rise at the onset of the core loss edge. Both images are taken from [21].

5.2. Influence of a second layer

The nanocrystals studied in this work are embedded in an amorphous titanium and cobalt matrix also in the direction of the electron beam or thickness direction. Thus, the measured chemical composition yield some average value between the chemical composition of the amorphous phase and the chemical composition of the nanocrystal. The amorphous phase and the nanocrystals can be seen as two separated layers. Let t_1 and t_2 denote the thicknesses of the two layers, n_a^1 and n_a^2 their total number of atoms per unit area and n_v^1 and n_v^2 their number densities of atoms. These quantities are then connected by:

$$\frac{n_a^1}{n_a^2} = \frac{t_1}{t_2} \frac{n_v^1}{n_v^2} \quad (\text{II-5})$$

The measured atomic concentration (c_A) of element A in a two layered specimen can be written as $(n_a^{1A} + n_a^{2A})/(n_a^1 + n_a^2)$ where n_a^{1A} denotes the number of A atoms per unit area in layer (1) for instance. Splitting the sum and using eq.II-5 to substitute n_a^1 or n_a^2 the measured atomic concentration yields a weighted average of the two layers with chemical concentrations c_{1A} and c_{2A} .

$$c_A = \frac{t_1 n_v^1}{t_1 n_v^1 + t_2 n_v^2} c_{1A} + \frac{t_2 n_v^2}{t_1 n_v^1 + t_2 n_v^2} c_{2A} \quad (\text{II-6})$$

If the EELS measurements truly reflect the mean chemical composition in beam direction, then eq.II-5 is valid for the measured chemical compositions.

5.3. Influence of the oxygen concentration

5.3.1. Nanocrystals as oxide particles

In the work presented here, nanocrystals are analyzed which are believed to contain the elements cobalt (Co) and titanium (Ti). In addition the influence of oxygen (O) on the obtained results must be considered because some of the analyzed nanocrystals could also be oxide particles for instance. The oxygen concentration is likely to change with the surface treatment of a specimen and could also change over time. So different measurements of the absolute oxygen concentrations or oxygen concentration ratios are not always comparable. If these quantities are unknown, the elemental concentration can not be determined for oxides by eq.II-2. A similar method for displaying the chemical data is to compare elemental concentration ratios of each element, between position at the nanocrystals and some background. Here the background is given by the amorphous matrix next to the nanocrystals. Based on eq.II-1 these ratios can be given in the form:

$$\frac{c_A^1}{c_A^2} \frac{t_1 n_v^1}{t_2 n_v^2} = \frac{n_a^{1A}}{n_a^{2A}} = \frac{I_k^{1A} I_0^2}{I_k^{2A} I_0^1} \quad (\text{II-7})$$

for each element (A). Here (1) denotes a specimen position at the nanocrystal and (2) denotes a specimen position at the amorphous matrix. A first estimation of the atomic titanium and oxygen concentrations (c_{Ti}^1 and c_O^1) of an oxide particle can be obtained by neglecting the influence of the amorphous matrix on the measurements at the position of the particle. This simplification is consistent with the relation $c_{Ti}^1 + c_O^1 = 1$. The titanium concentration of the oxide particle is then given in dependence of atomic concentration ratios.

$$c_{Ti}^1 = \frac{c_{Ti}^1/c_{Ti}^2 (c_O^1/c_O^2 - 1)}{(1 + c_O^1/c_{Ti}^2) c_O^1/c_O^2 - c_{Ti}^1/c_{Ti}^2} \quad (\text{II-8})$$

5.3.2. Oxygen in the amorphous matrix

A disadvantage of eq.II-5 is its dependence on absolute atomic concentrations. In addition, the atomic concentration of oxygen at the amorphous matrix is unknown for Specimen Co3Ti-I3. If only the elements titanium, cobalt and oxygen are present in the specimens, then the absolute atomic concentrations of the nanocrystal and absolute atomic concentrations of the amorphous phase can be related directly to integrated intensity measurements. For instance, the titanium and cobalt concentrations which are given by c_{Ti}^1 and c_{Co}^1 in eq.II-2 can be substituted by the mean titanium and cobalt concentrations given by eq.II-5. This method leads to three equations comparing integrated intensity ratios of titanium to cobalt, oxygen to cobalt and oxygen to titanium. Thus, the amount of titanium, cobalt and oxygen at the nanocrystal and the amount of oxygen in the surrounding amorphous matrix can be obtained by a numerical solution of the equation system.

Here two different models are evaluated for the oxygen distribution in the specimen.

- In model 1 the oxygen is assumed to be diffused inside the specimen and equally distributed over the specimen thickness. The oxygen concentration c_O^3 in the amorphous matrix next to a nanocrystal is equal to the oxygen concentration c_O^2 in the amorphous matrix that surrounds the nanocrystal in beam direction.
- In model 2 the oxygen is concentrated at the specimen surfaces. Then oxygen reveals a higher concentration in the amorphous matrix that surrounds the nanocrystal in beam direction than in the amorphous matrix next to a nanocrystal. Neglecting the influence of the oxygen on the density, the oxygen concentrations scale with $t_2 c_O^2 = t_3 c_O^3$ depending on the thickness t_3 of the specimen at a position next to the nanocrystal and the thickness t_2 of the amorphous matrix that surrounds the nanocrystal in beam direction.

If no oxygen is assumed to be present in the nanocrystal, both models lead to the same equation for the titanium atomic concentration of the nanocrystal c_{Ti}^1 .

$$c_{Ti}^1 = \frac{(R_{Co}^{Ti} - 1) n_v^2 t_2 c_{Ti}^2 / c_{Co}^2 + (1 + c_{Ti}^2 / c_{Co}^2) n_v^1 t_1 R_{Co}^{Ti}}{(1 + c_{Ti}^2 / c_{Co}^2) (1 + R_{Co}^{Ti} c_{Ti}^2 / c_{Co}^2) n_v^1 t_1} \quad (\text{II-9})$$

Variables corresponding to the nanocrystal are denoted with (1) whereas variables corresponding to the amorphous matrix are denoted with (2). If the considered nanocrystal is an oxide, then the cobalt concentration can be set to zero at the nanocrystal. This leads to different equations for c_{Ti}^1 depending on the oxygen model.

$$\text{model 1:} \quad c_{Ti}^1 = \frac{(R_{Co}^{Ti} - 1) ((R_{Co}^O - 1) n_v^2 t_2 - n_v^1 t_1) c_{Ti}^2 / c_{Co}^2}{((1 + c_{Ti}^2 / c_{Co}^2) R_{Co}^O - R_{Co}^{Ti} c_{Ti}^2 / c_{Co}^2 - 1) n_v^1 t_1} \quad (\text{II-10})$$

$$\text{model 2:} \quad c_{Ti}^1 = \frac{(R_{Co}^{Ti} - 1) ((t_3 - t_2 R_{Co}^O) n_v^2 + n_v^1 t_1) t_2 c_{Ti}^2 / c_{Co}^2}{((t_3 - t_2 R_{Co}^O) + (t_3 - t_2 (1 + R_{Co}^O - R_{Co}^{Ti})) c_{Ti}^2 / c_{Co}^2) n_v^1 t_1} \quad (\text{II-11})$$

6. Calculation of specimen thickness by EELS

6.1. Reduced thickness

The thickness of the specimen is estimated from the electron energy low loss spectrum by a log-ratio method and a parametrization for the total mean free path of the inelastic scattered electrons [23]. The energy loss integrated electron intensity I_n follows a Poisson distribution for uncorrelated n -fold inelastic scattered electrons,

$$I_n = I \frac{p^n}{n!} e^{-p} \quad (\text{II-12})$$

where I is the total integrated intensity and p is called the reduced thickness [22], [24]. The reduced thickness p is the ratio of the specimen thickness t and the total mean free path λ of all inelastic scattered electrons. Thus for $n = 0$ equation (referring to a probability of no inelastic scattering) II-12 gives the integrated intensity I_0 of the zero-loss peak in the electron energy low loss spectrum. Therefore, the reduced thickness can be calculated from the integrated intensities of an acquired low loss spectrum.

$$\frac{t}{\lambda} = p = \ln \frac{I}{I_0} \quad (\text{II-13})$$

The spectrum intensities measured in transmission are a good representation for all inelastically scattered electrons because inelastic scattering of the accelerated electrons is strongly forward directed.

6.2. Absolute specimen thickness from EELS

A detailed discussion on inelastic electron scattering for high energy electrons can be found in the book "Electron Energy-Loss Spectroscopy in the Electron Microscope" [22]. In the following the energy loss is denoted as E .

The cross section σ is a measure for the interaction area at a scattering event. Considering scattering on particles at a surface σ can be expressed as the probability of scattering on this surface per particle area density. The inelastic single scattering distribution $S(E)$ (without I_0) is a measure for the current of inelastically scattered electrons in EELS. Likewise, I_0 is a measure for the current of primary elastic, forward scattered electrons [21]. A small contribution $d\sigma$ to the total inelastic cross section for a small energy loss interval dE can be written in the form

$$d\sigma = \frac{S(E) dE}{I_0} (n_v t)^{-1} \quad (\text{II-14})$$

where n_v represents the number density of atoms and t is the specimen thickness.

The electron energy low loss spectrum of a material is related to the dielectric properties of that material. For small scattering angles the double differential cross section $d^2\sigma/d\Omega dE$ for inelastic scattering is proportional to the energy-loss function $\Im[-1/\varepsilon(E)]$ where $\varepsilon(E)$ is the relative permittivity. $d\sigma/d\Omega$ has a Lorentzian angle dependence at small scattering angles $\theta < \theta_C$, where θ_C denotes a cut-off angle. This angle regime is therefore called the dipole region. The cut-off condition is given by a Bethe ridge angle so that $\theta_C \approx (\bar{E}/E_0)^{1/2}$ with a mean energy loss $\bar{E}$ and acceleration energy E_0 . Only electrons with scattering angles θ smaller than the collection semi-angle β of the entrance of the electron energy loss spectrometer can contribute to the energy loss spectrum. Implying that $\beta \ll \theta_C$ the angular integration of $d^2\sigma/d\Omega dE$ only in the dipole region is valid and β is set as the new upper limit of the angular integral. After performing the angular integration of

$d^2\sigma/d\Omega dE$ in the dipole region $\Im m[-1/\varepsilon(E)]$ can be related to $S(E)$ and the specimen thickness by eq.II-14. Then one obtains a formula for the specimen thickness t by using the Kramers-Kronig relations to substitute $\Im m[-1/\varepsilon(E)]$.

$$t = \frac{4 a_0 F E_0}{I_0 (1 - n^{-2})} \int_0^\infty \frac{S(E)}{\ln(1 + \beta^2/\theta_E^2)} \frac{dE}{E} \quad (\text{II-15})$$

$a_0 \approx 53 \text{ pm}$ denotes the Bohr radius and n is the optical refractive index which can be set as $n \gg 1$ in most cases. F is a relativistic factor so that the relation between the kinetic energy E_0 , the velocity v and rest mass m_e of the electrons can be written as $F E_0 = m_e v^2/2$ similar to the non relativistic case. In terms of acceleration energy F takes the form:

$$F = \frac{1 + E_0/1022 \text{ keV}}{(1 + E_0/511 \text{ keV})^2} \quad (\text{II-16})$$

The scattering angle $\theta_E = E/(\gamma m_e v^2)$ in eq.II-15 then becomes $E/(2 \gamma F E_0)$. The Lorenz factor γ in terms of acceleration energy yields $\gamma = 1 + E_0/(511 \text{ keV})$. Because the scattering angle θ_E appears in a logarithmic function which suppresses errors, often the non relativistic expression $\theta_E = E/(2 E_0)$ is used.

The effect of plural scattering in an energy loss spectrum can be considered by dividing t in eq.II-15 by a correction factor

$$C = 1 + 0.3 p \quad (\text{II-17})$$

as long as the specimen is thin enough [25]. In the literature a reduced thickness value of $p < 1.2$ is given as a limit for this correction method.

In [25] an additional correction Δt for the obtained specimen thickness is proposed because of surface plasmon scattering. The authors suggest to subtract $\Delta t = 8 \text{ nm}$ of the obtained thickness value for a more accurate result, independent of material and specimen thickness. Surface plasmons have a lower energy range compared to bulk plasmons. Their influence on the energy loss spectrum is important in the 0-10 eV energy loss region. In [22] the authors comment that the surface correction Δt can be omitted by using a truncated spectrum for the calculation. The intensities in the energy loss spectrum including the zero-loss peak are set to zero for values prior to the first minimum after the peak. If this truncated spectrum is then used for the single scattering distribution, Δt can be set to zero to compensate the missing intensity contributions due to the truncation.

6.3. Total mean free path

In order to get real thickness values from the reduced thickness, we need to know λ for the material. The inelastic mean free path λ is related by $\sigma = 1/(n_v \lambda)$ to the inelastic scattering cross section. Thus, also λ can be represented in terms of energy loss integrals in an energy loss spectrum by integrating eq.II-14 and by applying eq.II-15 for instance.

$$\lambda = \frac{2 a_0 F E_0}{1 - n^{-2}} \frac{\int_0^\infty \frac{S(E)}{\ln(1 + \beta^2/\theta_E^2)} \frac{dE}{E}}{\int_0^\infty S(E) dE} \quad (\text{II-18})$$

The logarithmic term in the energy loss integral of eq.II-18 can be simplified using that $\beta \gg \theta_E$ for common E_0 in the range of 100 keV, for β in the range of 10 mrad and for the low energy loss regime where $S(E)$ does not vanish and thus $E \lesssim 100 \text{ eV}$. Neglecting the

energy loss dependence of the logarithmic term Malis et al. [23] give a parametrization for the remaining integrals in eq.II-18 which they interpret as an average energy loss $E_m = \int S(E)dE / \int S(E)E^{-1}dE$. Based on measurements of different materials at 100 kV acceleration voltage they suggest that:

$$E_m \approx 7.6 Z^{0.36} \quad \text{and} \quad \lambda \approx \frac{106 F E_0}{E_m \ln(2 \beta E_0 / E_m)} \quad (\text{II-19})$$

where λ is given in nm and the non relativistic expression is used for θ_{E_m} . For a compound material the atomic number Z can be replaced by an effective atomic number Z_{eff} based on Lenz atomic model of inelastic scattering [26]. Z_{eff} is similar to an average of the atomic numbers Z_i of the elements in the compound weighted with their atomic fraction f_i .

$$Z_{eff} \approx \frac{\sum_i f_i Z_i^{1.3}}{\sum_i f_i Z_i^{0.3}} \quad (\text{II-20})$$

Eq.II-18 can be also derived from the inelastic free mean path λ_p of a sharp plasmon energy loss E_p based on Drude model and shown in [22]. The total inelastic free mean path λ results from taking the average of λ_p over the energy low loss spectrum weighted by $S(E)$.

To summarize conditions behind the parametrization formula of Malis et al. in eq.II-19:

- The parametrization is realized at an acceleration voltage of 100 keV.
- Due to the restriction to the dipole regime for $d\sigma/d\Omega$ the collection semi-angle β has an upper limit:

$$E_m / (2 E_0) \ll \beta \ll (E_m / E_0)^{1/2} . \quad (\text{II-21})$$

For instance, $45 \cdot 10^{-6} \ll \beta \ll 9.5 \cdot 10^{-3}$

for Co_3Ti and $E_0 = 300$ keV. Here the average energy loss $\bar{E}$ is given by E_m .

- The formula does not consider the incident convergence semi-angle α .

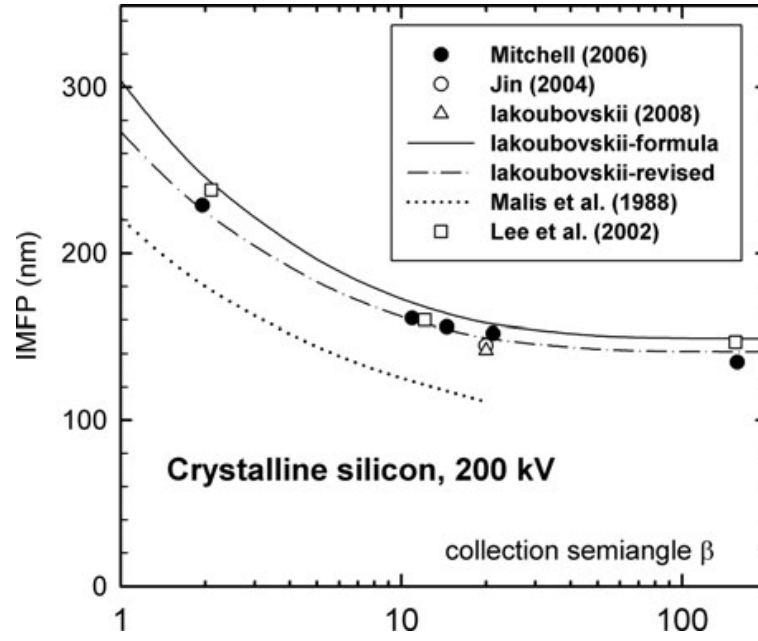
In STEM mode usually a convergent electron beam is used and the convergence semi-angle α can not be set as zero. It is even higher for aberration corrected STEM. Iakoubovskii et al. [27] derived a formula for λ by performing the angular integration of the inelastic differential cross section beyond the dipole regime and by relating the scattering angle to convergence and collection angles. This modifies the usual $\ln(1 + (\beta/\theta_E)^2)$ angular dependence. The mean energy loss E_m is here parameterized as a function of density ρ instead of atomic number Z and enters through the angle $\theta_{\bar{E}}$ in the equation. In [22] a further improvement to the equation is suggested by multiplying the relativistic factor F of the original work with the Lorentz factor γ . The so improved formula for the inelastic mean free path yields:

$$\theta_{\bar{E}} \approx \rho^{0.3} \frac{5.5}{\gamma F E_0} \quad \lambda \approx 100 \left(\theta_{\bar{E}} \ln \left(\frac{\alpha^2 + \beta^2 + 2\theta_{\bar{E}}^2 + |\alpha^2 + \beta^2| \theta_C^2}{\alpha^2 + \beta^2 + 2\theta_C^2 + |\alpha^2 + \beta^2| \theta_{\bar{E}}^2} \right) \right)^{-1} \quad (\text{II-22})$$

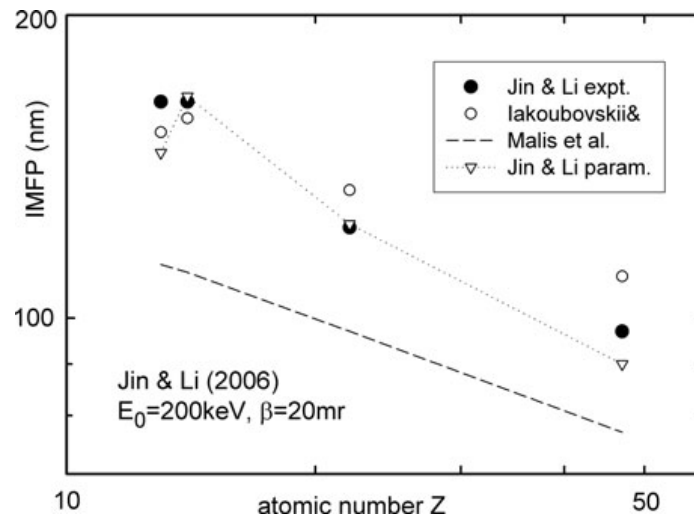
The saturation factor θ_C can be set to $\theta_C = 20$ mrad [27] and F is given in eq.II-16.

The expression for λ shown above has the advantage over eq.II-19 that the collection semi-angle is not limited for high acceleration voltages by the condition $\beta \ll (E_m/E_0)^{1/2}$ and that the convergence semi-angle α is considered in the expression. For the parametrization Iakoubovskii et al. used an acceleration voltage of 200 kV.

Because the parameterized formulas for λ are obtained by measuring specimen thicknesses, surface plasmon scattering has no influence on the formulas. A comparison of the two formulas for their collection angle dependence and for their atomic number dependence is shown in below in fig.II-6.



(a)



(b)

Figure II-6.: Comparison of the Malis et al. parameterization formula (eq.II-19) and the Iakoubovskii parameterization formula for λ to measurements for an acceleration voltage of 200 kV. The dash-dot curve in image (a) represents eq.II-22. The images are taken from the book Electron Energy-Loss Spectroscopy in the Electron Microscope [22].

7. Image processing

The company Gatan provides a commercial software package to analyze EELS data in the Gatan Microscopy Suite (GMS) software that can be downloaded from its homepage [28]. There are also free GMS versions available, but they do not include the package to analyze EELS data. A user guide to Gatan's EELS package is provided online from the Thin Film Physics research group of the Department of Physics, Chemistry and Biology at the University of Linköping [29]. In this work the EELS data evaluation is done without the use of the Gatan EELS package.

The acquired electron energy low loss spectra at one line scan are stored as a 32 bit real image. Each horizontal pixel line in the image corresponds to one spectrum. The horizontal pixel coordinate represents the energy loss value and the pixel value equals the intensity count. The vertical pixel coordinate gives the measurement position at the line scan. There is a scaling factor between a grayscale value in the 32 bit real image and the actual electron count like shown in fig.III-5. The use of electron counts or grayscale values is equivalent because in every derived quantity occurs at least one ratio of integrated intensities which correspond to the same spectrum. This nullifies the difference in intensity scales. Thus, in this work the spectra intensities are given as grayscale values.

The spectra images are processed with the Fiji software [30]. The "Cornell Spectrum Imager" plugin [31] is used for a numerical integration of the spectra. Note that Fiji defines the leftmost and upper most pixel in an images as pixel 0 by default. The terms "first" and "leftmost" are compatible when starting to count from the left and upper edge of the pixel. Here this pixel will be counted as pixel 1.

7.1. Energy loss shift

The energy loss values between spectra at one line scan are shifted like shown in fig.II-7.a for a low energy loss spectrum. The shift in the energy loss values must be corrected so that the same integration limits can be set for all spectra of one line scan in the "Cornell Spectrum Imager" plugin. The scripts for energy loss shift correction described below starts at the leftmost pixel of a given region of interest and proceeds to the right for each image row. This agrees with the positive energy loss direction.

7.1.1. Low energy loss spectra

For shifting low loss spectra, the correction was done by the Fiji macro script 1.a displayed in section VI-1. The script let the user select an energy loss region which should include the zero-loss peak. Then the pixel yielding the grayscale value maximum is found for each image row in the considered region. All grayscale values in an image row are then horizontally shifted for each row respectively, until the obtained grayscale maxima are vertically aligned with respect to the first row of the image. The values of the grayscale maxima and their initial pixel coordinates in scaled units are printed in a log file. This method leads again to a 32 bit real image with an energy shift correction at pixel accuracy between the image rows. Here pixel accuracy with an energy loss resolution of 0.25 eV per pixel (see tab.II-2) is sufficient for setting integration intervals over all image rows of one line scan image. Fig.II-7.b shows the energy shift corrected image in comparison to the uncorrected image (fig.II-7.a) of the line scan across particle A. The new zero-loss peak maximum and hence, the 0 eV energy loss pixel is now for all image rows at the 201 horizontal pixel.

7.1.2. High energy loss spectra

For the high loss spectra the Fiji macro script 1.b in section VI-1 is used. In the high loss spectra energy loss integrals over core loss edges need to be carried out. Therefore, these edges should be vertically aligned for all image rows of one image. In difference to script 1.a here the first steepest rise of the grayscale values is found instead of the maximum grayscale value for a considered energy loss range. The script aligns the image rows according to the horizontal pixel positions of the steepest rise. It applies a Gaussian blur filter on each image row separately before the slope is calculated by the grayscale value differences between neighboring pixels in an image row.

7.2. Truncated spectra

Truncated low loss spectra images are generated with the Fiji software for a direct calculation of the specimen thickness. Here a mean spectrum image is processed for each of the line scans A to D. The mean image is generated by averaging over all image rows of a low loss spectra image in the script 1.c in section VI-1. Now all horizontal pixels left to the zero-loss peak are cut off by the tool "Image/Adjust/CanvasSize...". Thus, the leftmost pixel yield the 0 eV energy loss. Then the grayscale values are set to zero for all pixels left to the first minimum in the energy loss spectrum using "Process/Math/Set...". The horizontal pixel coordinates and energy loss values are displayed in tab.II-5 for the first minima and the zero-loss peaks in the mean spectra of line scan A to D.

7.3. Zero-loss Peak subtraction

The energy loss integrated intensity I_0 of the zero-loss peak must be calculated to obtain the reduced thickness from the log-ratio method with eq.II-13. The zero-loss peak is broadened by the experimental setting like scattering of the electrons in the EELS device and especially by the energy spread of the incident electrons from the electron gun. An accurate separation of the zero-loss peak from the low loss spectrum is not

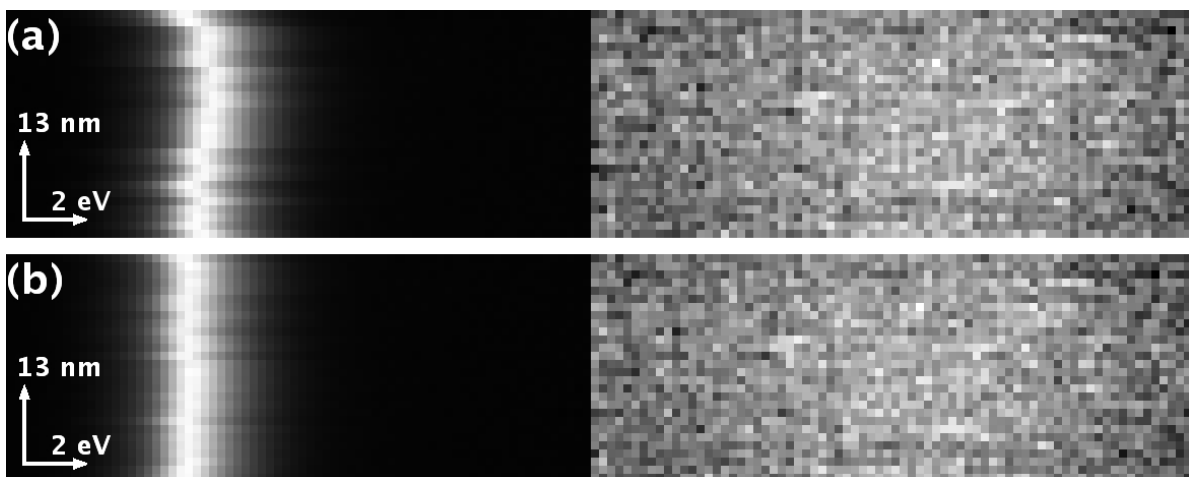


Figure II-7.: Image details of low-loss spectra showing the zero-loss peaks and the plasmon peaks for each position on line scan A. The recorded image is shown in (a) and the energy loss shift corrected image is shown in (b). The two images show two regions that are separated at 12.25 eV energy loss, respectively. A different contrast is used for the two regions so that the zero-loss peaks and the actually much weaker plasmon peaks can be visualized in the same image.

needed for calculating its integrated intensity. As shown in tab.II-5 the peak intensity is approximately 2 magnitudes higher than the intensities around the first energy loss minimum that could yield an upper limit of the integration interval.

But for the direct determination of the specimen thickness (section III-3.4.2) this separation is important, because the single scattering distribution $S(E)$ must be known. The $1/E$ scaling of $S(E)$ in eq.II-15 requires an accurate knowledge of $S(E)$ for very low energy losses or a huge error would be produced otherwise. Fig.II-9 shows a comparison of $S(E)$ and the integrand in eq.II-15 which features also this scaling. A spectrum revealing only the zero-loss peak can also be used in the deconvolution process that corrects high loss spectra for plural scattering which is discussed in section II-7.6.

During the study of specimen Co3Ti.L3 at the ASTEM (see section II-3.4) all EELS data is acquired at positions on the specimen. So there is no electron low energy loss spectrum recorded that would contain only the zero-loss peak without a plasmon loss region. To separate the zero-loss peak from the low loss spectrum, the negative energy loss region of the zero-loss peak can be mirrored to the positive energy loss region for instance. This would imply that the zero-loss peak is symmetric which need not be the case. The mirroring method can be used in the Gatan EELS package as described in the user guide [29]. There the width of the zero-loss peak's negative energy loss part is adjusted to the positive energy loss part to account for the asymmetry. The zero-loss peak can also be fitted with several functions [29].

A considerable amount of noise is present in the acquired electron low energy loss spectra for the intensity range of low energy losses like shown in fig.III-5. So instead of mirroring the experimental data in the negative energy loss region, a function is fitted to the data in the negative energy loss region and adjusted to the zero-loss peak's positive energy loss falling edge. When trying to just fit the positive energy loss falling edge of the zero-loss peak directly, this leads to an fitted falling edge with an onset that is too high in terms of intensity. The fitted function would roughly follow the measured intensities till the first minimum in the low loss spectrum. It can be assumed that in this region there is already an influence of the plasmon intensities when comparing the intensities with the intensities on the left, negative energy loss side of the zero-loss peak. There significant lower intensities are observed at the same energy loss distance from the zero-loss peak's maximum if the plasmon peak is considered for the intensity scale. The spectrum data for the just discussed intensity and energy loss range is displayed in fig.II-8.

Two functions are considered for different models of the intensity distribution I of the zero-loss peak's falling edge. Once a pure Gaussian function of the form

$$I(x) = \frac{I_0}{\sigma \sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-x_0}{\sigma}\right)^2} \quad (\text{II-23})$$

is used and another time a Pseudo-Voigt function was applied which contains a Lorentzian distribution in addition to a Gaussian distribution.

$$I(x) = I_0 \left(\frac{1-d}{\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-x_0}{\sigma}\right)^2} + \frac{d}{\pi \left(\left(\frac{x-x_0}{\sigma}\right)^2 + 1 \right)} \right) \quad (\text{II-24})$$

The standard deviation of the Gaussian part of the function is set equal to the scaling parameter of the Lorentzian part and both are denoted with σ . This simplifies the Pseudo-Voigt function by removing one fitting parameter and it stabilizes the fit. For the normalized Pseudo-Voigt function a factor of $1/\sigma$ would be in front of both, the Gaussian

part and the Lorentzian part of the function given here. This factor is included in the scaling parameter I_0 . The parameter d yields the Lorentzian fraction of the function so that $0 \leq d \leq 1$. Both fitting functions would also be available in the GMS software [29] but for a direct fit of the zero-loss peak for positive energy loss values.

Each image row of a line scan image is considered separately for fitting tit's zero-loss peak because the average peak of all image rows would be broadened due to the pixel accuracy of the peak position in each image row. Here the program Mathematica is used to process a whole line scan image and to fit the functions in eq.II-23 and eq.II-24, respectively to the zero-loss peaks in the image rows. The applied Mathematica script (section VI-1, script 2.a) is separated in four parts that can be executed successively: an image loading part, an evaluation part, a plotting part and an averaging part. In the image loading part the 32 bit real image is loaded as a matrix which indices correspond to pixel coordinates and which element values correspond to the intensity values. An intensity - pixel diagram displays one spectrum and a slider let the user switch between the spectra of the chosen image. In the evaluation part of the script a fitting interval in horizontal pixel coordinates is requested. Then the functions are fitted for each image row, the fitted peaks are saved as a 32 bit real image and displayed in an intensity - pixel diagram again. The plotting part lets one specify a custom region for plotting the functions and spectrum data. In the average part of the script the mean fitting parameters of all spectra of the line scan image are calculated with the option to exclude some spectra and the root mean square error for the fitted functions is calculated.

7.3.1. The Pseudo-Voigt fit

To adjust the Pseudo-Voigt function in eq.II-24 to the form of a zero-loss peak the 4 parameters I_0 , d , σ , and x_0 must be determined. Here the adjustment is done in 3 steps:

1. The Lorentzian fraction d of the zero-loss peak's falling edge is specified by fitting the function to the left, negative energy loss falling edge of the zero-loss peak. This fit has the constraint $0 \leq d \leq 1$. Therefore, the numerical fitting method "NMinimize" is used in Mathematica.
2. For the considered fit functions $I(x)$ the parameter I_0 scales the intensity values and σ the argument x or in other words, the width of the functions. Assuming that the falling edge intensities of the zero-loss peak are of similar values on both sides of the peak, the scaling parameter I_0 is determined by a second fit on the left, negative energy loss falling edge. For this second fit the Lorentzian fraction d is set as constant at the value obtained by the first fit. The Mathematica script 2.b in section VI-1 is applied for the fitting process. Here the Levenberg-Marquardt algorithm can be used instead of the "NMinimize" fitting method.

On the right, positive energy loss side of the zero-loss peak the plasmon peaks influences the falling edge of the zero-loss peak. Thus, the fitting interval should only include intensity values that are high enough compared to the intensity values of the plasmon peaks in order to minimize that influence.

The results of the second fit can be used to check the validity of the final fit on the right, positive energy loss falling edge in the region where plasmon intensities occur. Therefore, the fitting error is calculated for the intensity region of the plasmon intensities and compared to the fitting error (in the same region) of the first fit which fitting interval does include lower intensity values. In the low loss image of line scan A for instance, root mean square error values of 260 grayscale units for the first

fit and 190 grayscale units for the second fit could be obtained in the considered intensity region of approx. 400 to 3200 grayscale units. Detailed properties and values for these fits are shown in tab.II-6. The two obtained error values are of a similar size, although the second fit is already set at an intensity interval above the plasmon intensities with 1700 grayscale units as the lowest value. Thus, a function fitted to the zero-loss peak in an intensity region above the plasmon intensities is still in good agreement with the peak in a region where plasmon intensities occur.

3. The fitting interval for the final fit is placed on the right, positive energy loss falling edge of the zero-loss peak. It is chosen in such a way that the intensity values are higher than the plasmon intensity values. Only two free parameters σ and x_0 are determined by the fit. The value of d is taken from the first fit and the value of I_0 is taken from the second fit. The Mathematica script 2.c in section VI-1 is used for this third fit.

7.3.2. The Gaussian fit

For the Gaussian function in eq.II-23 the 3 parameters I_0 , σ , and x_0 must be found. Here the fitting process is similar as for the Pseudo-Voigt function, but now only 2 steps are needed:

1. The scaling parameter I_0 is calculated from a first fit on the left, negative energy loss falling edge of the zero-loss peak.
2. The final fit for the remaining parameters σ and x_0 is set on the right, positive falling edge of the zero-loss peak. Here I_0 is set constant at the value obtained from the first fit and the fitting interval is chosen to only include intensity values that are high enough when compared to the plasmon intensity values.

The fitting intervals are chosen from the mean spectrum image of all low loss spectra of a line scan. The parameter values, fitting intervals and calculated errors for the fitted functions are shown in tab.II-6 for line scan A. The characteristic values of the averaged spectrum image are shown in tab.II-5 and can be compared to the fitting intervals. In fig.II-8 the fitted Gaussian functions and the fitted Pseudo-Voigt functions are shown together with the measured low loss spectrum and the obtained single scattering distribution $S(E)$.

$S(E)$ is obtained for line scan A by subtracting the Pseudo-Voigt function image of the final (third) fit or the Gauss function image of the second fit from the low loss spectra image, respectively. The feature "Process/Image Calculator..." in the Fiji software can be used for subtracting the images. Negative grayscale values do occur in the fitted energy loss region and $S(E)$ reveals a buckling at the upper limit of the fitting interval like shown in fig.II-9 for a mean $S(E)$ image of line scan A. In the fitting region it is not possible to filter out the vanishing plasmon peak falling edge.

The Pseudo-Voigt function is fitted for line scans A to D to obtain images of zero-loss peaks. Minor changes on the fitting interval (in pixel coordinates) are applied between each line scan to account for the different averaged intensity values and energy loss positions of the zero-loss peak, the first minimum in the positive energy loss spectrum and the plasmon peak. The upper energy loss limit of the fitting intervals happens to be at 4 eV energy loss for all four line scans. The zero-loss peak images are obtained by replacing the low energy loss spectra images with Pseudo-Voigt function images of the final (third) fit for horizontal pixel coordinates that exceed the upper limit of the fitting regions.

line scan / spectrum feature		intensity (gray scale) value	horizontal pixel coordinate	energy loss value in eV
A	zero-loss peak max.	112540	201	0.00
	first intensity min.	1145	255	13.50
	plasmon peak global max.	1467	296	23.75
B	zero-loss peak max.	118936	198	0.00
	first intensity min.	748	255	14.25
	plasmon peak global max.	1238	294	24.00
C	zero-loss peak max.	109380	202	0.00
	first intensity min.	1439	252	12.50
	plasmon peak global max.	1909	297	23.75
D	zero-loss peak max.	119768	200	0.00
	first intensity min.	1311	252	13.00
	plasmon peak global max.	1744	293	23.25

Table II-5.: Characteristic values of the averaged low energy loss spectrum images for line scans A to D. The leftmost pixel value in the images is denoted with 1.

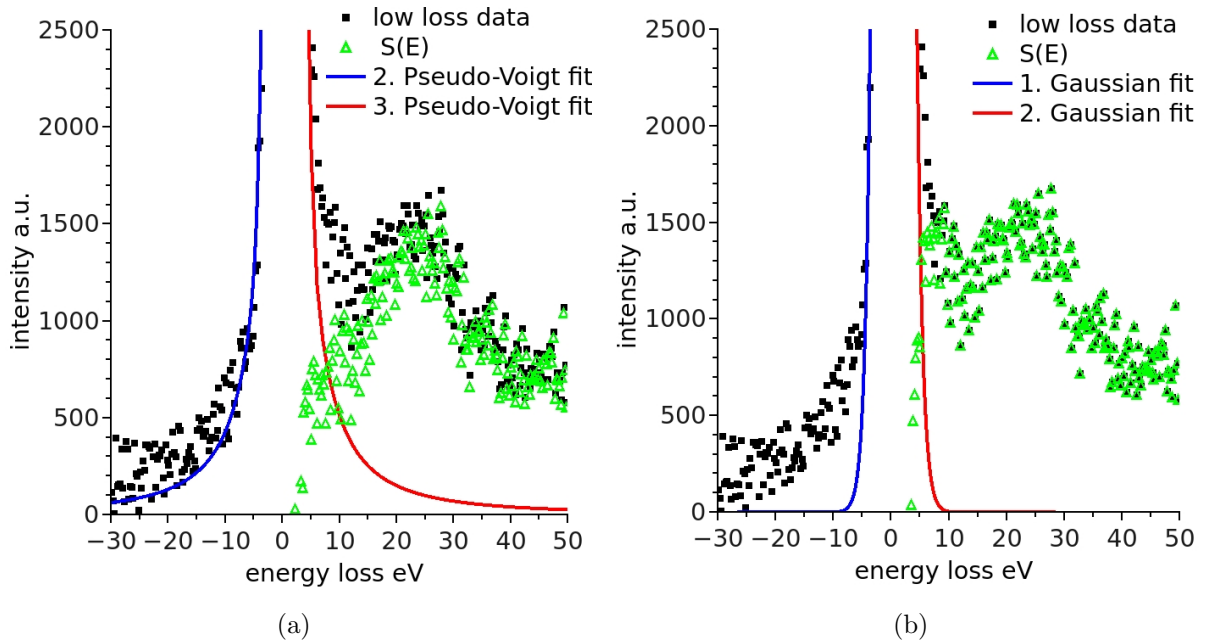


Figure II-8.: Both images show the same low loss spectra, the zero-loss peak subtracted spectra $S(E)$ but different fit functions. The higher onset of the zero-loss peak's falling edge for the positive energy loss region is revealed in the displayed low loss data. The Gaussian functions (b) are not able to follow the broad falling edges of the zero-loss peak. Fitting a Pseudo-Voigt function (a) to the zero-loss peak clearly leads to a more accurate single scattering distribution $S(E)$.

1. f i t	excluded image rows in vertical pixel coordinates	4, 11, 12, 18, 28			
	properties of fit	pixel range	intensity range	root mean square error	
	fitting region	150 - 192	400 - 12000	480	
	left falling edge region	150 - 187	400 - 3200	260	
	fitted parameters	d	I_0	σ	x_0
	parameter values	0.14	800000	1.30	211.2
	parameter errors	0.03	250000	0.29	1.3

2. f i t	excluded image rows in vertical pixel coordinates	2, 8, 14, 19, 23			
	properties of fit	pixel range	intensity range	root mean square error	
	fitting region	184 - 195	1700 - 26000	230	
	left falling edge region	150 - 187	400 - 3200	190	
	fitted parameters	I_0	σ	x_0	fixed parameter
	parameter values	425014	7.305	209.19	d
	parameter errors	140000	0.027	0.16	0.14

3. f i t	properties of fit	pixel range	intensity range	root mean square error	
	fitting region	209 - 217	28000 - 4200	290	
	fitted parameters	σ	x_0	fixed parameters	
	parameter values	7.727	194.175	d	I_0
	parameter errors	0.027	0.056	0.14	425014

Table II-6.: Properties of the Pseudo-Voigt fits of the zero-loss peaks falling edges in the low loss spectra image of the EELS line scan A. The fits 1-3 are carried out by the scripts 2.a - 2.c in section VI-1. The pixel coordinate origin is given by the upper and leftmost pixel in the image which is counted as pixel 1. The intensity values are taken from the averaged spectrum image. They are given in grayscale units. The fitted parameters are averaged over all image rows (spectra) except the excluded one. These exclusions are chosen manually by looking at the plotted fits and data. The parameter errors given here are yielding the propagated uncertainties calculated from the parameter errors of each image row except the excluded one. The root mean square errors are given in grayscale units. They are calculated from the difference between the data values and the fitted function values in the given pixel range considering all image rows, except the excluded one.

7.4. Manipulating low energy loss spectra

The absolute specimen thickness is calculated for line scan A to D based on eq.II-15 for a mean spectrum of each line scan, respectively. If the Cornell Spectrum Imager plugin [31] is used for the energy loss integration, the integrand in eq.II-15 must be given again as a line scan image. Here the mean images of the single scattering distribution $S(E)$ are processed to become the integrand images. The generation of these images is discussed in the previous section II-7.3. Mean images are obtained again by script 1.c in section VI-1. The width (energy scale) of a mean $S(E)$ image is cut so that the leftmost pixels correspond to the former positions of the zero-loss peaks, hence to the 0 eV energy loss.

It is not possible to obtain $S(E)$ in the fitting region of the zero-loss peaks by subtracting the fitted peaks, like already mentioned in the previous section. So a cubic polynomial of

1. f i t	properties of fit	pixel range	intensity range	root mean square error
	fitting region	150 - 195	400 - 26000	540
	left falling edge region	150 - 187	400 - 3200	580
	fitted parameters	I_0	σ	x_0
	parameter values	56804700000	19.06	283.1
	parameter errors	35000000000	0.94	8.7

2. f i t	properties of fit	pixel range	intensity range	root mean square error
	fitting region	209 - 217	28000 - 4200	290
	fitted parameters	σ	x_0	fixed parameter
	parameter values	19.392	219.44	I_0
	parameter errors	0.062	0.28	56804700000

Table II–7.: Properties of the Gaussian fits of the zero-loss peaks falling edges in the low loss spectra image of the EELS line scan across particle A. The fits 1-2 are carried out by the script 2.d and the script 2.e in section VI-1. Detailed information about the plotted values is given in tab.II–6 which refers to the Pseudo-Voigt fits.

the form $C_1 E + C_2 E^2 + C_3 E^3$ is fitted to the mean $S(E)$. The polynomial fit replaces $S(E)$ in the very low energy loss region that correspond to the fitting region of the zero-loss peaks. Because of the $1/E$ energy scaling in the integrand, this fit has strong influence on the calculated integrand as shown in fig.II–9. The energy loss region considered for the replacement spans 0 eV to 4 eV energy loss for all four line scans. The fitting interval for the polynomial fit itself is set from above 4 eV to about 12 eV energy loss. The fitted polynomial, the mean $S(E)$ and the resulting integrands are compared in fig.II–9.

The integrand in eq.II–15 is calculated also for the truncated mean spectra of line scans A to D that are discussed in section II-7.2.

A discussion about formula eq.II–15 and the occurring quantities like the energy loss dependent scattering angle Θ_E is given in section II-6.2. Here Θ_E enters as the relativistic expression $\Theta_E = E/(2 \gamma F E_0)$ in the calculation. The Fiji program is used again for the calculation. The grayscale values in the image are set by the tool "Process/Math/Macro...". A grayscale values v correspond to a value of the single scattering distribution $S(E)$ and a horizontal pixel position x to an energy loss E . The expression used for "Process/Math/Macro..." is:

$$v = 4 * v / (x * \log(1 + \text{pow}(\beta * 4 * (E_0 + 2 * m_e) / (x * (m_e / E_0 + 1)), 2)))$$

with a value of 300000 eV for the acceleration energy E_0 , a value of 511000 eV for the electron rest mass m_e equivalent energy and a value of 0.0205 rad for the collection semi-angle β . Note that the factor 4 in the equation comes from the pixel to energy loss conversion and that x is given in units of eV.

After applying this procedure the grayscale value of the first pixel in the integrand images must be set per hand. It corresponds to the 0 eV energy loss position and the program is not able to calculate the correct lines for that grayscale value. Here the value is set assuming a linear continuation from the grayscale values of the second and third pixel in the integrand image.

7.5. Integrating spectra

As mentioned before, the "Cornell Spectrum Imager" plugin [31] in Fiji is used to perform energy loss integrals in the spectra images. This plugin has the advantage to process a whole line scan image, to fit and subtract the background intensities for each spectrum in the line scan image and to perform the energy loss integration for all spectra at once. The integration intervals are the same for all spectra in one image and thus the image rows need to be aligned to each other as discussed in section II-7.1.

Note that in contrast to the Gatan DigitalMicrograph software the Fiji software does not take into account the offset of the energy loss origin given in tab.II-2 by the energy loss range. The first horizontal pixel is counted as 0 eV energy loss by default.

The integration result can be saved as a ".text" file yielding the line scan position and the integration value in two columns.

7.5.1. Low energy loss spectra

Low energy loss spectra must be integrated for calculating the specimen thickness. The energy loss scale is set as 4 pixel per 1 eV. It seems that background intensities in the low energy loss spectra are generated only by noise. Therefore, a background subtraction is omitted for low energy loss spectra. The integration intervals used for integrating the zero-loss peak images and the low energy loss images are displayed in tab.III-1 in units of eV. The horizontal pixel coordinate or energy loss value of the zero-loss peak in the first image row is used to set the integration intervals accordingly. This value is given in the output of script 1.a as described in section II-7.1.1. The integrand images for a direct determination of the specimen thickness by eq.II-15 are already cut so that the first pixel corresponds to the 0 eV energy loss position. Here the integration interval is set from 0 eV to 100 eV. energy loss.

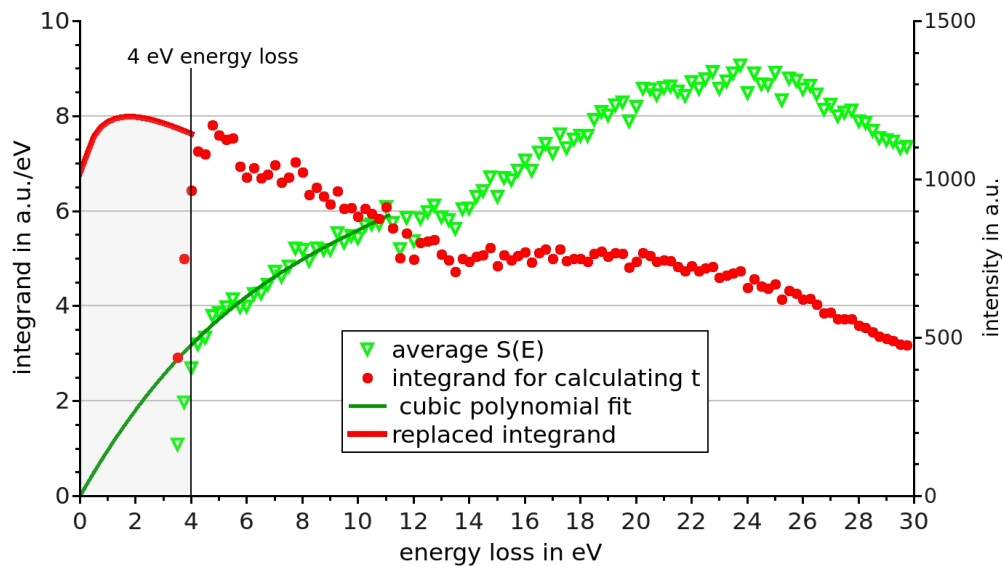


Figure II-9.: Integrand in eq.II-15 and the single scattering distribution $S(E)$ as a function of energy loss. $S(E)$ is obtained by subtracting the zero-loss peak using a Pseudo-Voigt function as a fit function. Because of the $1/E$ scaling, the integrand values at low energy losses have a strong influence on the calculation. Here mean images of line scan A are displayed. In the very low energy loss region of 0 eV to 4 eV $S(E)$ is replaced by a cubic polynomial. The corresponding change in the integrand is shown.

7.5.2. High energy loss spectra

Titanium, cobalt and oxygen core loss edges are considered for an energy loss integration in the high energy loss spectra. In fig.III–7 the line scan data of electron high energy loss spectra is shown for line scan VIII. The edges of the three elements are indicated in the figure. The edges are aligned at their steepest rise E_k as discussed in section II-7.1.2. This leads to three images that correspond to the three aligned edges for each line scan.

The energy loss scale is set as 4 pixel per 1 eV for images of line scans A to D (specimen Co3Ti_I3) and as 2 pixel per 1 eV for images of line scans I to VIII (specimen Co3Ti_I4) in accordance with tab.II–2. Each image is integrated using their energy loss values of E_k as the lower integration limit. These values are given in the outputs of script 1.b (section VI-1). The integration intervals and the parameters for background subtraction are displayed in tab.III–5 for the three edges. The values are rounded to 0.5 eV for line scan images of specimen Co3Ti_I4. A power law function is set to subtract the background with the Cornell Spectrum Imager plugin. The background subtracted images are saved for line scans A and C for further processing by deconvolution.

7.6. Deconvolution of high loss spectra

The line scan images selected for deconvolution are the background subtracted core loss edge images for line scan A and C as discussed in section III-3.5.1. The intensity values at the tail of the titanium and the oxygen core loss edge are extrapolated to zero by replacing them with a fitted linear function in the energy loss region yielding values that exceed the upper energy loss integration limit of the considered edge (energy loss values $\gtrsim E_k + \Delta$). The Cornell Spectrum Imager plugin [31] is used to perform the linear fit in Fiji [30]. When the intensity values of the fitted linear function become negative, the values are set to zero for each image row respectively by the script 1.d displayed in section VI-1. Intensity values in front of the edge onsets are also set to zero. Now the obtained images do only include the titanium, the oxygen or the cobalt core loss edges alone. The tail of the cobalt edge can not be extrapolated to zero because it is cut by the upper energy loss limit of the image.

Intensities in the low energy loss images and the zero-loss peak images are also set to zero for line scan A and C in energy loss regions that are dominated by noise or by the slowly decreasing tail of the zero-loss peak. The values given in tab.III–1 are used as references for this regions. In difference to the values presented there, the upper energy loss limit is set to 120 eV for the low energy loss images.

The Fourier-Ratio method is applied for a deconvolution of core loss edges in the electron high energy loss spectra. This method is described in section II-5.1. The software DigitalMicrograph from the Gatan company is used to implement a deconvolution for line scan images in a script file. A free version is available in GMS on the company’s homepage [28]. In DigitalMicrograph the Fourier transformation of an image can be processed easier than in Fiji because one can define complex images. The FELMI-ZFE provide a script database for DigitalMicrograph on their homepage [32] with useful scripts that are related to EELS. But a prepackaged script for deconvolution of line scan images could not be found. Another scripting database is maintained by Dave Mitchell at Dave Mitchell’s DigitalMicrograph Scripting Website [33]. The EELS tools package provided there does require Gatan’s EELS package for some applications to work.

Here the core loss edge images are deconvolved in script 3.a which is shown in section VI-1. The script applies eq.II-4 followed by an inverse Fourier transformation for every row of a line scan image. The image of a core loss edge, the low loss spectra image of the same EELS line scan and the corresponding zero-loss peak image are selected as input for the script.

The log-ratio deconvolution method using a zero-loss peak image as a smoothing image is compared to a method that is using a Gaussian function as smoothing image. The method to apply a Gaussian function in the deconvolution process is stated in the Electron Energy-Loss Spectroscopy in the Electron Microscope [22]. The procedure is realized in script 3.b in section VI-1 that features minor changes to 3.a to implement a Gaussian fit. Here an intensity profile of a zero-loss peak is selected as the third image. A region of interest (ROI), selecting the zero-loss peak at approximately its full width half maximum (FWHM) must be present in the image. The script 3.b uses a Gaussian function script written by Dave Mitchell and Bill Bertram that can be downloaded from [33]. This Gaussian function script must be implemented in DigitalMicrograph. A weighting factor reduces the contributions of the peak's tail for the Gaussian fit. Here a weighting factor of 3 is applied.

In fig.III-8 a comparison of the two deconvolution scripts for the core loss edges of line scan C is given.

III. Results & discussion

1. SEM imaging

Individual SEM images that show parts of the cross section of the disc shaped sample Co₃Ti-I are combined to an image of the whole cross section using the Fiji software [30]. This combined image is shown in fig.III-1. Secondary electrons (SE) generate an uniform contrast in the SE images of sample Co₃Ti-I and can not reveal different structures in the sample. SE are sensible to local changes in sample heights which could occur due to a preferred etching in a chemical polishing process. But the considered specimen is mechanically polished. Using the BSE detector two areas of different intensity can be recognized in the images. BSE are sensible to the atomic number and thus they are sensible to chemical composition and density of the material.

Like discussed in section II-1 and deduced in previous studies to this work, the two regions correspond to a still crystalline L1₂ long range ordered Co₃Ti phase and an amorphous phase that is formed during the HPT deformation. In fig.III-1 the contrast between the two phases is amplified by a factor of about 5 for a better visualization of the regions. Large amorphous regions are located at one half of the sample regarding the thickness direction. An increase of amorphous regions can also be observed in radial direction from the center of the disc towards its perimeter.



Figure III-1.: Combined SEM images of a cross section of the HPT deformed Co₃Ti-I disc. The images are acquired by the BSE detector using a high tension of 20 kV. The bright areas in the image correspond to amorphous regions whereas the dark areas are still crystalline. Amorphous regions are located at one half of the sample towards the surface indicated with (A). The other sample surface revealing more crystalline regions is marked with (C). The radial direction of the disc is indicated with an arrow (r). Just one half of a cross section is shown in the image.

2. TEM analysis

The TEM analysis on the PHILIPS CM200 electron microscope reveals the presence of crystalline and amorphous regions for all three specimen Co3Ti_I3, Co3Ti_I4 and Co3Ti_cross. Crystalline areas show a high density of lattice defects due to the HPT deformation. Amorphous bands cross these crystalline areas. A clear separation between amorphous regions and crystalline residuals is only possible at broader amorphous bands for the specimens Co3Ti_I3 and Co3Ti_I4. The specimen surface is oriented parallel to the surface of the HPT disc and parallel to sheared specimen planes for these specimens.

Embedded nanocrystals can be observed even at large amorphous regions that are clearly separated from residual crystalline regions. These nanocrystals are shown in fig.III–2 for the specimens Co3Ti_I3 and Co3Ti_cross. They reveal a similar size and shape in both specimens. Since specimen Co3Ti_I3 and specimen Co3Ti_cross display specimen planes that are perpendicular to each other, embedded nanocrystals are not elongated but they are of a roundish shape with some faceting. Thus, their shape can be roughly approximated by a sphere.

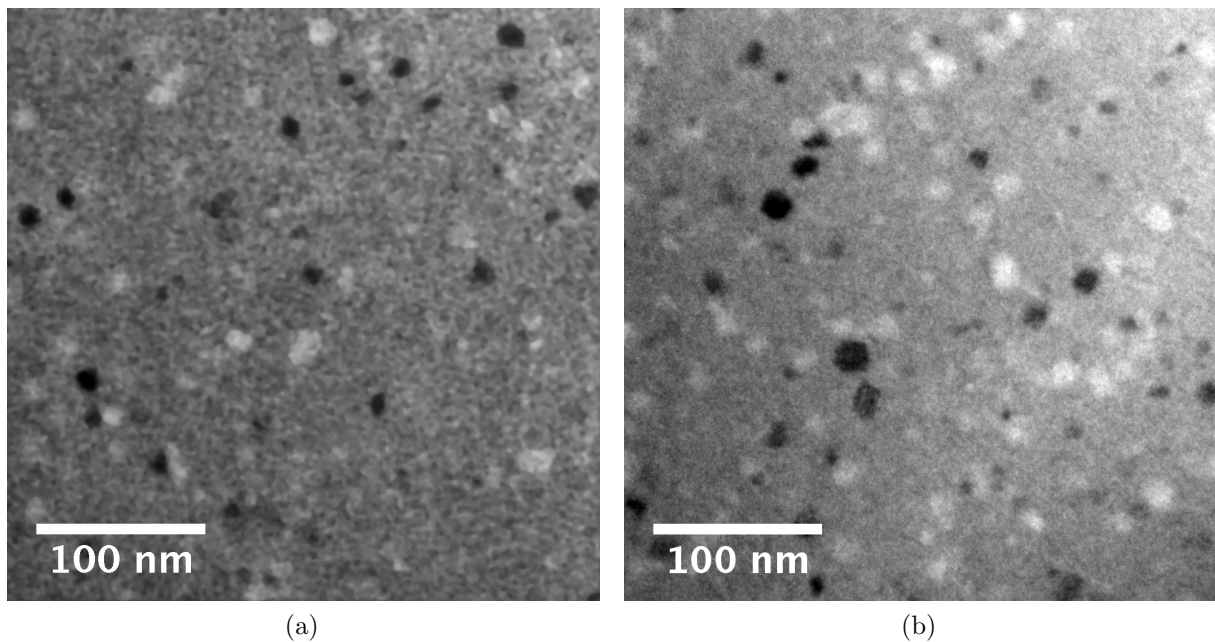


Figure III–2.: TEM bright field images of nanocrystals embedded in the amorphous matrix of the cobalt-titanium alloy. An amorphous region of specimen Co3Ti_I4 is shown in (a) and an amorphous region of specimen Co3Ti_cross is shown in (b). The nanocrystals reveal a similar size and shape for both images. They show dark and bright contrast with respect to the amorphous matrix.

III. Results & discussion

Size and quantity of embedded nanocrystals are analyzed from a bright field (BF) image of an amorphous area of approximately $1.1 \times 1.1 \mu\text{m}^2$ at specimen Co3Ti_cross. The nanocrystals reveal diameters between about 5 nm and 20 nm with a mean diameter of 12 nm and a standard deviation of 3 nm.

If one assumes that the specimen is thin enough so that nanocrystals are located roughly around one specimen plane, then the measured quantity of nanocrystals yields a good approximation for their area fraction. The calculated area fraction of nanocrystals from the BF image gives an upper limit for the actual area fraction. This implies the condition that most of the nanocrystals which are present at a considered specimen area must also be visible in the analyzed BF image. Here the influence of the amorphous phase on the image contrast becomes an advantage. Due to diffuse scattering contrast of the amorphous phase, nanocrystals that are not in Bragg condition can reveal bright contrast with respect to the amorphous phase in BF images.

Since a similar distribution of nanocrystals can be observed in specimen Co3Ti_I3 and in the cross-sectional specimen Co3Ti_cross, the area density of nanocrystals is similar for specimen planes that are oriented parallel and perpendicular to the surface of the HPT deformed disc. Thus, an upper limit for the volume fraction can be calculated from an estimated area fraction.

Embedded nanocrystals occupy a volume of $\lesssim 3 \%$ in the amorphous matrix at specimen Co3Ti_cross. This value is in good agreement with the value of 2 % that is obtained from a previous study at specimen areas parallel to the surface of the HPT deformed disc like already mentioned in section II-1. Therefore, the assumption of an isotropic distribution of embedded nanocrystals is valid.

3. Chemical analysis

The chemical composition of nanocrystals embedded in the amorphous phase of the HPT deformed samples is studied by EELS at the ASTEM. EELS line scans are acquired across individual nanocrystals and their surrounding amorphous phase for the TEM specimens Co3Ti_I3 and Co3Ti_I4.

3.1. EDX measurements

EDX measurements of specimen Co3Ti.I4 are received as recorded from a STEM session at the National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory. Specimen Co3Ti.I4 is not ion milled, thus a high carbon concentration could be measured at some areas. Seven measurements of amorphous areas of about $20 \times 30 \text{ nm}^2$ are taken from three different positions at the specimen. Neglecting the presence of additional elements beside titanium and cobalt in the specimen, the mean titanium concentrations are ranging from $25.0 \text{ at.\%} \pm 0.2 \text{ at.\%}$ to $25.7 \text{ at.\%} \pm 0.4 \text{ at.\%}$ between the measured positions. A total mean value is calculated from the mean values of the three positions.

A titanium concentration of $25.4 \text{ at.\%} \pm 0.4 \text{ at.\%}$ is obtained for the amorphous phase at specimen Co3Ti.I4 by neglecting additional elements present in the specimen.

3.2. Specimen Co3Ti.I3

Electron high energy loss spectra and electron low energy loss spectra are acquired simultaneously for each line scan at specimen Co3Ti.I3. This allows to calculate the specimen thickness at every line scan position. Knowing the plasmon distributions from the low loss spectra, the effect of multiple inelastic scattering in the high loss spectra can be reviewed. The influence of the amorphous matrix surrounding the nanocrystal on the measured chemical composition can be approximated by eq.II-5. Here the term "matrix corrected" is established for chemical data where this influence on the data is subtracted. EELS line scans of 4 different nanocrystals are evaluated. Both, the line scans and the corresponding nanocrystals are labeled with (A) to (D).

ADF and HRTEM images of nanocrystals A and B are compared in fig.III-3. In the HAADF image the weak contrast of nanocrystal A to the amorphous matrix indicates that a chemical difference between the nanocrystal and the matrix would only be a small one. In comparison, nanocrystal B reveals a strong negative contrast to the matrix which implies that it has a different chemical composition than the chemical composition of the amorphous matrix. In both cases the nanocrystals reveal a dark contrast compared to the contrast of the amorphous matrix. HAADF images reveal a Z contrast. If one considers the nanocrystals to contain just titanium and cobalt, this fact would indicate a higher titanium concentration at the nanocrystals, because titanium has the smaller atomic number Z of 22 than cobalt ($Z = 27$). The presence of carbon at the specimen should be reduced due to ion milling and plasma cleaning. A carbon contamination at the specimen surface would also lead to an increased signal in the HAADF images because the specimen thickness would increase. This phenomenon could not be observed here. An element that should be considered to be present at the specimen is oxygen. So observed nanocrystals could also be oxides. They also would reveal negative contrast in the HAADF images due to the low Z value of oxygen.

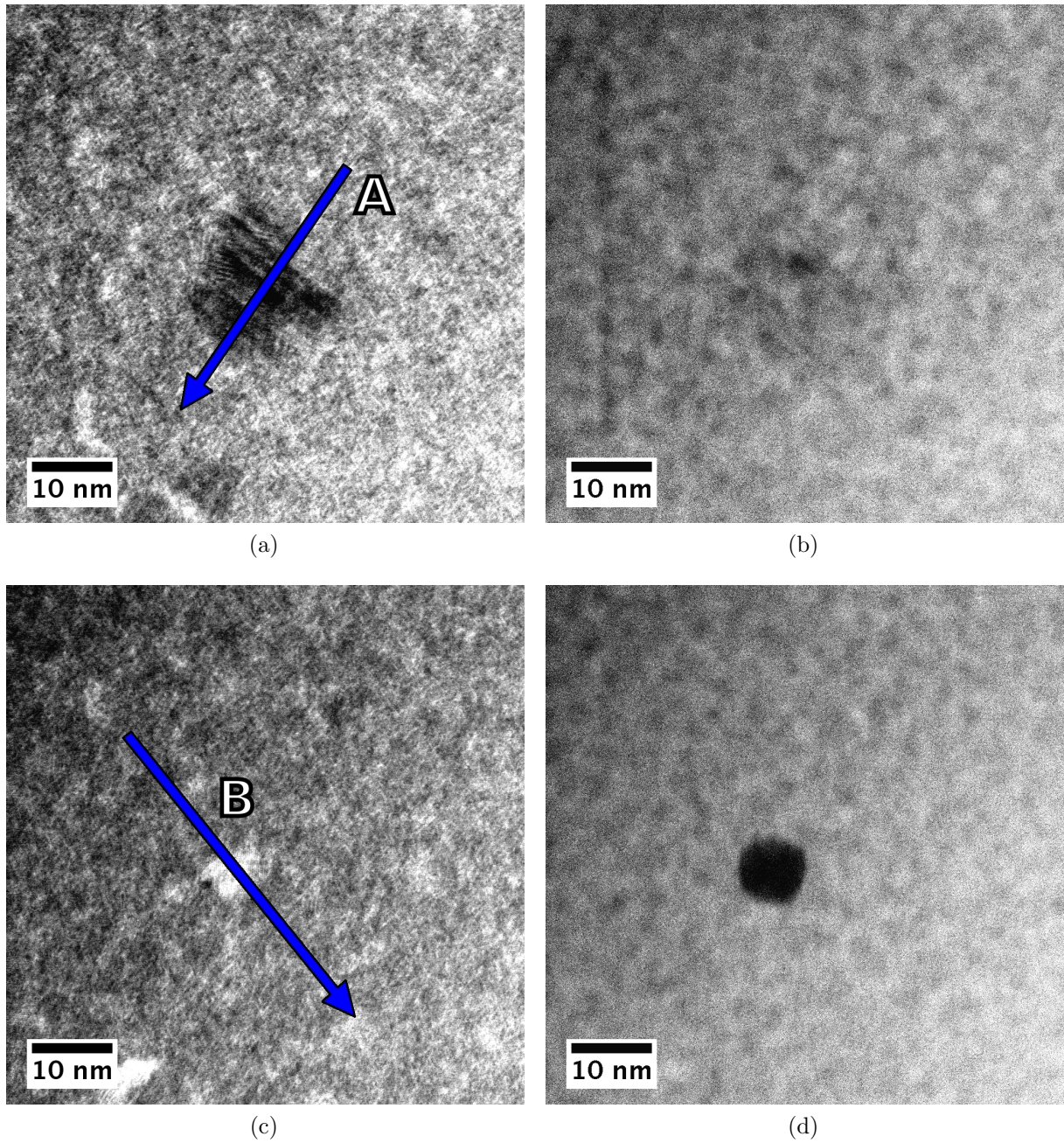


Figure III-3.: Images (a) and (b) show STEM images of nanocrystal A whereas images (c) and (d) display STEM images of nanocrystal (B). The ADF images ((a),(c)) and the HAADF images ((b),(d)) are acquired simultaneously for each nanocrystal. The EELS scan lines and the scan directions are indicated in the ADF images. Nanocrystal A has a very weak contrast to the surrounding amorphous matrix in the HAADF image (b). On the contrary, nanocrystal B reveals strong negative contrast to the amorphous matrix in HAADF image (d).

3.3. Specimen Co3Ti_I4

For specimen Co3Ti_I4 only electron high energy loss spectra are taken at each line scan. In return a higher number of line scans are acquired across nanocrystals than the number acquired at specimen Co3Ti_I3. Here EELS line scans of 8 different nanocrystals are evaluated. Both, the line scans and the corresponding nanocrystals are labeled with (I) to (VIII). Note that I and II correspond to the same line scan that is acquired across two nanocrystals which are separated by an amorphous matrix.

An image of the amorphous region with embedded nanocrystals IV to VII is shown in fig.III-4. Depending on their orientation relative to the focused, incident electron beam, the nanocrystals can reveal positive or negative contrast to the amorphous phase in images based on diffraction contrast.

3.4. Specimen thickness

In this work the specimen thickness is derived from the electron low energy loss spectroscopy data of specimen Co3Ti_I3. Three related calculation methods are compared for the data of line scan A. The results and ranges of validity are set in contrast to each other for these methods.

3.4.1. Log-ratio method & Malis et al. parametrization

This method is based on (eq.II-13) to derive the reduced thickness $p = t/\lambda$ and on the Malis et al. parametrization [23] (eq.II-19) for the total inelastic mean free path λ .

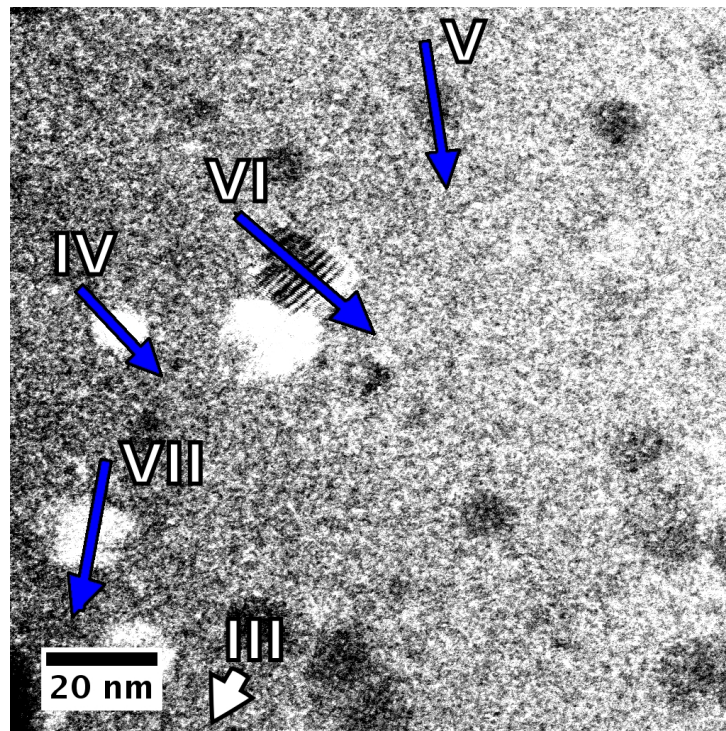


Figure III-4.: ADF image of an amorphous region containing nanocrystals in specimen Co3Ti_I4. The EELS scan lines across the nanocrystals IV to VII and the scan directions are indicated. Nanocrystal III is located near the displayed region at about 50 nm in the direction given by a white arrow.

III. Results & discussion

In our experimental setting we used an acceleration voltage of 300 kV instead of the 100 kV acceleration voltage at which the parametrization was derived. Thus a relativistic scattering angle dependence is used for the calculation even though the error which would occur otherwise is suppressed in a logarithmic term. This changes the logarithmic term in eq.II-13 from $\ln(2\beta E_0/E_m)$ to $\ln(2\gamma\beta F E_0/E_m)$.

The reduced thickness p is calculated from eq.II-13 for every position at the EELS line scans. Therefore, the energy loss integration of the acquired EELS line scans was carried

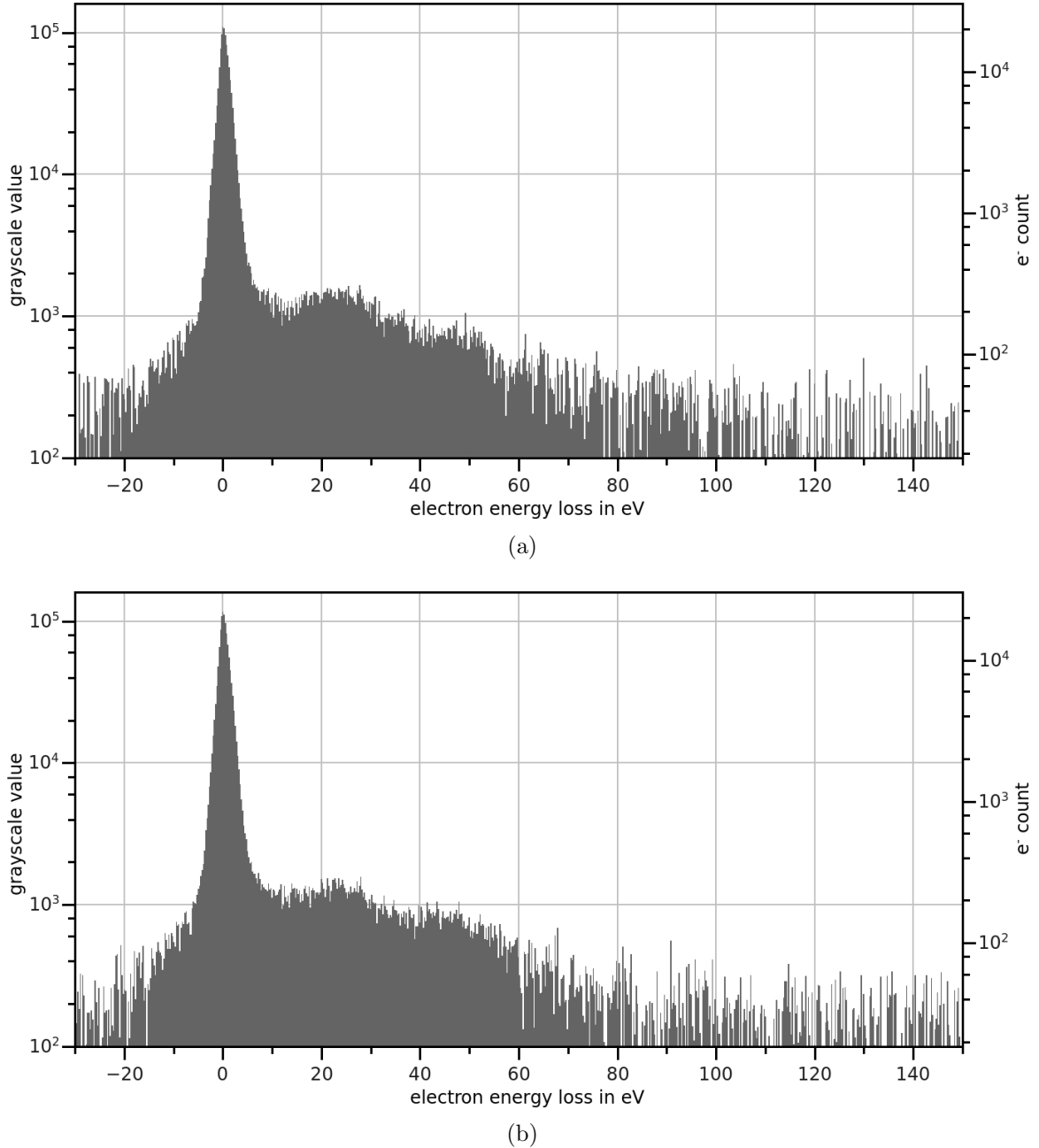


Figure III-5.: Electron low energy loss spectrum at one scan position at nanocrystal A (a) or nanocrystal B (b). A is assumed to be a nanocrystal of the titanium-cobalt alloy whereas B is assumed to be an oxide particle. Background noise dominates the spectra at energy losses $E \gtrsim 100$ eV in spectrum (a) and at energy losses $E \gtrsim 80$ eV in spectrum (b). Intensities are displayed in a logarithmic scale in form of grayscale values and in form of electron counts.

out with the image processing software Fiji [30] and the "Cornell Spectrum Imager" plugin [31] like discussed in section II-7.5. The energy loss integrated intensity of the zero-loss peak I_0 is obtained from a zero-loss peak image itself. The process to separate the zero-loss peak from the low loss spectrum is discussed in section II-7.3. To determine the integrated intensity I of the whole energy loss spectra, only the low energy loss region need to be considered. Above approx. 100 eV energy loss the intensities in the energy loss spectra are neglectable small as shown schematically in fig.II-5 and the error due to the background noise would increase in the integrated spectra (see fig.III-5). The energy loss integration limits for line scan A to D are shown in tab.III-1.

In general a remarkable change of the calculated reduced thickness along the line scan positions and especially at the positions of the nanocrystals could not be observed. These values are already proportional to the specimen thickness values that are shown in fig.III-9 for all scan positions of each line scan. Therefore, it is valid to specify the mean reduced thickness and the mean specimen thickness for each line scan, respectively. This results are shown in tab.III-2 for the the Malis et al. parametrization of λ .

The nanocrystals are embedded inside the amorphous phase of the specimen and they are not located on top of a specimen surface.

	lower energy loss limit in eV	upper energy loss limit in eV
zero-loss I_0	-26	34
low loss I	-26	100

Table III-1.: Integration limits in the low loss spectra for the integrated intensities I and I_0 .

The HAADF images of nanocrystals A, C and D indicate that the chemical composition of these nanocrystals is similar to that of the amorphous phase, if the influence of the surrounding amorphous matrix on the contrast of the nanocrystals is neglected. So the chemical composition of the amorphous phase with 25 at.% titanium and 75 at.% cobalt can be used to calculating the effective atomic number Z_{eff} . A value of 34.5 is obtained for Z_{eff} by eq.II-20. High tension and collection semi-angle β are given in tab.II-3.

A value of of 102 nm $\pm$ 15 nm is deduced for the inelastic mean free path.

A non relativistic angle dependence in the calculation would still lead to a similar value of 99 nm $\pm$ 15 nm.

mean values:	line scan A	line scan B	line scan C	line scan D
reduced thickness p	$0.174 \pm \begin{smallmatrix} 0.016 \\ 0.007 \end{smallmatrix}$	$0.149 \pm \begin{smallmatrix} 0.006 \\ 0.012 \end{smallmatrix}$	$0.244 \pm \begin{smallmatrix} 0.018 \\ 0.023 \end{smallmatrix}$	$0.188 \pm \begin{smallmatrix} 0.025 \\ 0.015 \end{smallmatrix}$
thickness t in nm	$17.8 \pm \begin{smallmatrix} 2.7 \\ 0.7 \end{smallmatrix}$	$15.2 \pm \begin{smallmatrix} 2.3 \\ 1.2 \end{smallmatrix}$	$24.9 \pm \begin{smallmatrix} 3.8 \\ 2.3 \end{smallmatrix}$	$19.2 \pm \begin{smallmatrix} 2.9 \\ 1.5 \end{smallmatrix}$

Table III-2.: Mean values of p and t for each EELS line scan of specimen Co₃Ti₁₃. The t values are derived using the Malis et al. parametrization.

Calculating the error values:

Reduced thickness values are calculated in addition using energy loss integration limits of 80 eV and 120 eV for I . The plasmon intensities in the low energy loss spectra are already decreased for both of these integration limits. The so obtained p values let one estimate the sensitivity of p to the integration limit in the low energy loss spectrum. The results show that the mean difference between p values calculated with 100 eV and 80 eV or 120 eV energy loss limits are higher than the standard deviation of the mean p values at each line scan. Therefore, the error values for p given in tab.III-2 are derived by the differences between mean p values. The difference between the mean p calculation at 100 eV and 80 eV integration limit for I yield the upper error value and the difference between the mean p calculation at 120 eV and 100 eV integration limit for I yield the lower error value.

Examples of measured maximal error values of 10% and 15% are given for the Malis et al. λ parametrization in [22]. These systematic error values are derived for an acceleration voltage of 100 kV. It is pointed out that this parametrization of λ leads to an underestimation of λ and t in most cases. Here a positive (systematic) error of 15% is assumed for λ . This leads to a propagated positive uncertainty of t . Note that the uncertainty is only valid if the parametrization of λ is also valid. The negative error value of t is given by the propagated negative uncertainty arising from the negative systematic error of the mean p value.

3.4.2. Direct determination of the absolute thickness

This method is based on eq.II-15 for a direct calculation of the specimen thickness t . By directly calculating the specimen thickness and comparing the result to the parameterized formula and the log-ratio method, the validity of the parameterization for the high acceleration voltage of 300 kV could be verified. Because λ is related to t via p , a comparison of t values is equal to a comparison of λ values. Mean absolute thickness values are calculated by truncated mean low loss spectra and by mean zero-loss peak subtracted spectra for line scans A to D. Averaging the spectra and calculating the specimen thickness or calculating the specimen thickness for each spectrum and then taking the mean value lead to equal results for the considered precision.

In general the energy loss spectrum contains also a plural scattering fraction especially in thicker specimen regions. Above a mass thickness of $p \gtrsim 0.3$ plural scattering effects must be considered for a specimen [22]. The acquired line scans reveal p values lower than 0.3 like shown in tab.III-2. This low values indicate thin specimen regions where plural scattering has a small influence and the energy loss spectrum is a good representation for $S(E)$. For example, fig.III-9.d shows that plural scattering can not be recognized in the atomic concentration results for line scan A.

The software Fiji [30] is used again for processing the line scan image of the low energy loss spectra and numerical integrations are done with the "Cornell Spectrum Imager" plugin [31]. The procedures to obtain the necessary integrals from the images of the measured spectra are discussed in detail in section II-7. Section II-7.2 describes the generation of truncated mean low energy loss spectra and section II-7.3 describes the generation of zero-loss peak subtracted low energy loss spectra which represent $S(E)$. The generation of an integrand image for the integrand in eq.II-15 is mentioned in section II-7.4.

Two fitting functions are considered in the process of subtracting the zero-loss peaks in the measured low energy loss spectra. A Gaussian function and a Pseudo-Voigt function. The fitting results reveal that the Gaussian function is not able to follow the broad tail of the zero-loss peaks like shown in fig.II-8.

The upper energy loss limit is set to 100 eV for integrating the manipulated mean spectra. In addition calculations are done using an integration limit of 120 eV energy loss to estimate the systematic error arising from this integration limit. Here the parameters E_0 and β are taken from tab.II-3 and the optical refractive index n is set to infinity. The obtained thickness values are then corrected for plural scattering by a factor C given in eq.II-17. Like discussed in section II-6.2 a thickness value of $\Delta t = 8$ nm is subtracted from the obtained mean specimen thickness for the calculations based on a mean $S(E)$ image. The final results are shown in tab.III-3 for calculations with and without plural scattering correction.

thickness t in nm	line scan A	line scan B	line scan C	line scan D
thickness value calculated from mean truncated spectrum				
without plural scattering correction	16.1 ($\pm$) 0.4	12.9 ($\pm$) 0.3	22.6 ($\pm$) 0.8	17.2 ($\pm$) 0.5
plural scattering corrected	15.3 ($\pm$) 0.3	12.4 ($\pm$) 0.2	21.0 ($\pm$) 0.6	16.3 ($\pm$) 0.4
thickness value calculated from mean single scattering distribution $S(E)$				
without plural scattering correction	16.3 ($\pm$) 0.4	11.9 ($\pm$) 0.3	25.9 ($\pm$) 0.8	17.8 ($\pm$) 0.5
plural scattering corrected	15.1 ($\pm$) 0.3	11.0 ($\pm$) 0.2	23.6 ($\pm$) 0.6	16.4 ($\pm$) 0.4

Table III-3.: Mean thickness values derived from truncated mean spectra or zero-loss peak subtracted single scattering distributions $S(E)$ by eq.II-15 for line scans A to D. An error is estimated from additional calculations using a 120 eV integration window instead of the 100 eV integration window.

Fig.III-6 shows a comparison between specimen thickness values which are calculated by eq.II-15 and between specimen thickness values which are calculated by the log-ratio method and the Malis et al. parametrization. Here the Malis et al. parametrization leads to an overestimation of the specimen thickness when compared to the direct thickness calculations. This is in contrast to literature [22] where an even higher underestimation of the specimen thickness is predicted for higher acceleration voltages by this parametrization (see fig.II-6). The differences in t between the parameterized thickness calculation and the plural scattering corrected direct thickness calculations yield error values between these methods. The so obtained relative error values for the parameterized thickness calculation are about 15% to 18% at the four line scans.

Line scan B reveals a higher relative error of about 28% if the mean $S(E)$ is considered for the error calculation. For line scan B a direct thickness calculation based on the mean $S(E)$ leads to a lower specimen thickness as expected from the direct calculation based on the truncated mean low energy loss spectrum. This deviation could be explained by the low specimen thickness of 11.0 nm ($\pm$) 0.2 nm obtained by the calculation based on the mean $S(E)$ image and eq.II-15. The method of subtracting $\Delta t = 8$ nm from the specimen thickness to correct for surface plasmon losses is only valid for a specimen thickness of $t \gtrsim 10$ nm. Thus, the low t value could already mean that a lower value should be considered for Δt which would lead again to a higher final value for the specimen thickness. A relative error of about 18% is obtained for the parameterized thickness if the truncated mean low energy loss spectrum is considered for the error calculation at line scan B.

To summarize these results:

The applied acceleration voltage of 300 kV leads to a mean deviation of about 17% for the specimen thickness calculated by the Malis et al. parametrization which was developed at 100 kV acceleration voltage to the direct thickness calculation. The deviation is comparable to error values of 10% to 15% given in literature for the Malis et al. parametrization [22] and for 100 kV acceleration voltage. It should be noted that the Malis et al. parametrization leads to an underestimation of the specimen thickness in most cases according to literature. But here the obtained t values are higher when compared to the direct calculations.

Plasmon losses in the sample are below approx. 100 eV energy loss. The kinetic energy of the accelerated electrons is 4 magnitudes higher and so all plasmons in the sample can already be exited. Therefore, a 3 times higher acceleration voltage should not change the energy loss spectrum.

3.4.3. Log-ratio method & Iakoubovskii et al. parametrization

This method is based on eq.II-13 and on the Iakoubovskii et al. parametrization given in eq.II-22 for the total inelastic mean free path. The use of a higher acceleration voltage of 300 kV should not have a significant influence on the electron low energy loss spectrum as motivated before. It can be assumed that an influence on the Iakoubovskii et al. parametrization that is derived at 200 kV is lower than on the Malis et al. parametrization that is derived at 100 kV.

The relative high value of 20.5 mrad for the EELS collection semi-angle β at an acceleration voltage of 300 kV violates the limiting condition for β given by eq.II-21. This means that the dipole approximation for the scattering angle dependence is not valid anymore and

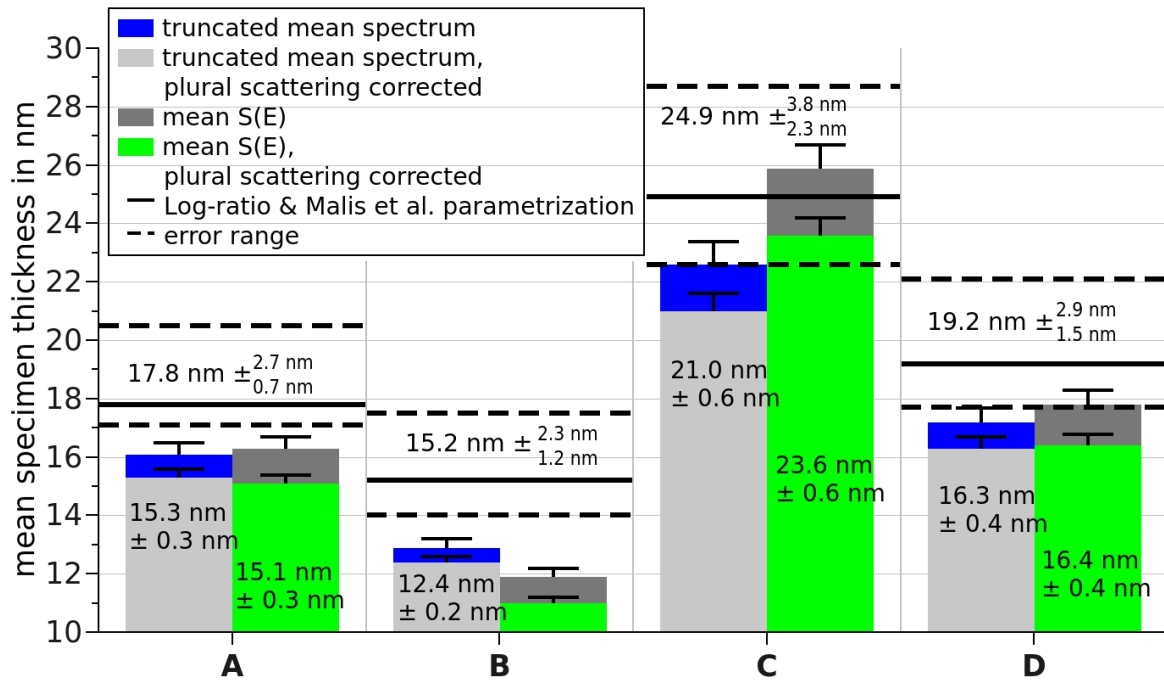


Figure III-6.: Comparison of mean specimen thickness values derived from the log-ratio method and Malis et al. parametrization and derived from direct thickness calculations by eq.II-15 for line scans A to D. Truncated mean spectra or zero-loss peak subtracted single scattering distributions $S(E)$ are used for a direct calculation.

that eq.II-19 is not a good method to calculate λ . In [22] upper limits for β of 15 mrad at 100 kV acceleration voltage and 10 mrad at 200 kV acceleration voltage are given, if eq.II-19 should be valid. Because the dipole approximation is applied in both, comparison of the Malis et al. parametrization of λ and the direct calculation of the specimen thickness by eq.II-15 is still valid, even if the derived thickness values themselves are not valid.

Iakoubovskii [27] derived a parametrization for the inelastic free mean path where the limiting condition for β does not occur. This calculation method for λ is not implemented yet in the EELS package of the GMS software [29]. The values for the two semi-angles α and β used in eq.II-22 are listed in tab.II-3. The saturation factor θ_C is set to 20 mrad and the density ρ is set to a value of 7.81 g/cm³ for Co₃Ti. This value is taken from the AtomWork database [14], [15].

A value of 129 nm $\pm$ 22 nm could be derived for the total inelastic mean free path λ by the Iakoubovskii et al. parametrization.

The final mean specimen thickness at line scans A to D is given in tab.III-4. The values for p that are discussed in section III-3.4.1 are displayed again in the table. Fig.III-9 shows specimen thickness values for every position on the line scans. In addition mean specimen thickness values are calculated for line scan positions at the corresponding nanocrystals only. These line scan positions are selected from ADF images and the titanium to cobalt atomic concentration ratio profiles in fig.III-9. The mean t values derived at the nanocrystals are displayed in fig.III-14.

mean values:	line scan A	line scan B	line scan C	line scan D
reduced thickness p	$0.174 \pm \begin{smallmatrix} 0.016 \\ 0.007 \end{smallmatrix}$	$0.149 \pm \begin{smallmatrix} 0.006 \\ 0.012 \end{smallmatrix}$	$0.244 \pm \begin{smallmatrix} 0.018 \\ 0.023 \end{smallmatrix}$	$0.188 \pm \begin{smallmatrix} 0.025 \\ 0.015 \end{smallmatrix}$
thickness t of: line scan, in nm	$22.5 \pm \begin{smallmatrix} 2.0 \\ 3.9 \end{smallmatrix}$	$19.2 \pm \begin{smallmatrix} 1.5 \\ 3.3 \end{smallmatrix}$	$31.5 \pm \begin{smallmatrix} 2.3 \\ 5.4 \end{smallmatrix}$	$24.3 \pm \begin{smallmatrix} 3.3 \\ 4.1 \end{smallmatrix}$
thickness t of: nanocrystal, in nm	$22.6 \pm \begin{smallmatrix} 2.0 \\ 3.9 \end{smallmatrix}$	$22.1 \pm \begin{smallmatrix} 1.6 \\ 3.5 \end{smallmatrix}$	$30.6 \pm \begin{smallmatrix} 2.3 \\ 5.4 \end{smallmatrix}$	$23.8 \pm \begin{smallmatrix} 3.3 \\ 4.1 \end{smallmatrix}$

Table III-4.: Final mean values of p and t for each EELS line scan of specimen Co₃Ti-I3. The t values are derived using the Iakoubovskii et al. parametrization.

Nanocrystal B has a different chemical composition than the chemical composition of the amorphous phase. Due to the strong negative contrast in the HAADF image (fig.III-3.d) it is thought to be an oxide particle. The fact that nanocrystal B is a titanium oxide particle is discussed in the next section III-3.5. The diameter of the nanocrystal is about one third of the specimen thickness as shown in fig.III-14. Thus, a weighted mean density ρ is used to calculate λ for line scan positions at nanocrystal B. Density values for titanium oxides are taken again from the AtomWork database [14], [15]. Here a mean density of 4.09 g/cm³ is obtained from the rutile, brookite and anastasia phase of titanium oxide. A value of 6.57 g/cm³ is obtained for ρ and a value of 135 nm is calculated for λ using a weighting of 1/3 oxide to 2/3 matrix. This leads to a thickness increase of about 3 nm at the position of the oxide. Note that the systematic errors given in tab.III-4 are of the same size as this variation and that the SD of the mean t value is with 1.5 nm half as large in size as this variation in t . A particle diameter of 6.5 nm $\pm$ 1 nm could be measured from profiles in the ADF and HAADF images. Therefore, the oxide particle seems to be embedded in the matrix and not located on its surface. This observation is in agreement

with the HAADF image. If the oxide particle would be located on top of the specimen's surface, it should reveal a positive contrast to the surrounding matrix due to the thickness contrast in the HAADF image. But this behavior could not be observed here.

Calculating the error values:

In [22] examples for error measurements of the Iakoubovskii et al. parametrization are given for an acceleration voltage of 200 kV. They list a maximal deviation of 10% between the parametrized λ values and the measured values. The measurements are shown in fig.II-6. The error in the Iakoubovskii et al. formula leads to an overestimation of the total inelastic mean free path. The mean relative error value of 17% between the Malis et al. parametrization and the direct t calculation that is discussed in the previous section III-3.4.2 could be interpreted as an calculation error due to the higher acceleration voltage. Taking a conservative point of view, an equal error value is assumed for the Iakoubovskii et al. parametrization. In accordance to literature [22] and to the observation in section section III-3.4.2 this error can be assumed to be negative. If the systematic error in p is neglected, a relative error of t equals a relative error in λ by eq.II-13. The negative error of 17% in λ leads to a negative propagated uncertainty of the mean t values. In tab.III-4 the positive error values for the mean t values are given by a propagated uncertainty due to the systematic error in p .

3.5. Chemical composition

Because the studied alloy is a cobalt-titanium alloy, the nanocrystals embedded in the amorphous phase should also contain the elements cobalt and/or titanium. Information on the chemical composition of the nanocrystals is derived from EELS high loss spectra by the ratio of the integrated core loss intensities of the elements titanium, cobalt and oxygen. In addition, the chemical composition of the amorphous matrix surrounding the nanocrystals is known from EDX measurements that are received from the NCEM as discussed in section III-3.1. Thus, atomic concentrations of titanium (c_{Ti}), cobalt (c_{Co}) and oxygen (c_O) can be calculated at the nanocrystals.

The consideration of the oxygen concentration in the specimen complicates the comparison of absolute atomic concentrations of titanium and cobalt and the comparison of these absolute concentrations to literature values. Here scaled concentrations (c^s) are given to specify atomic concentrations which neglect one of the three elements. Thus, using $c_{Ti} = c_{Ti}^s (1 - c_O)$ the equation $c_{Ti}^s + c_{Co}^s = 1$ holds for instance if no other elements are present in the specimen. The titanium to cobalt atomic concentration ratio is independent of this difference in declaration.

In the high energy loss spectra titanium, cobalt and oxygen core loss edges are recognized due to their energy loss values, their relative energy loss distances and their shape by comparing with literature values. Therefore, the Gatan company provides an EELS edge database that can be downloaded in form of an iPhone App for free at their homepage [28]. An EELS Atlas is build by Ahn and Krivanek [34]. The measured energy loss values (E_k) of the steepest rise of the edges are displayed in tab.III-5 for line scan A and compared to literature values. These values are measured (and aligned) by the Fiji script 1.b displayed in section VI-1 and discussed in section II-7.1.2. In fig.III-7 the line scan data of electron high energy loss spectra is shown for line scan VIII. The core loss edges of the three elements are indicated in the figure.

	Ti L3 edge	O K edge	Co L3 edge
width of Δ in eV	46.00	53.00	78.00
width of δ in eV	50.00	21.00	120.00
distance $d_{\delta k}$ in eV	6.25	3.50	5.25
steepest rise E_k in eV	458.25	533.00	779.75
steepest rise E_k in pixel units	354	653	1640
Gatan EELS database: E_k in eV	456.00	532.00	779.00

Table III-5.: Integration intervals (Δ) and fitting intervals for background subtraction (δ) at the considered titanium, oxygen and cobalt core loss edges. The energy loss distance ($d_{\delta k}$) between the upper limit of δ and the steepest rise E_k of the edge is displayed. Values for the steepest rise of the edges are given for line scan A as an example. The values correspond to the first spectrum in the line scan image and can be compared to given literature values [28]. The horizontal pixel coordinate of E_k in the high loss spectra image is also displayed.

3.5.1. Plural scattering in the high energy loss spectra

The small values obtained for the reduced thicknesses p (tab.III-4) indicate that the plural scattering contributions in the high energy loss spectra are small. Like already mentioned they satisfy the condition $p \lesssim 0.3$ for "thin" specimens [22]. To check the influence of

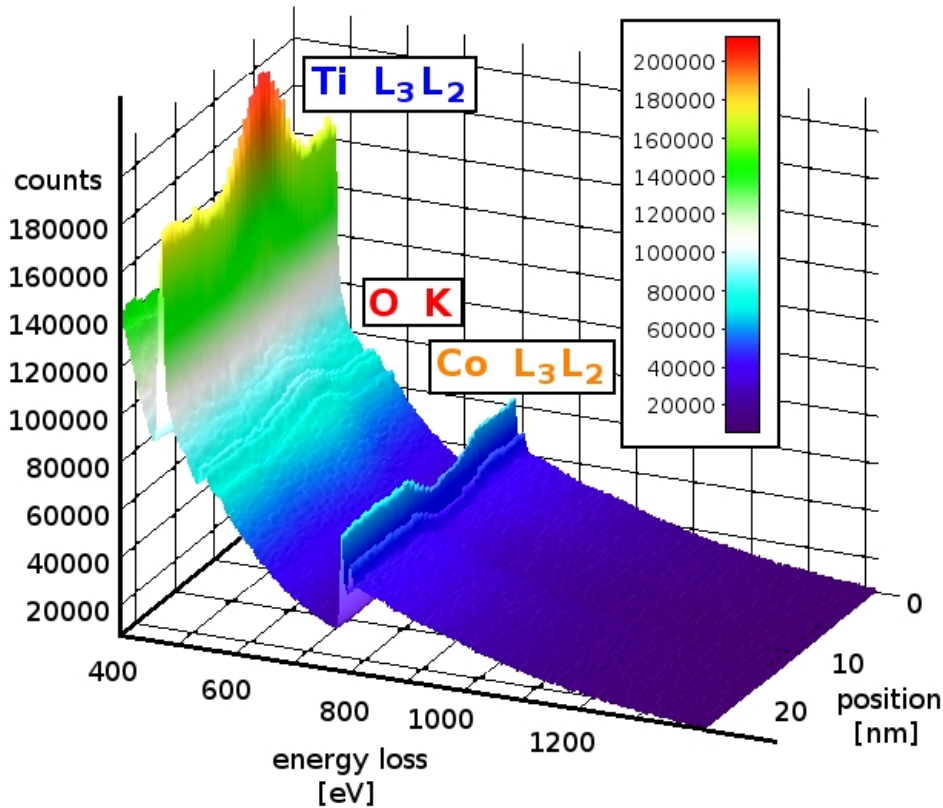


Figure III-7.: Electron high energy loss data for line scan VIII. The 3 dimensional plot shows the intensity values in dependence of the energy loss and the scan position. There is a significant higher signal coming from the titanium and oxygen core loss edges and a decrease of the cobalt signal at the position of the nanocrystal.

plural scattering on the high energy loss spectra, the core loss edges of titanium, cobalt and oxygen are deconvoluted as described in section II-7.6 for line scan C. Line scan C reveals the highest p value of $0.244 \pm \text{max. } 0.023$ for the four line scans at specimen Co3Ti_I3. In addition a deconvolution is applied on line scan A.

Since high and low energy loss spectra are acquired separately the Fourier Ratio method is applied to deconvolve the high energy loss spectra. This method is discussed in section II-5.1 and implemented in a DigitalMicrograph script as described in section II-7.6. The application of zero-loss peaks that are severed from the low energy loss spectra is compared to the application of a Gaussian function which is fitted to the zero-loss peaks in the deconvolution process. They are used to estimate the amount of plural scattering in the high energy loss spectra and to reduce the additional noise produced in the deconvolution process. These two methods are compared for line scan C in fig.III-8. Both methods reveal a decrease of the intensity in the tails of the edges due to the plural scattering subtraction in these regions. Setting the ROI for the Gaussian fit at the FWHM of the zero-loss peak leads to a smoother deconvolved profile and to a general decrease of intensity compared to the original intensity profiles and compared to the deconvolution method using a severed zero-loss peak. This behavior can be explained by the strong intensity decrease at the Gaussian fit's tails compared to the intensity decrease at the measured tails of the zero-loss peak. Thus, more of the high energy frequencies in Fourier space are cut off making the deconvolved profile smoother. The missing intensities in the fitted peaks leads to the general decrease of intensity for the deconvolved edges.

The removal of plural scattering contributions in the tails of the core loss edges leads to lower integrated intensities for the three elements. A change in the scan position dependence of integrated intensity profiles or in the resulting titanium to cobalt concentration ratios due to the deconvolution could not be observed like shown in fig.III-9.

Plural scattering seems to contribute here in equal amount to all elements and scan positions, independent of the presence of an embedded nanocrystal at some scan positions.

3.5.2. Integrated intensity & titanium concentration

The energy loss intervals for integrating core loss intensities and the fitting intervals for subtracting background in the high energy loss profiles are displayed in tab.III-5. The interval values presented there are used for all line scans A to D and I to VIII of the two specimens Co3Ti_I3 and Co3Ti_I4. They are set relative to the energy loss value E_k of the aligned steepest rises of a core loss edge in the spectra of a particular line scan. The width of the energy loss intervals is discussed in section II-5. Note that the width of the fitting interval is smaller than the suggested 10% of E_k for the oxygen edge. The presence of an additional feature in the high energy loss spectrum between the titanium and the oxygen core loss peaks would influence the background subtraction of the oxygen edge. This feature may be recognized in form of a faint buckling at the background region in front of the oxygen edge in fig.III-8.a. The energy loss integration in the images of high energy loss spectra is performed in Fiji [30] with the Cornell Spectrum Imager plugin [31] as discussed in section 7.5. Fig.III-9 and fig.III-10 show the resulting integrated intensity profiles for the elements titanium, cobalt and oxygen at all line scan positions of the line scans A to D, respectively.

A titanium to cobalt mean integrated intensity ratio (I_k^{Ti}/I_k^{Co}) is calculated for line scan positions at the amorphous matrix surrounding a nanocrystal. This mean value is used to obtain the titanium to cobalt atomic concentration ratio (c_{Ti}/c_{Co}) by eq.II-2 at all line scan positions of one line scan. The line scan positions for calculating a mean I_k^{Ti}/I_k^{Co} ratio are selected by comparing the corresponding ADF image, HAADF image and integrated intensity profile. Only those line scan positions are considered for the calculation where no

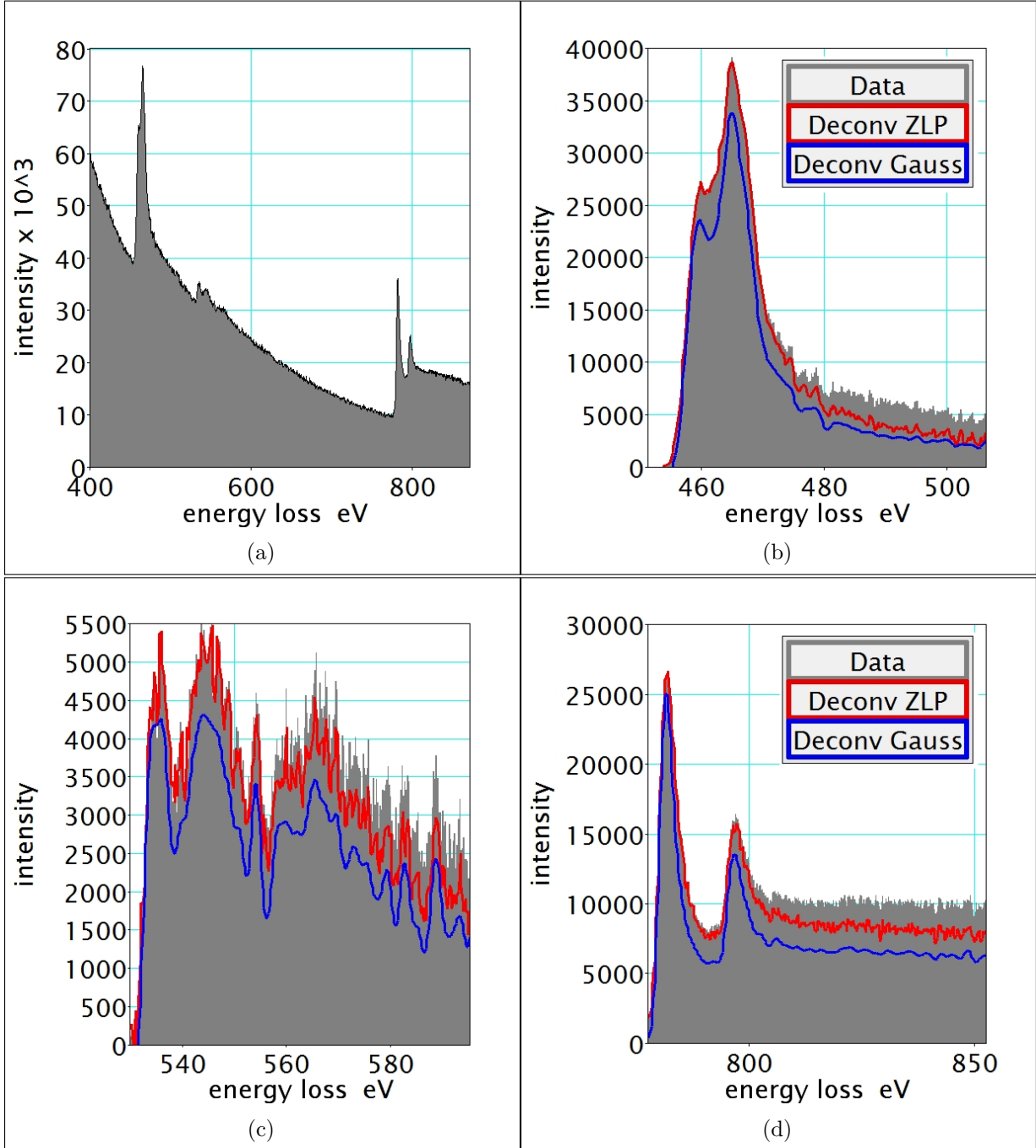


Figure III-8.: Image (a) shows one high energy loss spectrum of line scan C for a scan position at the nanocrystal. The deconvoluted core loss edges of the spectrum are displayed in (b) for the titanium edges, in (c) for the oxygen edge and in (d) for the cobalt edges. The background subtracted edges are printed in gray. Red curves show edges which are deconvoluted by using the zero-loss peaks to scale the plasmon intensities and to reduce noise (see eq.II-4). Blue curves show edges which are deconvoluted by using a Gaussian function instead.

nanocrystal is present. In addition, mean integrated intensity profiles are derived for line scan positions at the nanocrystals. There the values are taken only from scan positions of similar integrated intensities at the center of the nanocrystals to avoid an influence of the shape of the nanocrystals. Thus, a mean value can be calculated for c_{Ti}/c_{Co} at each nanocrystal. These mean values are given in tab.III–6 in form of scaled titanium concentrations.

Fig.III–9 and fig.III–10 show c_{Ti}/c_{Co} in dependence of the scan position for line scan A to D. The mean values are displayed again in form of scaled titanium concentrations in fig.III–14 for line scans of specimen Co3Ti.I3 and in fig.III–15 for line scans of specimen Co3Ti.I4. The derived chemical concentrations of nanocrystals in specimen Co3Ti.I3 are based on the assumption that a measurement of c_{Ti}/c_{Co} at the amorphous matrix yields the same result for specimens Co3Ti.I3 and Co3Ti.I4. The validity of this condition is shown in section III-3.5.6 by an EELS analysis using Gatan software.

scaled titanium concentrations of nanocrystals at specimen Co3Ti.I3 in at.%			
nanocrystal A	nanocrystal B	nanocrystal C	nanocrystal D
30.1 ± 0.7	72.1 ± 1.1	25.6 ± 1.0	31.9 ± 2.1
30.1 ± 0.7	(deconvolved)	25.7 ± 0.9	(deconvolved)

scaled titanium concentrations of nanocrystals at specimen Co3Ti.I4 in at.%			
nanocrystal I	nanocrystal II	nanocrystal III	nanocrystal IV
34.9 ± 1.0	34.8 ± 1.0	31.6 ± 0.7	28.3 ± 1.3
nanocrystal V	nanocrystal VI	nanocrystal VII	nanocrystal VIII
28.3 ± 0.9	30.1 ± 1.0	30.5 ± 0.9	58.1 ± 1.4

Table III–6.: Chemical composition of the nanocrystals derived by eq.II–2. The mean c_{Ti}/c_{Co} values at the amorphous matrix which were used to obtain these results are discussed in section III-3.5.3. Scaled titanium concentrations are calculated by neglecting the oxygen concentration. The given error values correspond to propagated uncertainties which are discussed in section III-3.5.4.

In eq.II–2 exact two measurement positions are compared for the total transmitted intensity I of eq.II–1 to cancel out. If one wants to calculate mean atomic composition ratios instead of atomic composition mean ratios, I has to be considered again for each measurement position that contributes to the mean values. Thus, the correct mean integrated intensities of high energy core loss edges would yield weighted mean values of the form

$$I_k^{\bar{I}A} = \frac{1}{N_{\bar{I}}} \sum_i^{N_{\bar{I}}} \frac{I_k^{iA}}{I^i} \quad (\text{III–1})$$

for a spatial region $\bar{I}$, element A and $N_{\bar{I}}$ averaged line scan positions. Here I^i is given by the integrated intensity in the low energy loss spectrum at line scan position i . The relative differences of I^i values are smaller than approximately 7% for each line scan at specimen Co3Ti.I3. Taking a double integrated intensity ratio at both averaged measurement positions in eq.II–2 reduces the influence of the weighting further.

Atomic concentration ratios are calculated in addition by neglecting the weighting of eq.III-1 in order to obtain the errors arising from this simplification for line scans at specimen Co3Ti-I3. The derived errors occur in a decimal digit that is smaller than the given decimal digit for the atomic concentration ratios and for the derived atomic concentrations. Thus, it is valid to calculate the required mean integrated intensities without the I weighting for EELS line scans of specimen Co3Ti-I4. For this specimen only high energy loss spectra are acquired and therefore the information on the total transmitted intensity is missing.

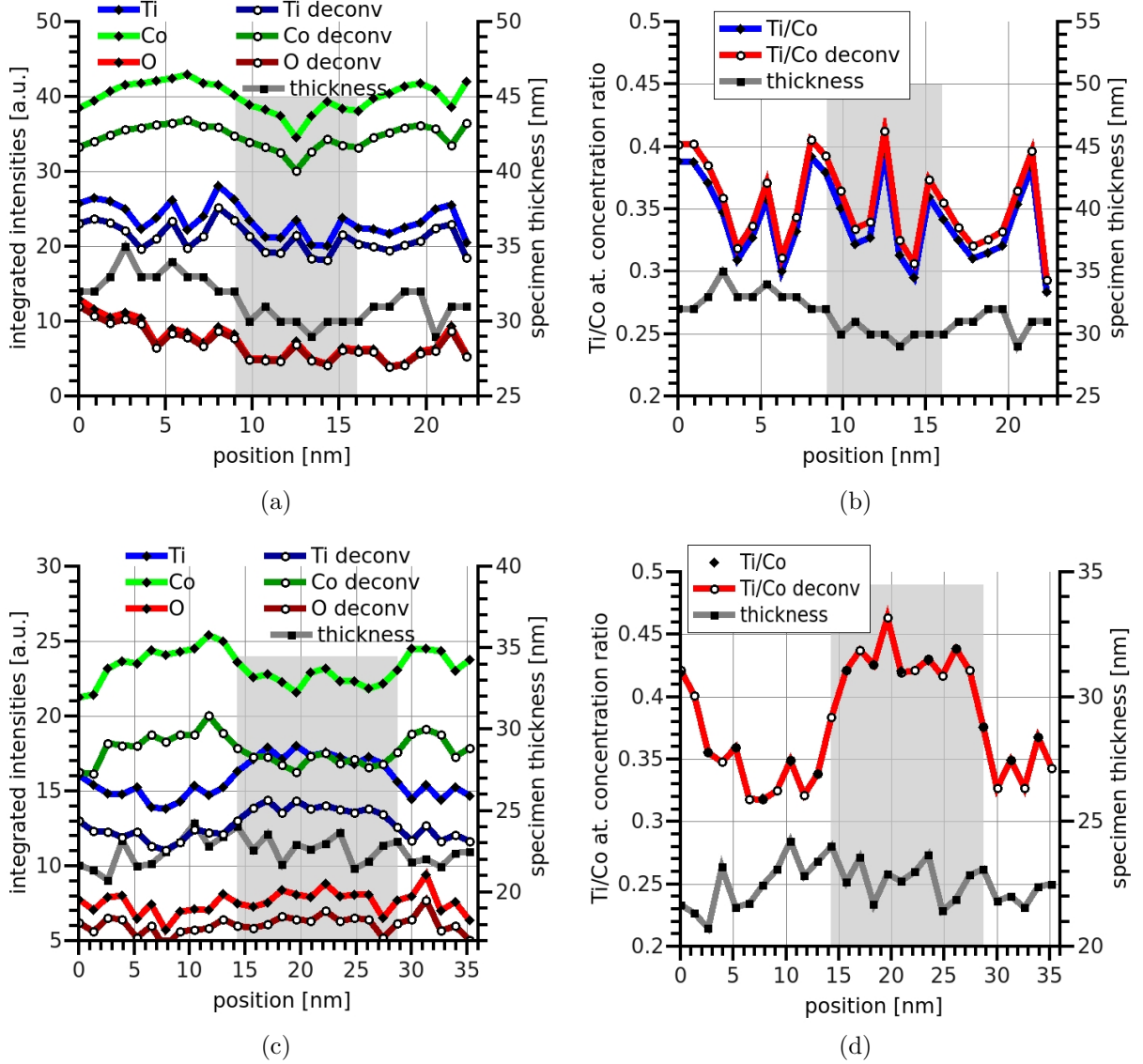


Figure III-9.: Integrated intensity profiles of core loss edges are shown in images (a) and (c). The titanium to cobalt atomic concentration ratios are displayed in images (b) and (d). **Data for line scan C is displayed in (a) and (b) and data for line scan A is displayed in (c) and (d).** The background is colored in gray at the position of a nanocrystal in each profile. The deconvolution changes the integrated intensities in (a) and (c) but the effect on the atomic concentration ratios displayed in (b) and (d) is neglectable. A variation of the titanium to cobalt atomic concentration ratio is uncorrelated to the position of nanocrystal C as shown in (b). But for line scan A an increase of this ratio can be seen in image (d) at the position of nanocrystal A.

III. Results & discussion

Nanocrystals B, D and VIII yield strong negative contrast to the surrounding amorphous matrix in HAADF images. The integrated intensity profiles of line scan B (see fig.III–10.c) and line scan VIII reveal a strong increase of the oxygen and titanium signal and a strong decrease of the cobalt signal at the positions of the nanocrystals. Thus, nanocrystal B and nanocrystal VIII are most likely titanium oxide particles. So the ratio c_{Ti}/c_{Co} and the scaled titanium concentration neglecting the oxygen is not informative for positions at those nanocrystals. In fig.III–11 the number of atoms per unit specimen area at positions (1) relative to a mean value at the amorphous matrix (2) are displayed for each element (A), respectively. These n_a^{1A}/n_a^{2A} ratios are calculated by eq.II–7 using the integrated low energy

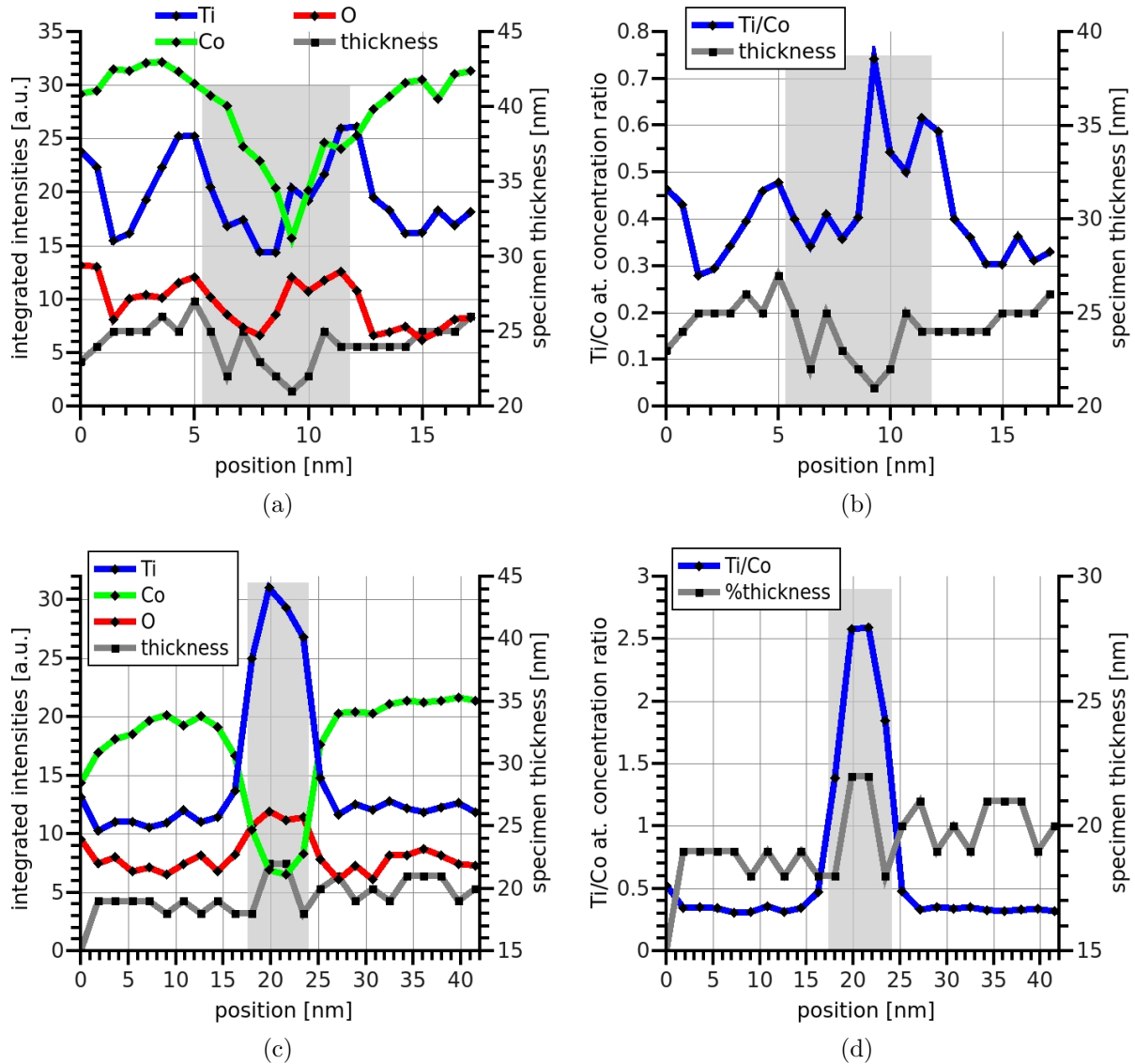


Figure III–10.: Integrated intensity profiles of core loss edges are shown in images (a) and (c). The titanium to cobalt atomic concentration ratios are displayed in images (b) and (d). **Data for line scan D is displayed in (a) and (b) and data for line scan B is displayed in (c) and (d).** The background is colored in gray at the position of a nanocrystal in each profile. An increase of the titanium and the oxygen signal correlates with a decrease of the cobalt signal at the position of the nanocrystal B in image (c). In image (a) this correlation is not as strong as in image (c). Here the oxygen signal reveals variations along the whole line scan and a decrease of the cobalt signal does not clearly match an increase of the titanium signal but rather a decrease of the specimen thickness.

loss intensities for I in case of line scan B. A I_k^{2A}/I^2 ratio of mean intensities is assigned to the amorphous matrix. The I scaling is neglected again for line scan VIII of specimen Co3Ti.I4. Mean atomic concentration ratios could also be calculated by eq.II-7 for each element, respectively. Therefore, the assumptions of same specimen thickness values but different number densities are made between averaged positions at the nanocrystal and averaged positions at the surrounding amorphous phase. The number density of Co_3Ti with a value of $8.38 \cdot 10^{28} \text{ m}^{-3}$ is used for the amorphous matrix. A mean number density of $9.25 \cdot 10^{28} \text{ m}^{-3}$ is assigned to the oxide particles by averaging number densities for the rutile, brookite and anastasia phase of TiO_2 . The literature values of number densities are taken from the AtomWorks database [14], [15].

Now eq.II-8 gives an estimation for the chemical composition of titanium oxide particles by neglecting the element cobalt at the scan position of the nanocrystals. In tab.III-7 the calculated titanium concentrations are displayed. Since TiO_2 has the lowest titanium concentration of possible titanium oxide phases according to literature (AtomWorks database [14], [15]), it agrees the best in chemical composition to nanocrystals B and VIII. Thus, the assumption that nanocrystals B and VIII are TiO_2 particles is valid. Note that the titanium concentration calculated by eq.II-7 and eq.II-8 varies with the number density ratio between the considered specimen positions. Depending on the assumption that nanocrystal B is of anatase or rutile phase, its titanium concentration has a value of $29.1 \text{ at.}\% \pm 2.9 \text{ at.}\%$ or a value of $20.5 \text{ at.}\% \pm 2.8 \text{ at.}\%$, for instance.

Fig.III-10.a shows integrated intensity profiles for line scan D at specimen Co3Ti.I3. A relation between a decrease of the cobalt signal and the oscillations of the titanium and oxygen signals is not obvious in these profiles. The ratios n_a^{1A}/n_a^{2A} are plotted for each element in fig.III-11.a. The profile of $n_a^{1\text{Co}}/n_a^{2\text{Co}}$ agrees well to an intensity profile of the HAADF image along the line scan. It yields the low spatial frequency variation of the grayscale values that corresponds to the strong negative contrast of the nanocrystal relative to the surrounding amorphous matrix in the HAADF image. The ratios of the elements titanium and oxygen coincide in the figure. This fact indicates a constant amount of oxygen relative to the amount of titanium at the observed specimen area. Variations in

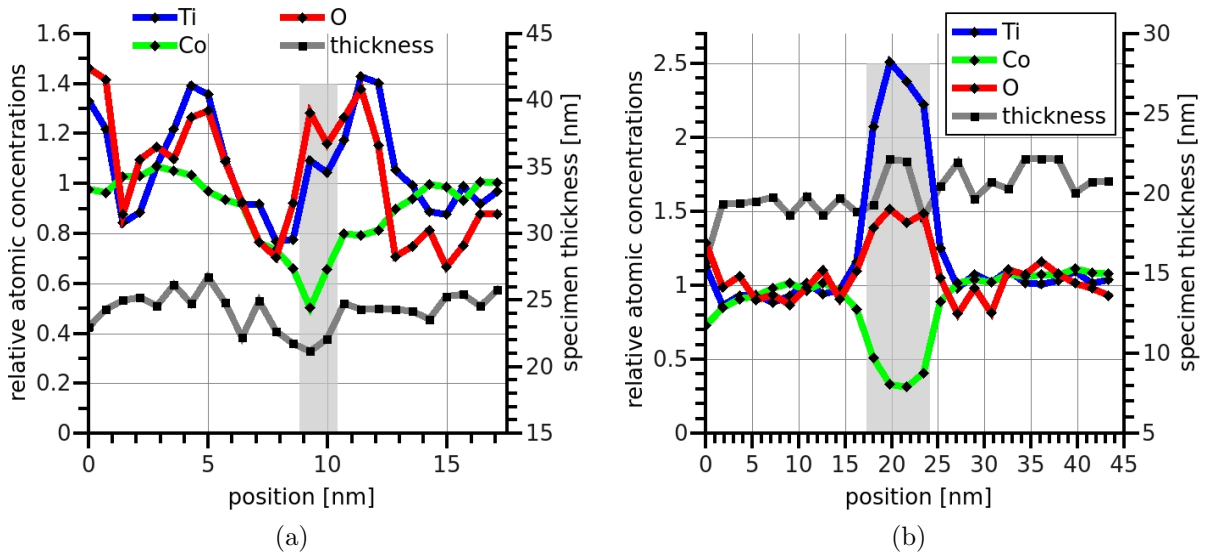


Figure III-11.: Relative number of atoms per unit specimen area for the elements titanium, cobalt and oxygen at line scans D (a) and B (b). The numbers at each line scan position are set relative to mean numbers at the amorphous matrix for each element, respectively.

chemical concentration and in n_a values along the EELS line scan could be related to contrast changes in HAADF images. They are high spatial frequency variations compared to signal changes due to nanocrystals. Contrast oscillations in HAADF images can be seen in fig.III-3.b and fig.III-3.d at areas corresponding to the amorphous matrix for instance. Their size is consistent to the spatial size of oscillations in integrated intensity profiles with wavelength scales between about 5 nm and about 10 nm. These compositional variations at the amorphous matrix are discussed again in section IV-2.3.

Variations of about 5 nm to 10 nm in size can be recognized for the chemical composition or for the number of atoms per specimen area at the amorphous matrix.

The cobalt ratio does not decrease as clearly for nanocrystal D as for nanocrystal B in the line scan profiles of fig.III-11. Therefore, neither the cobalt, nor the oxygen concentration should be neglected in the chemical analysis of nanocrystal D. The deduced chemical composition of nanocrystal B that is shown in tab.III-7 can be used to calculate the mean oxygen concentration in the surrounding amorphous matrix at line scan B. Then the mean oxygen concentration in the amorphous matrix surrounding nanocrystal D can be estimated by the use of tab.III-8 which is discussed in the next section III-3.5.3. Knowing the absolute atomic concentrations of the amorphous matrix let one calculate the absolute atomic concentrations of nanocrystal D by eq.II-2. In fig.III-11.a a small titanium and oxygen peak can be recognized at the line scan position where n_a^{1Co}/n_a^{2Co} has its minimum. Here only two scan positions at those peaks are used to calculate mean values for quantities corresponding to the nanocrystal. The considered scan positions are indicated in the figure. At these scan positions the presence of a titanium oxide particle can be assumed due to the high c_{Ti}/c_{Co} value of the resulting atomic concentrations shown in tab.III-7. The obtained titanium concentration of $13.7 \text{ at.\%} \pm 6.1 \text{ at.\%}$ yields a value of $17.4 \text{ at.\%} \pm 8.1 \text{ at.\%}$ for the scaled titanium concentration by neglecting the cobalt concentration again. A restriction to just two line scan positions at nanocrystal B leads to huge error values for the calculated mean concentrations of the nanocrystal. The low c_{Ti}^s value compared to the value for TiO_2 could be explained by a high oxygen concentration in the material that surrounds nanocrystal D in the direction of the electron beam.

results based on eq.II-8	c_{Ti}^s in at.%	mean c_{Ti}^1/c_{Ti}^2	mean c_o^1/c_o^2
nanocrystal B	24.3 ± 2.8	2.214 ± 0.070	1.332 ± 0.057
nanocrystal VIII	27.9 ± 1.7	1.583 ± 0.020	1.472 ± 0.045
results based on eq.II-2	c_{Ti} in at.%	c_{Co} in at.%	c_o in at.%
nanocrystal D	13.7 ± 6.1	21.8 ± 9.8	64.6 ± 28.8

Table III-7.: Chemical composition of nanocrystals B, VIII and D. The given titanium concentrations of nanocrystals B and VIII are calculated by eq.II-8. The given atomic concentrations of nanocrystal D are calculated by eq.II-2.

3.5.3. Atomic concentrations of the amorphous matrix

Chemical compositions at the amorphous matrix can also be compared between the acquired EELS line scans. In tab.III-8 the calculated values for mean integrated intensity

ratios (R_{Co}^{Ti} , R_{Co}^O) at the amorphous matrix and their propagated uncertainties are listed. These ratios give a scaling factor between the compared mean atomic concentration ratios of the amorphous matrix from different line scans. The results show that the amorphous matrix reveals a constant average chemical composition regarding the elements titanium and cobalt between different positions at specimen Co3Ti.I3. The maximum deviation between these line scans corresponds to an error of about 0.8 at.% in the scaled titanium concentration (c_{Ti}^s) of the amorphous matrix. This is consistent to an uncertainty of ± 0.4 at.% for c_{Ti}^s measured by EDX as discussed in section III-3.1. The measured c_{Ti}^s value of 25.4 at.% that is discussed there yields a c_{Ti}/c_{Co} ratio of 0.340 ± 0.007 . This value is assigned to the amorphous matrix surrounding the nanocrystals at specimen Co3Ti.I3.

A higher variation of the titanium and cobalt concentrations can be observed at specimen Co3Ti.I4. Here the maximal deviation correspond to an error of about 10 at.% in the scaled titanium concentration. Especially for line scans I, II and VIII which reveal a high c_{Ti}/c_{Co} ratio the ratio c_{Ti}/c_{Co} is also high. It is equivalent to explain this fact by higher oxygen and titanium concentrations or by a lower cobalt concentration without further knowledge of absolute atomic concentrations. The uncertainty of the EDX measurements is much smaller than the deviation in c_{Ti}/c_{Co} for some of the line scans at specimen Co3Ti.I4. Line scans IV, V, VI and VII reveal similar concentration ratios and their maximal difference in c_{Ti}^s is 1.4 at.%. Therefore, the c_{Ti}/c_{Co} value measured by EDX is assigned to a mean chemical composition of the amorphous matrix between these four line scans. A mean value of 0.835 ± 0.014 is obtained for R_{Co}^{Ti} in tab.III-8 between the four line scans. Mean values for c_{Ti}/c_{Co} at the amorphous matrix are now obtained for each line scan by scaling the c_{Ti}/c_{Co} value measured by EDX with the R_{Co}^{Ti} value corresponding to the considered line scan in tab.III-8 and by inverse scaling it with the mean R_{Co}^{Ti} value. Tab.III-9 shows the final mean values for c_{Ti}/c_{Co} at the amorphous matrix for line scans of specimen Co3Ti.I4. These values are used to calculate the chemical composition at all line scan positions and they are used to calculate the mean chemical composition of the nanocrystals.

relative atomic concentration ratios at specimen Co3Ti.I3			
line scan A	line scan B	line scan C	line scan D
c_{Ti}/c_{Co}	0.966 ± 0.031	0.958 ± 0.029	0.975 ± 0.054
c_{O}/c_{Co}	1.219 ± 0.074	0.682 ± 0.067	0.972 ± 0.097

relative atomic concentration ratios at specimen Co3Ti.I4			
line scan III	line scan I & II	line scan IV	line scan V
c_{Ti}/c_{Co}	1.270 ± 0.028	0.854 ± 0.028	0.803 ± 0.014
c_{O}/c_{Co}	2.258 ± 0.105	0.770 ± 0.096	0.078 ± 0.056
	line scan VI	line scan VII	line scan VIII
c_{Ti}/c_{Co}	0.863 ± 0.021	0.822 ± 0.014	1.293 ± 0.011
c_{O}/c_{Co}	0.618 ± 0.048	0.456 ± 0.055	2.359 ± 0.042

Table III-8.: Comparison of atomic concentration ratios of the amorphous matrix for the two specimens. Integrated intensity ratios R_{Co}^{Ti} and R_{Co}^O are displayed. The values represent the titanium to cobalt ratio c_{Ti}/c_{Co} and the oxygen to cobalt ratio c_{O}/c_{Co} of the listed line scans relative to the ratios of line scan A or III by eq.II-2.

line scan number at specimen Co3Ti.I4							
	I & II	III	IV	V	VI	VII	VIII
c_{Ti}/c_{Co}	0.518	0.408	0.348	0.327	0.352	0.335	0.527
propagated error $\pm$	0.018	0.011	0.015	0.011	0.013	0.011	0.015
c_{Ti}^s in at. %	34.1	29.0	25.8	24.7	26.0	25.1	34.5
propagated error $\pm$ in at. %	0.8	0.6	0.8	0.6	0.7	0.6	0.7

Table III–9.: Mean titanium to cobalt atomic concentration ratios c_{Ti}/c_{Co} of the amorphous matrix for line scans at specimen Co3Ti.I4. The corresponding scaled titanium concentrations c_{Ti}^s are also given for comparison with the measurement in section III-3.1.

3.5.4. A discussion of error values

Systematic errors

Systematic error values for the atomic concentration ratios derived by eq.II–2 due to plural scattering can be found in literature. In Williams Carter’s book Transmission Electron Microscopy [21] a systematic error of 10% to 20% is stated for this method. A quantitative analysis of the systematic errors due to plural scattering is done by A.P. Stephens in [35]. Stephens specifies two types of errors. One error occurs due to an energy convolution of the inelastic scattering distribution like discussed in section II-5.1 and another error occurs due to a scattering angle convolution by plural scattering. This second error becomes only noticeable for small collection semi-angles $\beta \lesssim 5$ mrad and vanishes for the β value of 20.5 mrad that is use in the EELS measurements discussed here. Note that Stephens’s discussion about the collection angle dependence is based on an acceleration voltage of 80 kV. Relative errors due to the energy convolution are displayed in [35] depending on the reduced thickness p , the energy loss value of the plasmon peak maximum, the energy loss value of the considered core loss edges and the energy loss integration widths. A positive relative systematic error of +2.5 % is given for the obtained c_{Ti}/c_{Co} ratios of line scans A and B. This error becomes +3.8 % for line scans C and D because of their higher p values. The relative difference in c_{Ti}/c_{Co} calculated from spectra with and without plural scattering correction by deconvolution is much smaller than these error values from literature. The ratio obtained from deconvolved spectra is about +0.3% higher relative to the ratio obtained from not deconvolved spectra for line scan C. At line scan A a relative difference of about +0.03% is obtained. Calculations of specimen thickness values based on assumed chemical compositions of nanocrystals indicate that specimen Co3Ti.I4 reveals similar thickness values at the position of EELS line scans than specimen Co3Ti.I3. This calculations are discussed in section 3.5.5. Therefore, systematic errors at specimen Co3Ti.I4 are similar to systematic errors at specimen Co3Ti.I3.

Statistical errors

Standard deviations of mean integrated intensity ratios for the amorphous matrix and the nanocrystals and SD of mean chemical compositions of the amorphous matrix measured by EDX lead to propagated uncertainties for derived quantities. The uncertainties given in tab.III–6 yield propagated uncertainties for c_{Ti}/c_{Co} of about 3% at nanocrystal A, of about 5% at nanocrystal B and C and they yield a value of about 10% at nanocrystal D. Similar uncertainties between 3% and 5% are obtained for line scans at specimen Co3Ti.I4. The values are comparable to the systematic error values given in literature [35] which are discussed previously. Thus, the propagated uncertainties of chemical quantities that are given in this work are based on the statistical error values.

3.5.5. Influence of the amorphous matrix on the chemical composition

Nanocrystals are also surrounded by the amorphous matrix in the direction of the electron beam or thickness direction like discussed in section II-5.2. Therefore, the measured chemical compositions at the nanocrystals yield average values between these two structural components. EELS has the advantage to provide information on the specimen thickness. The size or thickness of the nanocrystals can be measured in the ADF and HAADF images. Therefore, the measured elemental concentrations at the nanocrystals can be corrected for the influence of the surrounding amorphous matrix by the methods discussed in section II-5.3.2. Here the term "matrix corrected" is introduced for chemical compositions which consider this influence.

The specimen thickness is given in tab.III-4 for mean line scan positions at the amorphous matrix and for mean line scan positions at the nanocrystals of line scans A to D. Mean diameters are displayed for nanocrystals A to D and III to VII in tab.III-10. They are obtained from grayscale value profiles of ADF and HAADF images. Multiple profiles are selected across a nanocrystal and its surrounding amorphous matrix in different directions in each image. The diameters are then measured by the full width half maximum (FWHM) of the grayscale peak corresponding to the nanocrystal in each profile. The results of the TEM analysis in section III-2 show that the nanocrystals are approximately of spherical shape with some faceting. Thus, it can be assumed that the derived mean diameters are a good approximation for the size of the nanocrystal in thickness direction.

The size of nanocrystal IV is derived only from an ADF image, because of a difference in the measured diameters between the HAADF image and the ADF image. Nanocrystal IV reveals a mean diameter of $14.5 \text{ nm} \pm 0.9 \text{ nm}$ in the HAADF image but it shows a much weaker contrast in that image compared to the contrast in the ADF image. Thus the larger size of the nanocrystal in the HAADF image could also be related to a variation of the chemical composition or a variation of the specimen thickness at the amorphous matrix that surrounds the nanocrystal.

For nanocrystal D two different compositions are considered. Once it is seen as titanium oxide particle denoted with "D (oxide)" and another time it is seen as nanocrystal "D" of the cobalt-titanium alloy. The results of section III-3.5.2 indicate that there is an oxide particle at line scan D.

mean diameter of nanocrystals in specimen Co3Ti.I3 given in nm				
nanocrystal A	nanocrystal B	nanocrystal C	nanocrystal D	D (oxide)
14.5 ± 1.2	6.5 ± 0.9	7.3 ± 0.3	6.5 ± 0.7	3 ± 1

mean diameter of nanocrystals in specimen Co3Ti.I4 given in nm				
nanocrystal III	nanocrystal IV	nanocrystal V	nanocrystal VI	nanocrystal VII
10.0 ± 0.8	6.2 ± 0.2	9.0 ± 0.2	15	11.3 ± 0.2

Table III-10.: Mean diameters of nanocrystals deduced from profiles of ADF and HAADF images. A given mean value is averaged from two mean values derived from the two image types. The corresponding error value represents the SD of the mean that is calculated from the two averaged mean values. The size of D (oxide) is approximated by the negative cobalt peak and the weak oxygen and titanium peaks in fig.III-11.a.

Numerical calculations:

Tab.III–11 shows numerically calculated results for the chemical composition of nanocrystals. The calculated variables are the atomic concentrations of titanium and oxygen at a nanocrystal and the amount of oxygen in the amorphous matrix that surrounds the nanocrystal in thickness direction. If one guesses the exact chemical composition of a nanocrystal, the specimen thickness and the oxygen concentration of the amorphous matrix can be calculated instead. This method is used to estimate the specimen thickness for line scans at specimen Co3Ti.I4. Here the specimen thickness can not be deduced from EELS data because only high energy loss spectra are acquired. The evaluated nanocrystals III to VII are located at the same amorphous specimen region. Thus, the obtained thickness results can be compared to each other. The relative positions of the considered line scans and nanocrystals at the amorphous specimen region are indicated in fig.III–4. Numerically calculated specimen thickness values are displayed in tab.III–12. Only solutions of non-vanishing c_O concentration (different to analytical solutions) are considered.

The results for mean chemical compositions of nanocrystals and surrounding amorphous matrix which are discussed in section III-3.5.2 reveal scaled titanium concentrations in the range of 30 at.% titanium for nanocrystals III to VII (see tab.III–6). Laves phases $\text{Co}_{2.1}\text{Ti}_{0.9}$ and Co_2Ti occur in this titanium concentration range according to the cobalt-titanium binary alloy equilibrium phase diagram [10] that is shown in fig.I–1. Thus, titanium concentrations of 30 at.% titanium ($\equiv \text{Co}_{2.1}\text{Ti}_{0.9}$) and 33.3 at.% ($\equiv \text{Co}_2\text{Ti}$) titanium are assumed for the considered nanocrystals.

nanocrystal & oxygen model	atomic concentrations in at.%			c_{Ti}^s	c_O^2 (matrix)
	c_{Ti}	c_{Co}	c_O	in at.%	in at.%
A & model 1	27.5	55.9	16.6	33.0	14.7
A & model 2	20.3	42.0	37.7	32.6	57.3

Table III–11.: Numerical solutions for the matrix corrected elemental concentrations of titanium (c_{Ti}), cobalt (c_{Co}) and oxygen (c_O) at a nanocrystal and for the oxygen concentration (c_O^2) in the amorphous matrix at the given line scan. Only solutions that are different to analytical solutions are shown. They reveal not vanishing oxygen concentrations. The titanium concentration c_{Ti}^s is scaled by neglecting c_O .

nanocrystal & oxygen model (m)	assumed c_{Ti}^s in at.%	calculated c_O^1 in at.%	calculated c_O^2 in at.%	calculated t in nm	t in nm, given by tab.III–4
A & model 1	33.3	70.4	67.2	23.1	$22.6 \pm \begin{smallmatrix} 2.0 \\ 3.9 \end{smallmatrix}$
A & model 2	33.3	50.2	67.7	29.2	
III & model 1	33.3	89.2	87.9	15.8	
III & model 2	33.3	91.7	85.5	21.4	
V & model 1	33.3	96.4	85.9	12.0	
V & model 2	33.3	74.6	54.3	15.5	

Table III–12.: Numerical solutions for the specimen thickness (t), the oxygen concentration at the nanocrystal (c_O^1) and the oxygen concentration at the amorphous matrix (c_O^2). Here the fixed c_{Ti}/c_{Co} ratios at nanocrystals are given in form of scaled titanium concentrations (c_{Ti}^s). Only solutions that are different to analytical solutions are shown. They reveal not vanishing oxygen concentrations. Data for nanocrystal A is also displayed to see the influence of the specimen thickness on the chemical composition.

Analytical calculations:

Matrix corrected chemical compositions of nanocrystals can be calculated analytically by eq.II-9. Therefore, it is assumed that no oxygen is present at the nanocrystals. This simplification is valid because the oxygen concentration at a nanocrystal has only a weak influence on the concentration of titanium relative to the concentration of cobalt at the nanocrystal as shown for instance in fig.III-12 for nanocrystal A. In fig.III-12 the matrix corrected scaled titanium concentration is displayed in dependence of the oxygen concentration, the specimen thickness and the amount of titanium relative to the amount of cobalt at the surrounding amorphous matrix. Oxygen model 2 assumes the oxygen to be concentrated in layers at the specimen surface. Here the oxygen concentration of the embedded nanocrystal has a stronger influence on the chemical composition of the nanocrystal. But an additional amount of 50 at.% oxygen at nanocrystal A would lower the matrix corrected c_{Ti}^s value only for about 1 at.% in this model. The oxygen concentration vanishes also at the amorphous matrix if the oxygen concentration is set to zero at the nanocrystal for both models. Tab.III-13 shows the obtained matrix corrected titanium concentrations for nanocrystals A, C and D. In tab.III-14 specimen thickness values are displayed again for EELS line scans III to VII at specimen Co3Ti.I4. The values are deduced by solving eq.II-9 for the specimen thickness and guessing the titanium concentration of the nanocrystals.

If one assumes the nanocrystal III, IV, V and VII to reveal the Laves phase Co_2Ti , then similar specimen thickness values can be obtained for those nanocrystals. A slight decrease of the grayscale values at the amorphous matrix can be recognized in HAADF images at the specimen region where line scans III to VII are acquired. This decrease is also visible in the ADF image shown in fig.III-4 and can be related to a decrease of the specimen thickness. Now the calculated thickness values for nanocrystals III, IV, V and VII can be associated to the positions of these nanocrystals in the considered specimen region. Then the direction of the decrease of calculated thickness values that are shown in tab.III-14 matches the direction of the thickness decrease seen in HAADF images. Besides, the not matrix corrected titanium concentration at nanocrystals III and VII are already too high for these nanocrystals to reveal the Laves phase $\text{Co}_{2.1}\text{Ti}_{0.9}$ (see tab.III-6).

The diameter of nanocrystal VI is with approximately 15 nm larger than the diameters of nanocrystals III, IV, V and VII (see tab.III-10). Furthermore, nanocrystal VI reveals a negative contrast relative to the surrounding amorphous matrix in the HAADF image. This contrast is stronger than the contrast of the other nanocrystals that are considered here and could be explained by a decrease of the specimen thickness at the position of nanocrystal VI. Thus, the amorphous matrix surrounding nanocrystal VI in thickness direction should not have a considerable influence on the measured chemical composition. Nanocrystal VI is therefore assumed to reveal the Laves phase $\text{Co}_{2.1}\text{Ti}_{0.9}$ according to the measured c_{Ti}^s value of $30.1 \text{ at.\%} \pm 1.0 \text{ at.\%}$ that is given in tab.III-6.

nanocrystal:	A	A deconv.	C	C deconv.	D
c_{Ti}^s in at.%	32.8 ± 1.7	32.9 ± 1.7	26.5 ± 3.7	26.8 ± 3.6	51.5 ± 9.7

Table III-13.: Matrix corrected scaled titanium concentration (c_{Ti}^s) of nanocrystals in specimen Co3Ti.I3 calculated by eq.II-9.

Instead of presenting derived specimen thickness value based on assumed chemical compositions for nanocrystals III to VII, the results are presented again in form of derived chemical compositions. Therefore, a mean specimen thickness is calculated from the thickness values of nanocrystals III, IV, V and nanocrystal VII which are shown in tab.III–14. These nanocrystals are assumed to reveal a Co_2Ti Laves phase. A mean specimen thickness value of $18.1 \text{ nm} \pm 2 \text{ nm}$ is obtained. Now the matrix corrected chemical composition of nanocrystals III to VII is calculated by eq.II–9. The results are displayed in fig.III–15.

Calculations concerning oxide particles:

The matrix corrected chemical composition of oxide particles is based on the neglect of the element cobalt at the particles themselves. Concerning oxide particles, neither the numerical calculations nor the analytical calculations yield valid solutions for the resulting chemical compositions at specimen thickness values given in tab.III–4. This fact is represented in fig.III–13 that shows the mutual dependencies between the titanium and oxygen concentrations at the nanocrystal, the specimen thickness and the concentration of titanium relative to the concentration of cobalt at the amorphous matrix. Smaller specimen thickness values are expected at the assumed c_{Ti}/c_{Co} value of the amorphous matrix from these calculations than the specimen thickness values derived from the electron low energy loss spectra in section III-3.4.3. If the titanium concentration is set to the value of 33.3 at.% for TiO_2 , the specimen thickness can be calculated by eq.II–10 for each oxygen model, respectively. In oxygen model 2 the specimen thickness (t_3) at an amorphous area next to a nanocrystal is set equal to the specimen thickness ($t_1 + t_2$) at the nanocrystal.

analytically calculated specimen thickness values for specimen Co3Ti.I3				
nanocrystal & oxygen model (m)	assumed c_{Ti} in at.%	calculated c_O^2 in at.%	calculated t value in nm	t in nm, given by tab.III–4
A	33.3	0.0	24.0 ± 2.9	$22.6 \pm \frac{2.0}{3.9}$
oxide particles				
B & m 1	33.3	48.4 ± 1.8	9.3 ± 1.0	$22.1 \pm \frac{1.6}{3.5}$
B & m 2	33.3	63.7 ± 2.0	10.4 ± 1.1	
D (oxide) & m 1	33.3	27.9 ± 4.3	10.2 ± 2.9	$23.8 \pm \frac{1.6}{3.5}$
D (oxide) & m 2	33.3	36.7 ± 6.3	11.2 ± 3.3	
analytically calculated specimen thickness values for specimen Co3Ti.I4				
nanocrystal	assumed c_{Ti}^s in at.%		calculated t value in nm	
III	33.3		16.5 ± 3.1	
IV	33.3	(30.0)	18.1 ± 6.2	(10.2 ± 3.9)
V	33.3	(30.0)	20.7 ± 3.5	(12.9 ± 2.5)
VI	(33.3)		(26.5 ± 4.5)	
VII	33.3		16.9 ± 2.0	

Table III–14.: Calculated specimen thickness value (t) based on an assumed chemical composition of a nanocrystal given by its titanium concentration (c_{Ti}). The calculations are based on eq.II–9 except for the oxide particles B and D (oxide). Here eq.II–10 is used to calculate the specimen thickness and the oxygen concentration in the amorphous matrix (c_O^2) that surrounds the nanocrystal in the direction of the electron beam.

Calculated values for the specimen thickness and the amount of oxygen in the amorphous matrix are given in tab.III-14 for the oxide particles B and D (oxide).

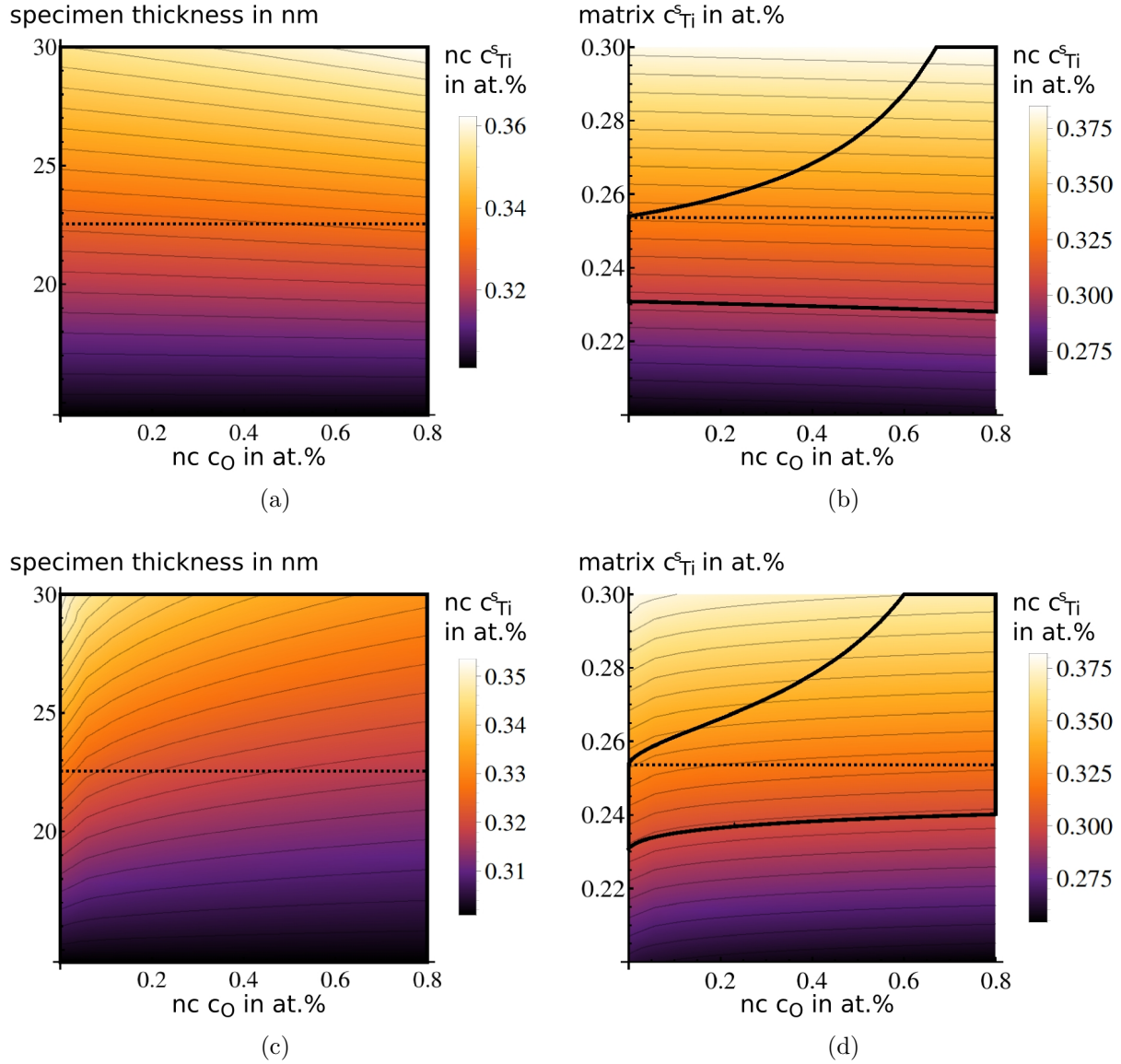


Figure III-12.: The scaled titanium concentration of nanocrystal A ($nc\ c_{Ti}^s$) is plotted as function of specimen thickness and oxygen concentration of the nanocrystal ($nc\ c_O$) in image (a) for the oxygen model 1 and in image (c) for the oxygen model 2 which are discussed in section II-5.3. Image (b) and (d) compare the dependence on the scaled titanium concentration of the amorphous matrix ($matrix\ c_{Ti}^s$) with the dependence on $nc\ c_O$ for model 1 and model 2. The titanium concentrations are scaled to neglect the oxygen concentrations. The images are cross sections of four dimensional data cubes. Image (a) and (c) are plotted at $matrix\ c_{Ti}^s = 0.254$ at.%. This value is measured at the NCEM as discussed in section III-3.1 for specimen Co3Ti-I4. Image (b) and (d) are plotted at the derived specimen thickness of 22.6 nm. The derived value for the specimen thickness and the derived value for $matrix\ c_{Ti}^s$ are indicated in the images. In addition the boundaries of the range of validity are indicated by black curves. Inside this region the oxygen concentration (c_O) of the surrounding amorphous matrix satisfies the condition $0 \leq c_O \leq 1$.

3.5.6. Chemical analysis by the Gatan EELS package

EELS analysis of nanocrystals

EELS data is also evaluated at the FELMI-ZFE in Graz by the Gatan Microscopy Suite Software using the Gatan EELS package [28]. Recorded spectra are corrected for plural scattering by a Fourier-Log deconvolution method for line scans A and B. This method is discussed in literature like in Egerton's book [22]. Here plural scattering is removed from a whole spectrum and background intensities can be subtracted from the spectrum afterwards. The energy differential cross sections are calculated in the EELS analysis of GMS. The calculation is based on a Hartree-Slater model as described in the user guide [29]. Thus, the number of atoms per unit specimen area are obtained for each element. This leads to the deduction of absolute atomic concentrations without the need of chemical data from additional measurements. Therefore, it is assumed again that only the elements titanium, cobalt and oxygen are present in the specimen. Elemental compositions at line scans A and B are given in tab.III–15 in form of mean values for the nanocrystals and in form of mean values for the surrounding amorphous matrix using the same spatial regions in the averaging process as for the mean values that are obtained in section III-3.5.2. Reduced thickness values and absolute thickness values are shown in tab.III–16 for the two line scans. The absolute thickness is calculated from λ values derived in section III-3.4.3. The results obtained here are compared to previous results in fig.III–14.

An EELS area scan is acquired at an amorphous specimen region of about $45 \times 55 \text{ nm}^2$ to measure the mean chemical composition of the amorphous matrix at specimen Co3Ti.I3. Only the elements titanium and cobalt are considered for the measurement at the specimen region shown in fig.III–16.a. The obtained scaled titanium concentration of $25.8 \text{ at.}\% \pm 2.7 \text{ at.}\%$ is in good agreement with the value of $25.4 \text{ at.}\% \pm 0.4 \text{ at.}\%$ for c_{Ti}^s that is

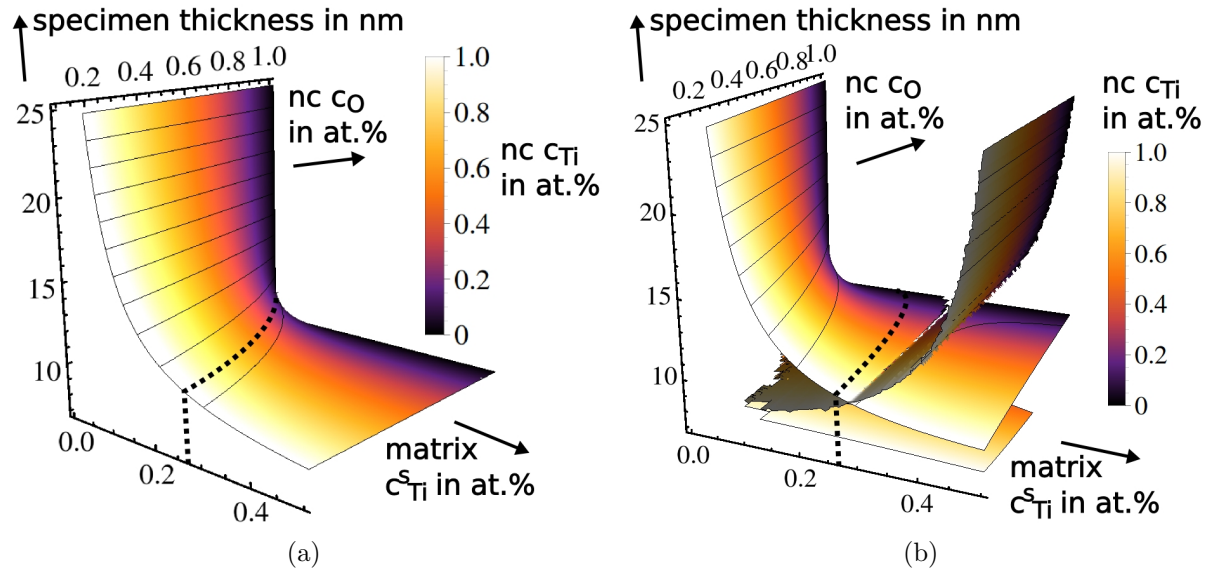


Figure III–13.: Titanium concentration of nanocrystal B ($nc\ c_{Ti}$) as function of specimen thickness, the oxygen concentration of the nanocrystal ($nc\ c_O$) and the scaled titanium concentration of the matrix ($matrix\ c_{Ti}^s$). Image (a) shows these dependencies for oxygen model 1 and image (b) displays oxygen model 2. Both images show the dependencies for an oxide particle (see section II-5.3). Therefore, it is assumed that the element cobalt is not present at the nanocrystal. The derived value for ($matrix\ c_{Ti}^s$) is indicated in the images.

measured by EDX at specimen Co3Ti.I4 (see section III-3.1). Although the EELS analysis reveals a higher error of the measurement, one can conclude that specimens Co3Ti.I3 and Co3Ti.I4 yield the same chemical composition at the amorphous matrix. This result can be expected because the additional specimen treatment of ion milling should not influence the chemical composition at specimen Co3Ti.I3.

	line scan	atomic concentrations in at.%			c_{Ti}^s
	mean values for:	c_{Ti}	c_{Co}	c_O	in at.%
A	nanocrystal	24.1 ± 0.2	50.6 ± 0.3	25.3 ± 0.3	32.2 ± 0.3
	amorphous matrix	21.0 ± 0.2	53.7 ± 0.4	25.3 ± 0.3	28.1 ± 0.3
B	nanocrystal	40.9 ± 0.4	18.3 ± 0.5	40.8 ± 0.8	50.0 ± 0.6
	amorphous matrix	19.8 ± 0.3	50.2 ± 0.7	30.0 ± 0.5	28.2 ± 0.4

Table III–15.: Mean values for elemental concentrations of titanium (c_{Ti}), cobalt (c_{Co}) and oxygen (c_O) at a nanocrystal and at the surrounding amorphous matrix calculated by the GMS software and the Gatan EELS package. Titanium concentrations c_{Ti}^s are scaled by neglecting c_O except for the value at nanocrystal B. There c_{Ti}^s is scaled by neglecting c_{Co} instead. The SD of the mean is displayed for each atomic concentration value.

mean values:	line scan A	line scan B
reduced thickness p	0.058 ± 0.005	0.065 ± 0.006
thickness t of: line scan, in nm	7.4 ± 1.5	8.5 ± 1.7
thickness t of: nanocrystal, in nm	6.2 ± 1.9	7.8 ± 1.4

Table III–16.: Mean values of p and t derived by the GMS software and the Gatan EELS package. Reduced thickness values correspond to mean values that are averaged over all line scan positions. The t values are calculated using the Iakoubovskii et al. parametrization.

EELS analysis of surface layers

A narrow region of negative contrast to the amorphous matrix can be observed in HAADF and ADF images along the specimen edge that encircles the specimen hole. This occurrence is shown in fig.III–16. It indicates the presence of a surface layer. Therefore, EELS area scans are acquired at elongated areas parallel to the specimen edge. Fig.III–16.b shows the specimen region where three area scans are located. The scan areas are about $1.2 \times 22 \text{ nm}^2$ in size. Here the area scans are denoted with the numbers 1, 2 and 3. Their distances to the specimen edge are approximately 2.5 nm for area scan 1, 6 nm for area scan 2 and 17 nm for area scan 3. Mean high loss spectra are only evaluated for area scans 1 and 2 by GMS and the Gatan EELS package. The mean chemical composition at area scan 3 is calculated by eq.II–2 using the data of area scan 2 as reference. The energy loss integration intervals and intervals for background subtraction in the high energy loss spectra are chosen again according to tab.III–5. The resulting mean chemical compositions are shown in tab.III–17.

In addition, data of area scan 1 is also evaluated by eq.II-2 using data of area scan 2 as reference. This calculation is in good agreement with the Gatan EELS analysis for area scan 1 as shown in tab.III-17. Thus, the obtained results for area scan 3 should be valid too.

The high concentration of the elements oxygen and cobalt compared to the titanium concentration at the very edge of specimen Co₃Ti.I3 indicates the presence of a cobalt oxide layer on the specimen's surfaces.

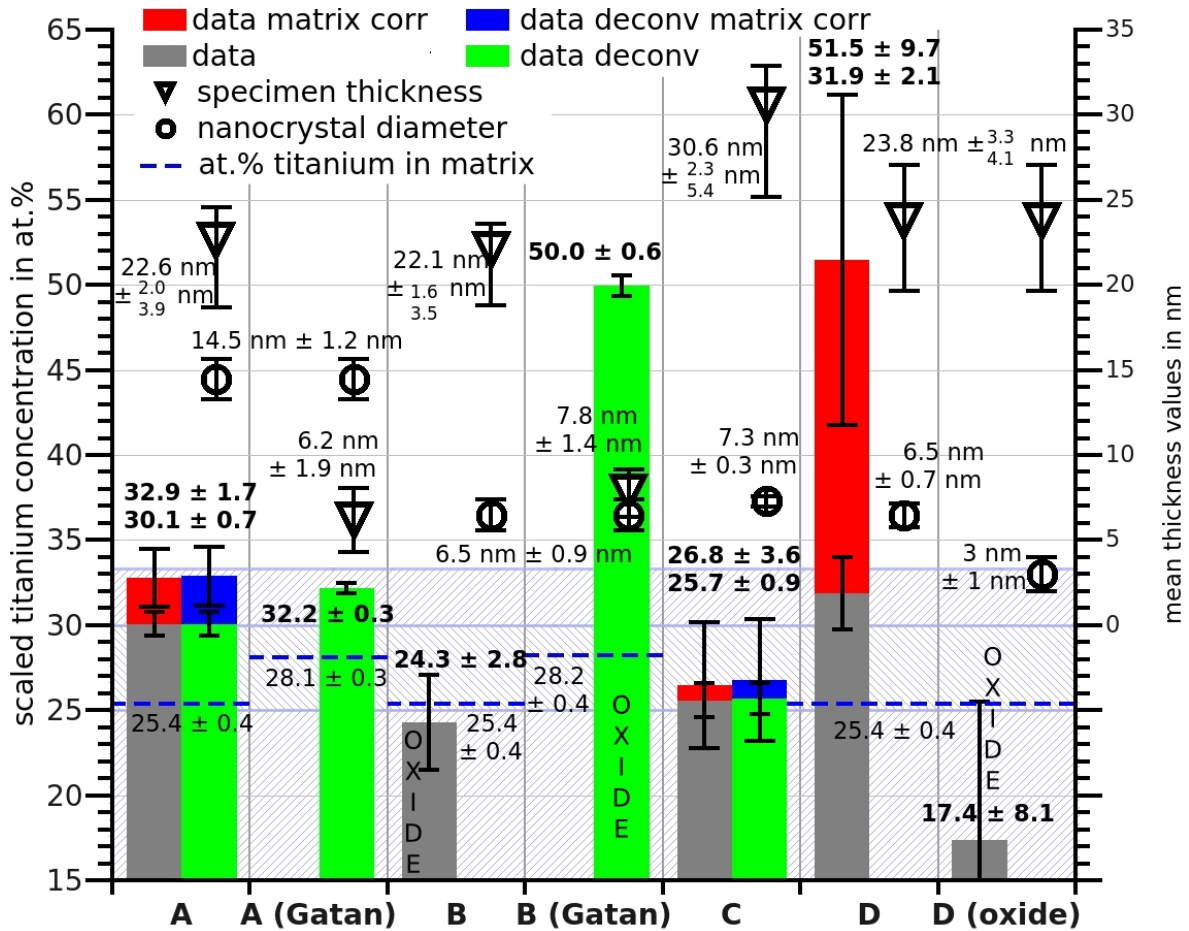


Figure III-14.: Graph of scaled titanium concentrations at nanocrystals, diameters of nanocrystals and specimen thickness values at the position of nanocrystals for specimen Co₃Ti.I3. Mean c_{Ti}^s values are scaled by neglecting c_{Co} for nanocrystals that are assumed to be oxide particles or otherwise the values are scaled by neglecting c_O . The specimen thickness mean values shown here are derived in section III-3.4.3. Chemical results obtained in section III-3.5.2 are compared to matrix corrected results by analytical calculations that are discussed in section III-3.5.5. The deconvolution of high energy loss spectra at line scans A and C has no influence on the results at the given propagated uncertainties as shown here. In addition the EELS analysis by the GMS software is displayed for nanocrystals A and B denoted as "A (Gatan)" and "B (Gatan)". This analysis is described in section III-3.5.6. The mean scaled titanium concentrations at the amorphous matrix which is surrounding the nanocrystals are shown in the figure. Stoichiometric c_{Ti} values for Co₂Ti and TiO₂ (33.3 at.% titanium), for Co_{2.1}Ti_{0.9} (30 at.% titanium) and for Co₃Ti (25 at.% titanium) are indicated in the background of the figure.

The HAADF profile displayed in fig.III-16.b shows a vague plateau in the grayscale values up to a distance of approximately 5 nm from the specimen edge. Then the intensities increase for regions further away from the edge. At area scans 1 and 2 which are located near that plateau region, twice as much oxygen is present as at area scan 3 which has a higher distance from the edge. Thus, the increase of intensity in the HAADF profile can be related to the decrease of oxygen rather than to a rapid increase of the specimen thickness. A considerable amount of titanium is already present at a distance of 6 nm from the specimen edge at area scan 2. But the oxygen concentration is unchanged at area scan 2 compared to the oxygen concentration at area scan 1. So one can assume that the occurrence of oxygen in the specimen is not restricted to the cobalt oxide surface layer.

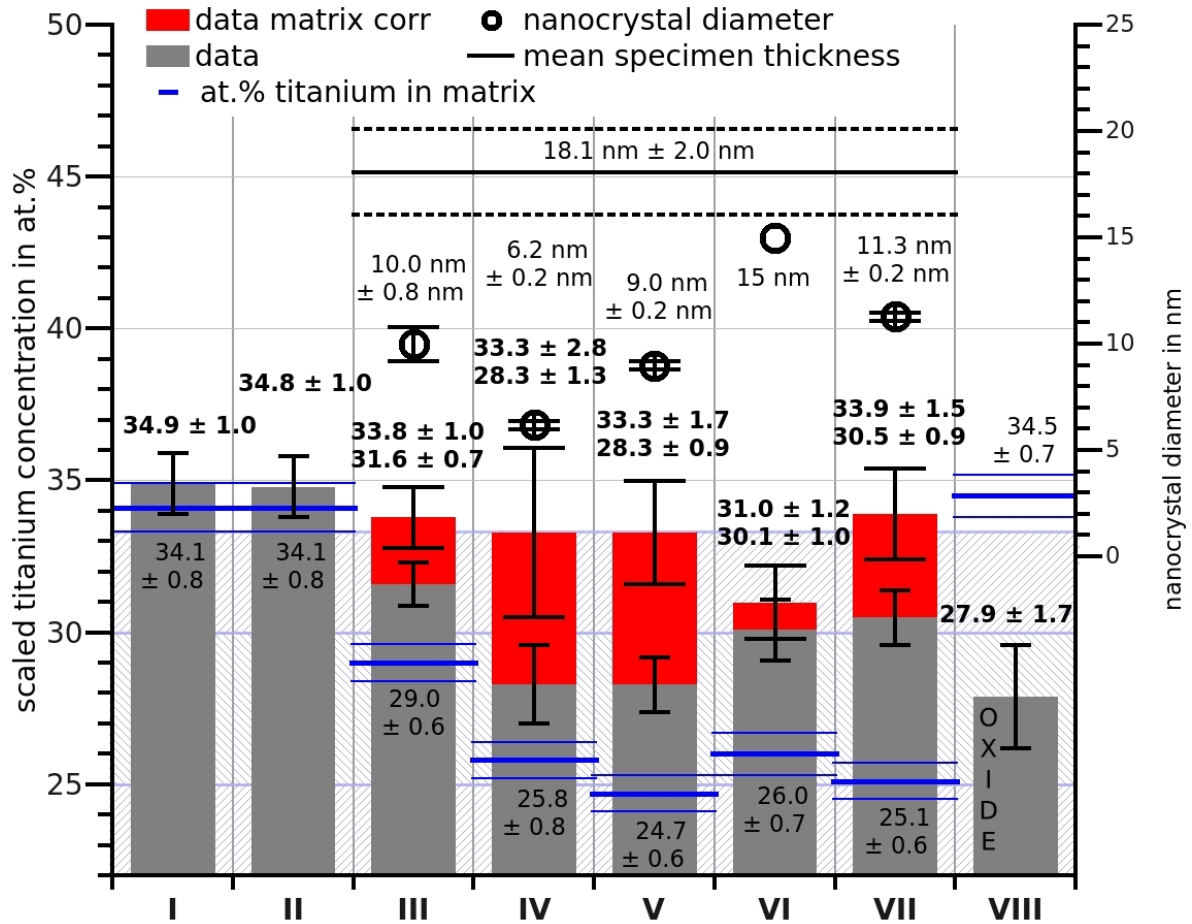


Figure III-15.: Graph of scaled titanium concentrations at nanocrystals and diameters of nanocrystals for specimen Co₃Ti₁₄. The mean c_{Ti}^s value is scaled by neglecting c_{Co} instead of c_O at the oxide particle VIII. The matrix corrected titanium concentrations of line scans III to VII are calculated analytically from a mean specimen thickness at the specimen region shown in fig.III-4. This procedure is discussed in section III-3.5.5. Mean c_{Ti}^s values at the amorphous matrix are shown for each line scan as derived in section III-3.5.3. Stoichiometric c_{Ti} values for Co₂Ti and TiO₂ (33.3 at.% titanium), for Co_{2.1}Ti_{0.9} (30 at.% titanium) and for Co₃Ti (25 at.% titanium) are indicated again in the background of the figure.

III. Results & discussion

A rough estimation of about $3 \text{ nm} \pm$ approximately 2 nm can be given for the thickness of the cobalt oxide layer from the positions of the area scans and the plateau in the HAADF profile.

area scan numbers	atomic concentrations in at.‰			c_{Ti}^s in at.‰	distance from edge in nm
	c_{Ti}	c_{Co}	c_O		
1	2.9 ± 0.4	37.7 ± 4.2	59.3 ± 4.2	7.2 ± 1.1	2.5
2	9.4 ± 1.1	26.3 ± 2.9	64.2 ± 4.3	26.4 ± 4.3	6.0
results calculated by eq.II-2 and by data from area scan 2					
3	13.6 ± 3.2	53.5 ± 9.1	32.8 ± 3.7	20.3 ± 4.8	17.0
1	2.2 ± 0.5	38.3 ± 5.1	59.6 ± 1.9	5.3 ± 1.2	2.5

Table III-17.: Mean chemical composition at area scans 1 to 3. The scan areas are located near the edge of the specimen at different distances to the edge. The atomic concentrations are deduced from a mean spectrum at each area scan, respectively. The scaled titanium concentration c_{Ti}^s represents the titanium to cobalt atomic concentration ratio by neglecting the oxygen.

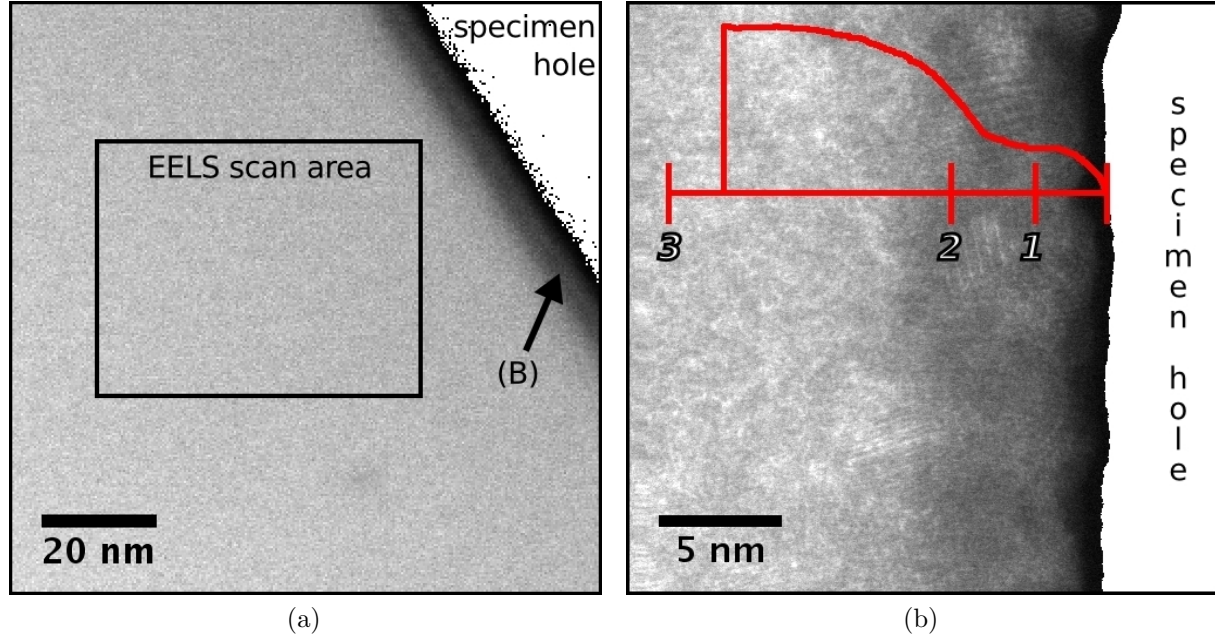


Figure III-16.: Image (a) shows a HAADF image of an amorphous region at specimen $\text{Co}_3\text{Ti}_1\text{I}_3$. The marked area of $45 \times 55 \text{ nm}^2$ displays the region of an acquired EELS area scan. A band (B) which reveals a sharp negative contrast to the amorphous matrix is visible at the edge of a specimen. The ADF image (b) shows a detail of the specimen edge at higher magnification. A HAADF image profile is overlaid in (b). The profile is taken from a similar specimen region as the specimen region visible in (b). It is an average profile of same distances from the specimen edge. The EELS area scans 1, 2 and 3 which are acquired parallel to the specimen edge are indicated by their distances to the edge.

4. HRTEM analysis

The chemical analysis shows that nanocrystals having a chemical compositions of Co_2Ti , $\text{Co}_{2.1}\text{Ti}_{0.9}$ and Co_3Ti are present in the amorphous phase of the specimens. These chemical compositions correspond to the Laves phases C15 (Co_2Ti), and C36 ($\text{Co}_{2.1}\text{Ti}_{0.9}$) and to the L_{12} long range ordered phase (Co_3Ti).

HRTEM images of the TEM specimen Co_3Ti .I4 are received as recorded at an uncorrected FEI Titan microscope from the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory. In addition HRTEM images of the TEM specimen Co_3Ti .I3 are taken at a PHILIPS CM30 ST at the Physics of Nanostructured Materials research group at the University of Vienna.

In HRTEM images received from the NCEM lattice structures smaller than the Kagomé lattice plane distances of the considered Laves phases are resolved. This complicates the identification of nanocrystals with possible Laves phases due to the more complex structures in the images. The HRTEM images taken at the PHILIPS CM30 ST microscope should show less detailed lattice structures and so the large Kagomé lattice of the Laves phases could be recognized more easily in these images than in the images received from the NCEM.

HRTEM images of nanocrystals are analyzed by their Fast Fourier transformation (FFT) and by the stacking order of densely packed lattice planes in the images. The HRTEM images of nanocrystals received from the NCEM are compared to simulated HRTEM images. By analyzing the images of both transmission electron microscopes it is shown that the same lattice structures occur in both cases but that indeed the images received from the FEI Titan microscope show more details of the atomic structures. The FFTs in fig.III–19 and in fig.III–20 show higher indexed reflections for HRTEM images acquired at the FEI Titan microscope than for HRTEM images acquire at the PHILIPS CM30 ST microscope and the HRTEM image details in fig.III–21 (FEI Titan) show finer lattice structures than the HRTEM images in fig.III–18 (PHILIPS CM30 ST) when comparing the same structure and orientation.

Literature values of lattice parameters and X-ray diffraction data for the three considered phases are taken from the Atomwork database [15], [14]. The data provided there is taken from measurements that are given in [16] for Co_2Ti , in [16] for $\text{Co}_{2.1}\text{Ti}_{0.9}$ and in [18] for Co_3Ti .

The imaged nanocrystals are located inside large amorphous regions in the specimens. The distance to remaining crystalline specimen areas is large enough to distinguish them from crystalline remnants of the initial material.

The results of the HRTEM analysis show that nanocrystals of the Co_3Ti L_{12} long range ordered phase, the Co_2Ti Laves phase C15 and the $\text{Co}_{2.1}\text{Ti}_{0.9}$ Laves phase C36 are embedded in the amorphous regions in the specimens.

4.1. Fast fourier transformation of HRTEM images

The HRTEM images are analyzed in the software DigitalMicrograph from the GATAN company. The FFT of a HRTEM image is calculated from a region of interest set at the nanocrystal shown in the image. The nanocrystals are embedded in an amorphous matrix. The restriction to the ROI should prevent an influence of the surrounding amorphous matrix on the FFT. Due to the small size of the nanocrystals the FFT images have a low pixel resolution of visible reflections.

The reciprocal lattice of the $L1_2$ long range ordered Co_3Ti structure is a body centered cubic (bcc) lattice with additional superlattice reflections. An important orientation for Co_2Ti and Co_3Ti is the $[110]$ orientation where densely packed lattice planes are in projection and the ABC stacking order can be recognized. The reciprocal lattices planes for these two structures in $[110]$ orientation are shown in fig.III–17. The symmetric unit cell of Co_2Ti is much bigger than the symmetric unit cell of Co_3Ti . Therefore, the reciprocal Bravais lattice of the Co_2Ti structure is a bcc lattice with much smaller reciprocal lattice spacings than the reciprocal lattice spacings of the Co_3Ti structure.

The evaluated FFT images of HRTEM (fig.III–18) images are shown in in fig.III–19 and fig.III–20. The PASAD plugin [36] for DigitalMicrograph is used to measure reciprocal distances in the FFTs. The central spot is defined by the center of the FFT image. Thus, the azimuthal averaged, or averaged integrated intensities are calculated by PASAD for an angular sector containing only the considered reflection. Then the peak maximum in the integrated intensity profile yields the reciprocal distance. If multiple reflections of the same species occur in one FFT, an average value is calculated. Measured reciprocal distances and characteristic angles between reflections are compared to calculated distances and angles from literature values of lattice spacings [16], [17] and [18] in tab.III–19. The distances yield the inverse lattice spacings in the HRTEM images and the angles correspond to the angles between the visible lattice planes. An error value for the measured reciprocal lattice distance of approx. $\pm 0.1 \text{ nm}^{-1}$ arises from the pixel resolution of the integrated intensity profile images and thus from the size of the ROI used for the FFT calculation. The error of $\pm 1.5^\circ$ for the measurement of the angle between two reciprocal vectors is a deduced error from the difference between two measured angles with an error of approx. $\pm 1^\circ$, respectively.

4.1.1. Calibration of HRTEM and FFT images

HRTEM images displayed in fig.III–18 are acquired at the PHILIPS CM30 ST microscope. It shows that there was a slight error in the pixel to nanometer scale of the acquired

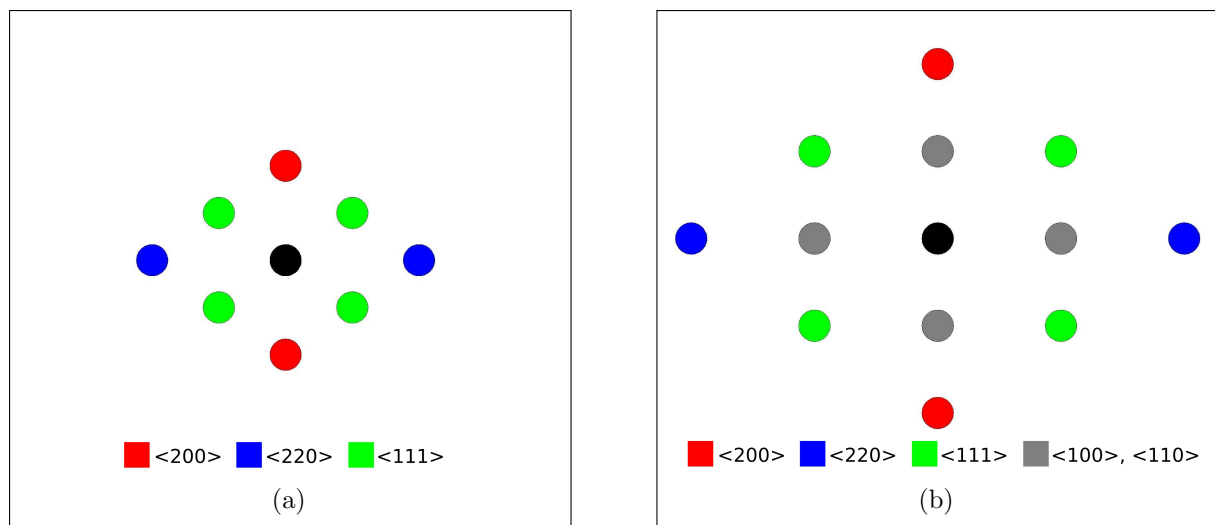


Figure III–17.: Sketches of the reciprocal lattice plane for Co_2Ti (a) and Co_3Ti (b) in $[110]$ orientation at the same magnification. Only the Kagomé lattice or fundamental lattice packages are considered for the Co_2Ti pattern (a). Visible superlattice reflections of $\langle 110 \rangle$ reflections and of $\langle 100 \rangle$ reflections are marked in gray for the Co_3Ti pattern (b).

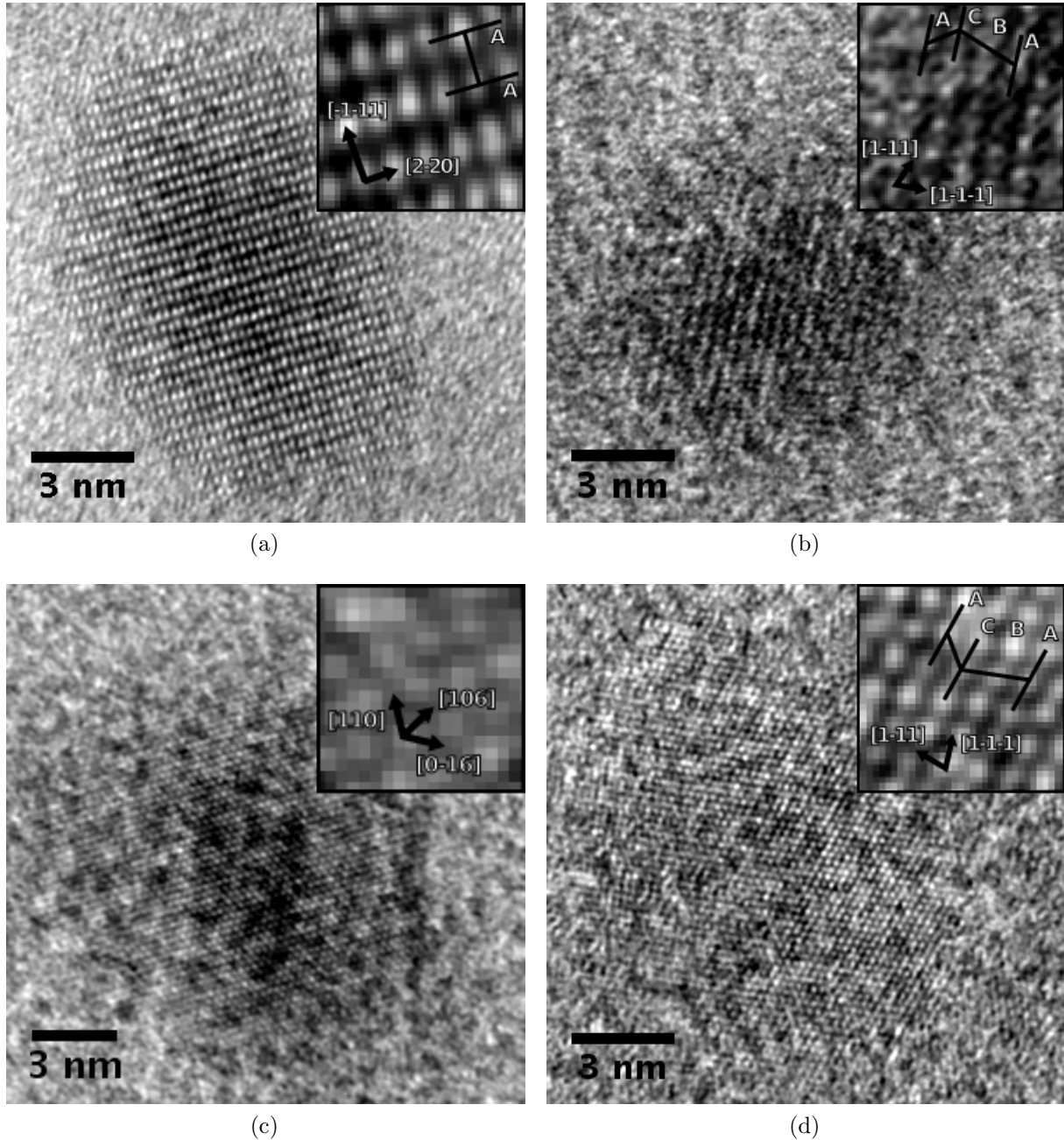


Figure III-18.: HRTEM images of nanocrystals acquired at the PHILIPS CM30 ST microscope. Image (a) and (b) reveal Co_2Ti Laves phase structures (C15) in $[112]$ and in $[110]$ real space orientations. Image (c) matches a $\text{Co}_{2.1}\text{Ti}_{0.9}$ Laves phase (C36) in $[-661]$ real space orientation and image (d) shows a Co_3Ti structure in $[110]$ real space orientation. The length of reciprocal lattice vectors that are marked in the inserted magnified image details is given by the lattice spacings of the related (perpendicularly arranged) lattice planes. Their indexing is in accordance to the corresponding FFT images shown in fig.III-19 and fig.III-20. In image (a) and (b) the stacking order of Kagomé lattice planes is sketched. The ABC stacking order of densely packed $(1-11)$ planes is marked in (d) for Co_3Ti .

images when comparing the measured lattice spacings to theoretical values. This deviation is due to a calibration error that could occur from the applied high tension values at the HRTEM sessions. These values of 280 kV or 295 kV (see section II-3.3) differ from the stated high tension of 300 kV for the transmission electron microscope.

The Co_2Ti nanocrystal shown in fig.III–18.a is used to calibrate the nanometer scale of HRTEM images acquired at the PHILIPS CM30 ST microscope using a high tension of 295 kV. Therefore, measured reciprocal distances of marked reflections in the FFT image in fig.III–19.b are compared to theoretical reciprocal distances. These distances are calculated from literature values of lattice plane spacings [16]. A mean correction factor is calculated from ratios between measured and calculated reciprocal distances. The obtained ratios are given in tab.III–18. The correction factor for HRTEM images is then given by the reciprocal factor for the FFT image. Since the FFT image (fig.III–19.b) is used for the scaling of the images, it is not part of the results shown in tab.III–19.

HRTEM images are corrected by a factor of 1.17 in addition to their original nanometer scale for images acquired on 5.11.2015 by a high tension of 295 kV. The same correction method is applied to HRTEM images that are acquired on 8.10.2015 by a high tension of 280 kV. Here a correction factor of 1.11 is obtained for the original nanometer scale in HRTEM images. A HRTEM image of a Co_2Ti nanocrystal is used again in the process.

The assumption that fig.III–18.a shows a Co_2Ti nanocrystal in $[112]$ orientation is based on the following facts:

- The AAA stacking order of Kagomé layers along the $[-1-11]$ direction can be recognized in the image. The pattern in the corresponding FFT image (fig.III–19.b) matches that of the Co_2Ti structure oriented in this crystallographic direction.
- The lattice visible in the image is similar to the lattice of a Co_2Ti nanocrystal in $[112]$ orientation shown in a HRTEM image received from the NCEM and acquired at a FEI Titan microscope (see fig.III–21.a). Lattice points on $(-1-11)$ planes dominate the visible structure revealing a bright contrast to the background for both images. The difference between the two images is an additional lattice structure that is visible between the $(-1-11)$ planes for the HRTEM image received from the NCEM. These additional structure reveals lower brightness values in the image and it is probably not resolved for the HRTEM image acquired at the PHILIPS CM30 ST microscope.
- Simulated HRTEM images of Co_2Ti in $[112]$ orientation agree well to the HRTEM image received from the NCEM as shown in fig.III–21.a.

reciprocal lattice vectors	$[-1-11]$	$[2-20]$	$\langle 113 \rangle$
measured reciprocal distance $[1/\text{nm}]$	3.08	4.86	5.75
literature value $[1/\text{nm}]$	2.59	4.23	4.96
scaling factor	0.84	0.87	0.86

Table III–18.: Reciprocal distances measured by PASAD [36] from the FFT shown in fig.III–19.b compared to values calculated from literature [17] for the Co_2Ti structure in $[112]$ orientation. A scaling factor is obtained for each reciprocal vector.

4.1.2. Analysis of the FFT images

The nanocrystal shown in fig.III-18.b is a Co_2Ti nanocrystal in $[110]$ orientation. Smaller lattice structures than lattice structures corresponding to fundamental layer packages (see section II-3) are indicated in the image but not clearly resolved. The ABC stacking order can be recognized. Fig.III-19.d shows the corresponding FFT image. The reciprocal lattice distances and the angles between the reflections are in agreement with literature values (cf. tab.III-19).

The lattice structure revealed in fig.III-18.c is in agreement with a $\text{Co}_{2.1}\text{Ti}_{0.9}$ nanocrystal in $[-661]$ real space orientation. Fig.III-20.c shows the corresponding FFT image. The measured uncommon angle of 54.5° between the two $\langle 106 \rangle$ reflections matches the theoretical angle very well as shown in tab.III-19). Literature values are taken from [17].

Fig.III-18.d reveals a Co_3Ti nanocrystal in $[110]$ orientation. The ABC stacking order of densely packed $\{111\}$ planes is clearly visible in the image. The corresponding FFT image is shown in fig.III-20.b. Superlattice reflections as indicated in fig.III-17.b could not be observed in the FFT. They would correspond to a periodic contrast change at atom positions in the $[002]$ and $[2-20]$ directions in the HRTEM images. But these contrast changes are not even recognizable in simulated HRTEM images of a thin L_{12} long range ordered Co_3Ti crystal. Therefore, no conclusion on the ordering is made from the lack of the superlattice reflections.

Fig.III-19.a displays a FFT of a nanocrystal imaged by HRTEM. The image is received from the NCEM. This FFT could correspond to two possible orientations of a Co_2Ti nanocrystal: a $[112]$ or a $[110]$ orientation. From comparison with simulated HRTEM images the considered crystal seems to be in $[112]$ orientation. However the reflections indicated with blue circles in fig.III-19.a can not be explained by that orientation. There is a 30° tilt between the $[112]$ orientation and the $[110]$ orientation along an axis in $[2-20]$ direction. A deviation from the $[112]$ orientation towards the $[110]$ orientation of the nanocrystal could explain the higher difference between measured reciprocal distances or measured angles and literature values compared to other FFTs. The values plotted in tab.III-19 are in between the expected values for both directions. The dominance of the $[2-20]$ reflection and the faint $\langle 111 \rangle$ reflections support this suggestion. Therefore, a deviation is also applied for the simulated HRTEM image like discussed in the next section III-4.2.

The FFT image shown in fig.III-20.d corresponds to a HRTEM image that is acquired at the PHILIPS CM30 ST microscope. If only the reflections with large reciprocal distances and strong dark contrast to the background are considered, the pattern could be identified as a pattern of a $\text{Co}_{2.1}\text{Ti}_{0.9}$ nanocrystal in a $[-443]$ orientation. There are some weak additional reflections visible in the FFT. The strong reflections with large reciprocal distances and some weak reflections indicated in fig.III-20.d match a Co_2Ti structure in $[110]$ orientation. In addition to the indicated but very weak $\langle 111 \rangle$ reflections for the Co_2Ti structure one can recognize their $\langle 222 \rangle$ multiples in the FFT image. In comparison to the FFTs of Co_2Ti nanocrystals in $[110]$ orientation shown in fig.III-19.c and fig.III-19.d the $\langle 111 \rangle$ reflections and the $[002]$ reflection are even weaker for this FFT image. The results are shown in tab.III-19.

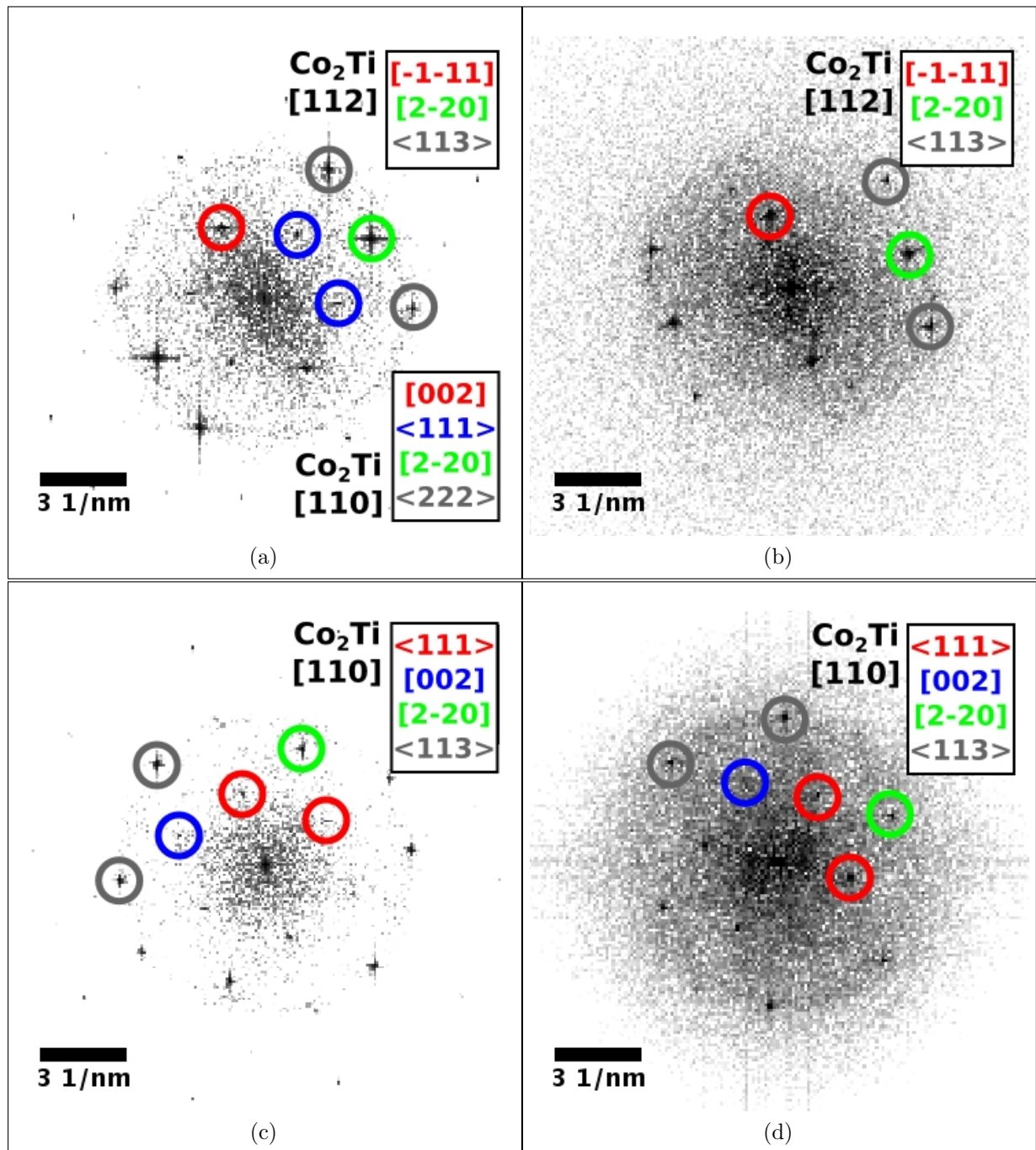


Figure III-19.: Fast fourier transformations of HRTEM images of Co_2Ti nanocrystals. The FFTs (a) and (c) correspond to HRTEM images received from NCEM and acquired at a FEI Titan microscope. The FFTs (b) or (d) correspond to HRTEM images that are shown in fig.III-18.a or in fig.III-18.b. These HRTEM images are acquired at the PHILIPS CM30 ST microscope. For the FFT image (a) two orientations of the Co_2Ti nanocrystal are possible. Assumed crystalline phases, crystalline orientations in real space and corresponding reciprocal lattice vectors are given in the images.

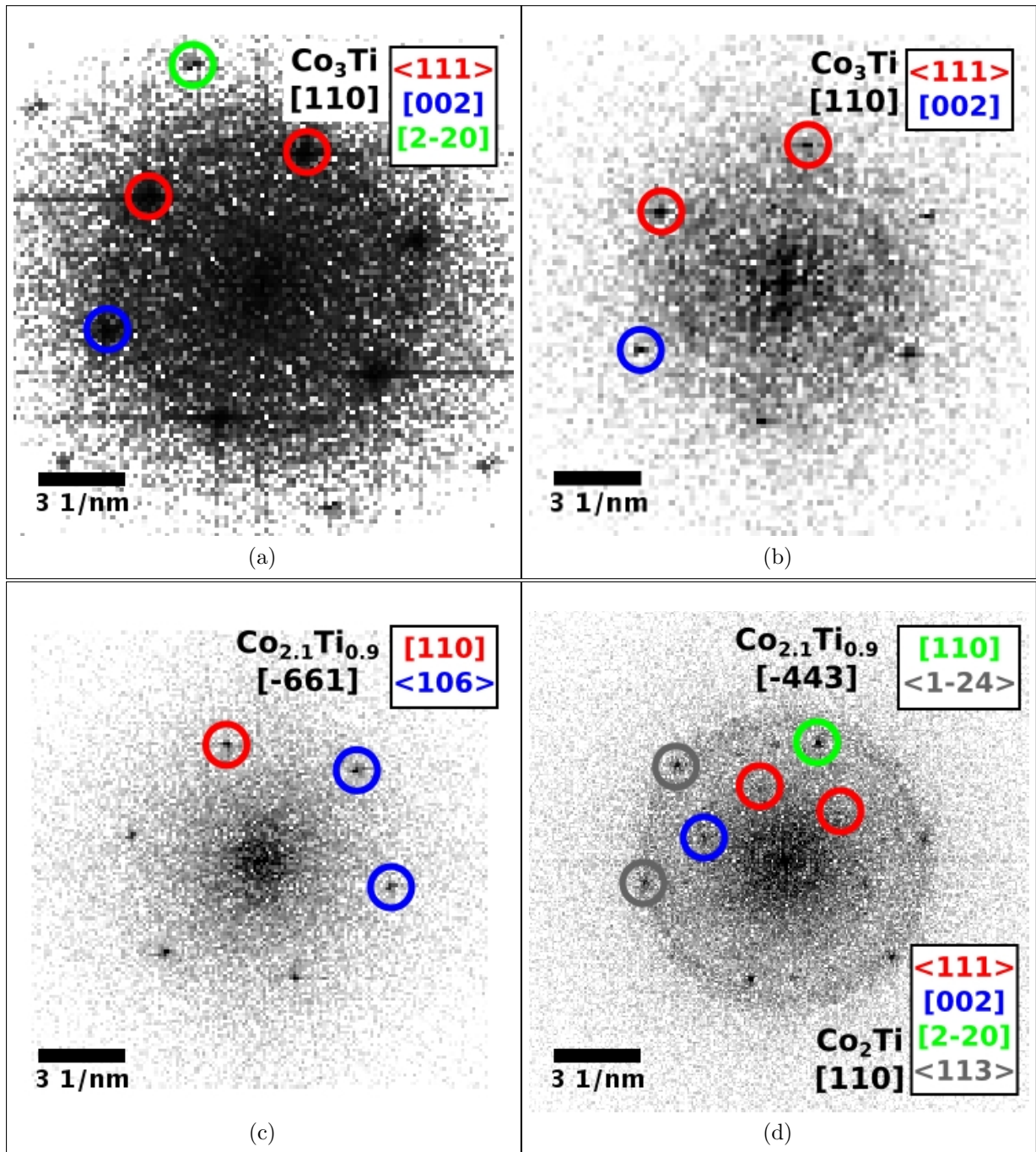


Figure III-20.: Fast fourier transformations of HRTEM images of Co_3Ti and $\text{Co}_{2.1}\text{Ti}_{0.9}$ nanocrystals. FFT (a) correspond to a HRTEM image received from NCEM and acquired at a FEI Titan microscope. Image (b) or (c) show FFTs of the HRTEM images displayed in fig.III-18.d or in fig.III-18.c. These HRTEM images are acquired at a PHILIPS CM30 ST microscope. The FFT image (d) is also calculated from a HRTEM image acquired at a PHILIPS CM30 ST. The pattern shown in (d) matches the structures of two different Laves phases. Assumed crystalline phases, crystalline orientations in real space and corresponding reciprocal lattice vectors are given in the images.

Analyzed FFTs of the HRTEM images received from the NCEM (FEI Titan)				
assumed reflections	reciprocal distances [1/nm]		characteristic angles [degree]	
	measured distance	literature value	measured angle	literature value
FFT shown in fig.III–19.a (Co ₂ Ti, [112] orientation)				
[-1-11]	2.76 ± 0.10	2.59	$\angle([1-3-1],[3-1-1])$	
[2-20]	4.18 ± 0.10	4.23	67.7 ± 1.5	62.96
<113>	5.01 ± 0.10	4.96		
FFT shown in fig.III–19.c (Co ₂ Ti, [110] orientation)				
<111>	2.58 ± 0.10	2.59	$\angle([1-11],[1-1-1])$	
[002]	3.05 ± 0.10	2.99	72.0 ± 1.5	70.53
[2-20]	4.16 ± 0.10	4.23		
FFT shown in fig.III–20.a (Co ₃ Ti, [110] orientation)				
<111>	4.81 ± 0.10	4.77	$\angle([1-11],[1-1-1])$	
[002]	5.52 ± 0.10	5.51	70.2 ± 1.5	70.53
[2-20]	7.88 ± 0.10	7.80		

Analyzed FFTs of the HRTEM images acquired at a PHILIPS CM30 ST microscope				
assumed reflections	reciprocal distances [1/nm]		characteristic angles [degree]	
	measured distance	literature value	measured angle	literature value
FFT shown in fig.III–19.d (Co ₂ Ti, [110] orientation)				
<111>	2.57 ± 0.10	2.59	$\angle([1-11],[1-1-1])$	
[002]	3.04 ± 0.10	2.99	71.0 ± 1.5	70.53
[2-20]	4.20 ± 0.10	4.23	$\angle([1-13],[1-113])$	
<113>	4.93 ± 0.10	4.96	50.4 ± 1.5	50.48
FFT shown in fig.III–20.c (Co _{2.1} Ti _{0.9} , [-661] orientation)				
[110]	4.19 ± 0.10	4.23	$\angle([106],[0-16])$	
<106>	4.49 ± 0.10	4.59	54.5 ± 1.5	54.81
FFT shown in fig.III–20.b (Co ₃ Ti, [110] orientation)				
<111>	4.75 ± 0.10	4.77	$\angle([1-11],[1-1-1])$	
[002]	5.39 ± 0.10	5.51	70.1 ± 1.5	70.53
FFT shown in fig.III–20.d (Co ₂ Ti, [110] orientation)				
<111>	2.45 ± 0.20	2.59	$\angle([1-13],[2-20])$	
[002]	2.92 ± 0.10	2.99	64.4 ± 1.5	64.76
[2-20]	4.19 ± 0.10	4.23	$\angle([1-13],[1-113])$	
<113>	4.89 ± 0.10	4.96	50.2 ± 1.5	50.48

Table III–19.: Reciprocal distances measured by PASAD [36] from FFTs of HRTEM images. The values are compared to values calculated from literature values of lattice spacings in [16] for the Co₂Ti structure, in [17] for the Co_{2.1}Ti_{0.9} structure and in [18] for the Co₃Ti structure. The error values are approximated from the pixel resolution of the FFT images. Crystalline orientations are given in form of real space lattice vectors.

4.2. HRTEM simulations

HRTEM images are simulated using the JEMS software [13]. The simulation is done for a FEI Titan electron microscope. Different crystallographic directions are considered for Co_2Ti , $\text{Co}_{2.1}\text{Ti}_{0.9}$ and Co_3Ti , respectively. Slight deviations from these directions are chosen in such a way that the final simulated HRTEM images match the acquired images as good as possible. During the HRTEM session the orientation of a nanocrystals in the specimen is not chosen by tilting but it is given by chance. Therefore, a nanocrystal which is suited for HRTEM is likely to be in an orientation having a slight deviation from a perfect crystallographic direction. The simulated images are compared to the HRTEM images received from the NCEM at Lawrence Berkeley National Laboratory acquired at a FEI Titan electron microscope.

The simulated HRTEM image of Co_2Ti in $[112]$ orientation agrees nicely to the acquired HRTEM image like shown in fig.III–21.a. The intensity values of the lattice points and their positions are conform.

In fig.III–21.b the HRTEM simulation for $[110]$ oriented Co_2Ti is compared to an acquired HRTEM image. Artificial noise is added in the lower part of the simulated image. The simulation and the HRTEM image are in good agreement. It should be noted that the simulation shows a lattice with oscillating intensities of lattice points for a large defocus range. This oscillation is weak in the displayed pattern.

The simulated HRTEM image of Co_3Ti in $[110]$ orientation is in good agreement to the acquired image. Both images are shown in fig.III–21.c. The intensity values of the lattice points and there positions are conform. A periodic oscillation of the lattice point intensities can not be observed, even so the long range ordered L_{12} structure is used for the simulation. The acquired HRTEM image does also not show such a periodic oscillation.

It should be noted that also other orientations were simulated, e.g. for $[112]$ oriented Co_3Ti the simulated image shows only lattice fringes for the $(-1-11)$ plane since the lattice spacing for the $(2-20)$ plane can not be resolved anymore.

Simulations of Co_2Ti oriented in $[112]$ direction and $\text{Co}_{2.1}\text{Ti}_{0.9}$ oriented in $[120]$ direction reveal a similar projected structure and stacking order of Kagomé layers. Therefore, a clear distinction of the structure based on HRTEM images in these directions is not possible. The lattice distances of 0.386 nm for the (-111) plane and 0.237 nm for the $(2-20)$ plane of Co_2Ti [16] are the same as for the (004) plane and the $(1-20)$ plane of $\text{Co}_{2.1}\text{Ti}_{0.9}$ [17] up to the third decimal digit in nm. As an example, simulated HRTEM images of $\text{Co}_{2.1}\text{Ti}_{0.9}$ in $[120]$ orientation are shown in fig.III–21.d. The simulations differ in defocus values and deviation from the exact orientation.

On the other hand, the ABAC stacking order of the Kagomé layers of the $\text{Co}_{2.1}\text{Ti}_{0.9}$ structure can be recognized in the simulated images when the beam direction is parallel $[100]$ as shown in fig.III–21.d. The ABAC stacking sequence is present in the $[001]$ direction. The appearance of the layers in the simulation depends on defocus and deviation from the exact orientation.

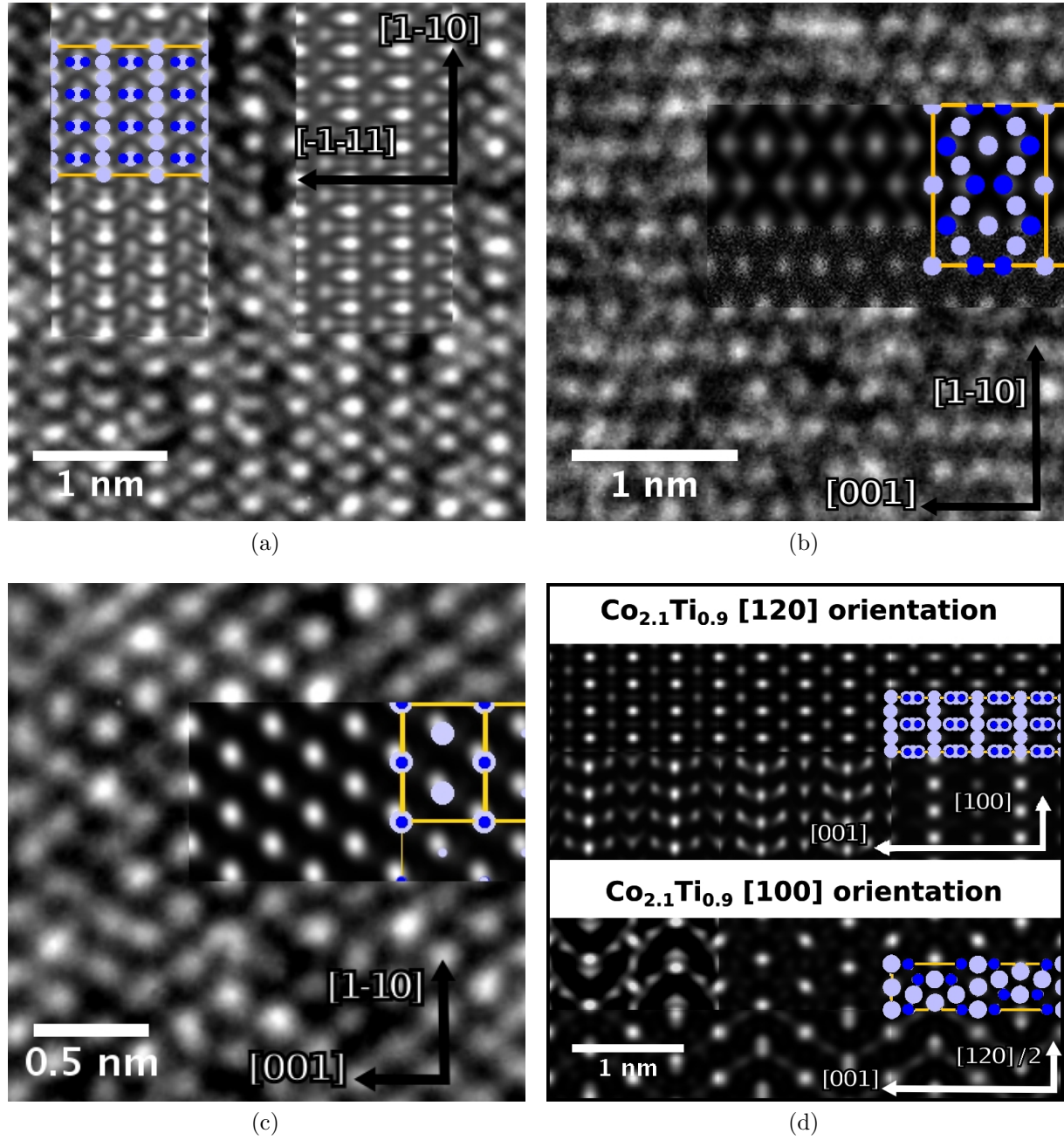


Figure III-21.: Comparison of HRTEM images received from the NCEM and HRTEM images that are simulated using the JEMS software [13]. The atom positions in one unit cell and lattice vectors are indicated for every image. Titan atoms are marked in blue. Image (a) shows a HRTEM image of a Co₂Ti nanocrystal in [112] orientation. Two simulated images revealing different defocus values and different slight deviations from the [112] pole are overlayed in the image. Image (b) shows a Co₂Ti nanocrystal in [110] orientation and the overlayed simulated image. In image (c) a HRTEM image of a Co₃Ti nanocrystal in [110] orientation is compared to the simulated image. Image (d) shows simulated HRTEM images of Co_{2.1}Ti_{0.9} in two low indexed orientations. Defocus values and deviations from the poles are varied again leading to different patterns.

4.3. Analysis of a surface oxide layer

4.3.1. Phase structure of the oxide layer

The chemical analysis at the edge of the TEM specimen reveals a high amount of oxygen and cobalt indicating the presence of a cobalt oxide layer at the specimen surfaces. The atomic concentrations of the elements cobalt and oxygen yield a cobalt to oxygen concentration ratio of 0.64 ± 0.09 at the very edge of the specimen as discussed in section III-3.5.6 and shown in tab.III-17. Therefore, the cobalt oxides Co_2O_3 and Co_3O_4 are considered in this study. Structural data of HRTEM images is analyzed again by FFTs and compared to data that is deduced from literature values for the cobalt oxide phases. Literature values given at the AtomWork database are taken from [37] for the hexagonal Co_2O_3 phase, they are taken from [38] for the tetragonal Co_3O_4 phase and they are taken from [39] for the cubic Co_3O_4 phase.

The analyzed HRTEM images of specimen Co3Ti-I3 are acquired at a PHILIPS CM30 ST. In addition an ADF image of that specimen acquired at the ASTEM is analyzed in the same way. Continuous lattice fringes are visible for areas of about several nanometers to the square in HRTEM images of the specimen edge. The small sizes of this connected areas indicate that the cobalt oxide layer consists of nanometer scaled domains. Regions of interests are set at areas that have a favorable orientation to the incident electron beam. They reveal lattice contrast which indicates that more than one lattice plane is in projection. About eight areas in different HRTEM images are analyzed. They are smaller than approximately 30 nm^2 . Most ROI are set at the very edge between the specimen and the specimen hole. But two ROI are also set at an edge along one of the long cracks that are visible in the sketch of specimen Co3Ti-I3 shown in fig.II-4. Although the specimen is too thick for TEM at positions next to the cracks, a thin region could be found that spans one crack locally. This region is not located near the specimen hole but it is located at the propagating edge of the crack instead. Reciprocal distances and angles are measured from the reflections visible in the FFT of a considered ROI. The small ROI areas lead again to a low pixel resolution for the FFTs. Thus, a single reciprocal distance measurement could have a large error in between $\pm 0.1 \text{ nm}^{-1}$ and $\pm 0.3 \text{ nm}^{-1}$. The error of an angle measurement could also yield values between approximately 2° and 4° .

The Measurements reveal reciprocal distances of $2.1 \text{ nm}^{-1} \pm 0.1 \text{ nm}^{-1}$, $3.5 \text{ nm}^{-1} \pm 0.1 \text{ nm}^{-1}$, $4.0 \text{ nm}^{-1} \pm 0.2 \text{ nm}^{-1}$ and $4.9 \text{ nm}^{-1} \pm 0.1 \text{ nm}^{-1}$ depending on the particular ROI. Note that the error values given here represent the range of measured values and not the uncertainty of a single measurement like discussed previously. The FFT patterns do not match with any diffraction pattern of hexagonal Co_2O_3 .

The measured reciprocal distances and angles in the FFT patterns coincide with literature values for diffraction patterns of Co_3O_4 at all considered ROI.

Co_3O_4 yields very similar lattice distances and angles for the two phases, one with a cubic crystal system and the other one with a tetragonal crystal system. They reveal differences in reciprocal distances of less than 0.1 nm^{-1} and differences in angles between reciprocal lattice vectors of less than 1° . Thus, every FFT pattern which is observed here is in agreement with one diffraction patterns of the cubic phase and it is in agreement with at least two diffraction pattern of the tetragonal phase. Recognized orientations of the oxide nanocrystals relative to the incident electron beam are given in form of real space lattice vectors in tab.III-20. The cobalt oxide surface layer is visible in HRTEM images of the specimen edge at amorphous specimen regions and at residual crystalline regions.

4.3.2. Size estimation for the oxide crystals

The projected size of the oxide nanocrystals is estimated from two HRTEM images displaying different specimen edge regions of about $50 \times 50 \text{ nm}^2$. Therefore, single reflection pairs, consisting of a reflection and its negative counterpart, are selected from the FFT of a whole image. Recognized reflections with reciprocal distances of approximately 2.1 nm^{-1} , 3.5 nm^{-1} and 5 nm^{-1} are chosen for the process. These reflections can be assigned to reciprocal lattice vectors of the cobalt oxide. Inverse FFT (IFFT) images are calculated for each pair of reflection. The IFFT images display lattice fringes in a specific direction revealing high brightness values compared to the average value at image areas where these lattice fringes are visible in the original HRTEM image. Thus, the size of the connected areas where a specific lattice plane is in projection can be obtained by a segmentation of the IFFT images using a grayscale threshold. Striped areas in the resulting binary images can be transformed to solid areas by the binary operations dilatation and eroding in digital image processing.

Fig.III-22.a shows one of the two HRTEM images that are analyzed for a size estimation of the oxide nanocrystals. $\langle 111 \rangle$ reflections of cubic Co_3O_4 or $\langle 101 \rangle$ reflections of tetragonal Co_3O_4 that feature a valid angle of about $70^\circ \pm 4^\circ$ between them are indicated by the symbols $\circ$, Δ , ∇ and $\square$. They would correspond to a $[110]$ real space orientation of the cubic phase or to a $[100]$ or $[111]$ orientation of the tetragonal phase relative to the incident electron beam. But IFFT images of those reflections show that specimen areas of matching reflection pairs do not overlap significantly. This statement is also true for most of the other selected reflections. Reflections having a reciprocal distance of about 3.5 nm^{-1} do not occur at a position in the FFT image at which they would be expected to occur if one of the previously discussed orientations should be present at the considered specimen area. Thus, each selected reflection pair in the FFT image can be assumed to originate from a different crystalline orientation. Then each segmented area in the IFFT images represents the size of an individual oxide nanocrystal.

In addition the orientation of two oxide nanocrystals could be deduced from the HRTEM image and the FFT shown in fig.III-22.a. Reflections indicated by the symbols $\triangleleft$ and $\triangleright$ can be associated to a $[103]$ orientation of the cubic Co_3O_4 phase or a $[331]$, $[113]$ or $[120]$ orientation of the tetragonal Co_3O_4 phase. The segmented areas of IFFT images show a clear overlap for reflections that are part of the corresponding diffraction patterns.

cubic Co_3O_4	tetragonal Co_3O_4	cubic Co_3O_4	tetragonal Co_3O_4
$[112]$	$[311]$ $[101]$	$[141]$	$[351]$ $[102]$
$[103]$	$[331]$ $[113]$ $[120]$	$[152]$	$[371]$ $[321]$

Table III-20.: Real space lattice vector indices in Co_3O_4 . The third index refers to the c axis in case of the tetragonal crystal system. Each column in the two tables represents recognized possible orientations of an oxide nanocrystal in a HRTEM image. Some of the analyzed oxide nanocrystals reveal the same possible orientations.

Crystalline areas between 1 nm^2 and 160 nm^2 in size are obtained for the oxide surface layer from the segmented binary IFFT images of both analyzed HRTEM images. The shape of the oxide nanocrystals can be approximated by squares in a specimen plane that is parallel to the specimen surface. This results in a recalculated lateral length (d) of about 1 nm to 13 nm for the oxide nanocrystals. The size of segmented areas is evaluated individually for each of the two HRTEM images. Segmentation artifacts could lead to the occurrence of very small and very large areas in the segmented binary images. Different quantities of d values are selected by their size to consider those segmentation errors. The different lateral length quantities are chosen by the following conditions: $0 < d$, $2 \text{ nm} < d$, $3 \text{ nm} < d$, $2 \text{ nm} < d < 9 \text{ nm}$, $3 \text{ nm} < d < 9 \text{ nm}$, or $d < 9 \text{ nm}$. The resulting mean values for the recalculated lateral length are all in between 3 nm and 6 nm for both HRTEM images when rounded off to the nearest 1 nm. They all yield standard deviations for single length values of about 2 nm. A final mean value for the size of the oxide nanocrystals can be calculated from the obtained mean d values of the different quantities. Then an uncertainty is given by the SD of the final mean value.

The cobalt oxide surface layer consists of Co_3O_4 nanocrystals with a mean lateral length of $4 \text{ nm} \pm 1 \text{ nm}$ assuming they are square shaped in a plane that is parallel to the specimen surface.

4.3.3. Lattice fringes at the amorphous phase

Lattice fringes in HRTEM images could be recognized not just at specimen positions where nanocrystals of the cobalt-titanium alloy are embedded in the amorphous matrix but also at the amorphous matrix itself which is surrounding the nanocrystals. This lattice fringes occur despite the fact that the specimen regions considered here are located further away from a specimen edge when compared to the specimen regions used to identify the phase of the surface oxide layer. The HRTEM images of nanocrystals and their surrounding amorphous matrix display again specimen areas of about $50 \times 50 \text{ nm}^2$. A specimen edge is not visible in these images.

Reciprocal distances corresponding to these lattice fringes are still in good agreement with literature values for Co_3O_4 . Especially the occurrence of reflections yielding a reciprocal distance of $2.1 \text{ nm}^{-1} \pm 0.1 \text{ nm}^{-1}$ in the FFTs of HRTEM images can be assigned to the presence of Co_3O_4 . Co_3Ti , $\text{Co}_{2.1}\text{Ti}_{0.9}$ and Co_2Ti do not show this reciprocal distance according to the X-ray diffraction data given at the AtomWork database [14], [15]. Reciprocal distances calculated for the rutile, brookite and anastasia phases of titanium oxide using literature data of the AtomWork database do also not show a value of $2.1 \text{ nm}^{-1} \pm 0.1 \text{ nm}^{-1}$. Diffraction patterns of Co_3O_4 could be recognized in FFT images of ROI that are set at the amorphous matrix in three different HRTEM images of nanocrystals and surrounding amorphous matrix. The corresponding real space orientations relative to the incident electron beam are the same in all three images. The oxide is oriented in [141] direction for the cubic Co_3O_4 phase and in [351] direction or [102] direction for the tetragonal Co_3O_4 phase.

An example for the presence of lattice fringes at the amorphous matrix is given in fig.III-22.b. The figure shows a detail of a HRTEM image displaying both a $\text{Co}_{2.1}\text{Ti}_{0.9}$ nanocrystal in [252] orientation and the surrounding amorphous matrix.

In addition the FFT of the whole image is overlaid in the figure. IFFT images of selected reflection pairs are calculated again. Reflections marked with the symbol $\square$ in the FFT correspond to the nanocrystal. The visible additional reflections do not originate from specimen positions at the nanocrystal but rather from areas at the surrounding amorphous matrix. Reciprocal lattice vectors of $2.1 \text{ nm}^{-1} \pm 0.1 \text{ nm}^{-1}$ length yield again an angle of about $70^\circ \pm 4^\circ$ between them. This condition would be in agreement with a specific orientation of the cobalt oxide like discussed previously in section III-4.3.2. The corresponding reflections are marked by the symbol $\triangle$ in the overlaid FFT image in fig.III-22.b. But real space areas displaying the related lattice fringes do not overlap in the HRTEM image.

In conclusion of this section, a crystalline cobalt oxide surface layer can lead to recognizable lattice fringes and lattice contrast in HRTEM images of an amorphous cobalt-titanium matrix.

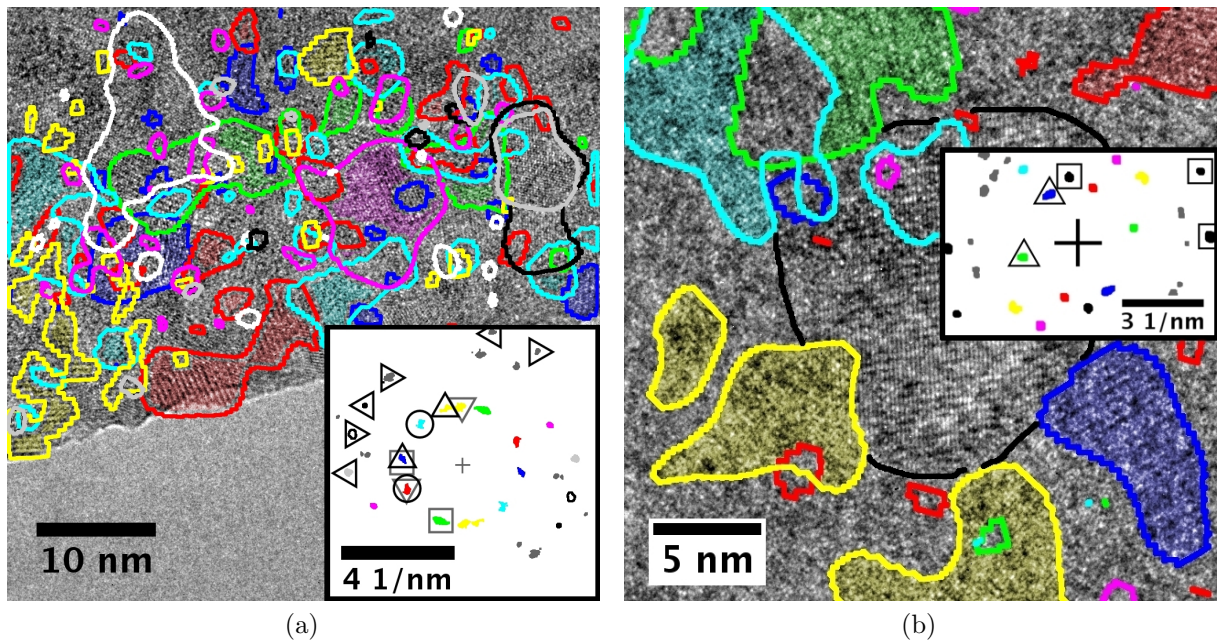


Figure III-22.: HRTEM images of specimen Co₃Ti.I3. The edge region between the specimen and the specimen hole is displayed in (a). Image (b) shows an amorphous specimen region with an embedded Co_{2.1}Ti_{0.9} nanocrystal in [252] real space orientation relative to the incident electron beam. Areas revealing the same lattice fringes are bordered with a line of the same color. The areas are segmented in IFFT images which are calculated from one reflection pair visible in the FFT of a HRTEM image. Pairs of reflections related to image areas of same lattice fringes are displayed in color in the overlaid FFT images in (a) and (b). The overlaid FFT images are segmented images and visible reflections appear broader due to the segmentation process and also for a better recognizability in the images. Reflections which could be part of one specific crystal orientation are marked with the symbols $\circ$, $\triangle$, ∇ , $\square$, $\triangleleft$ and $\triangleright$. Co₃O₄ crystals oriented in [103] real space direction for the cubic phase or in equivalent directions for the tetragonal phase (see tab.III-20) show reflections marked with $\triangleleft$ and $\triangleright$ in (a). Reflections related to the displayed Co_{2.1}Ti_{0.9} nanocrystal are marked with $\square$ in (b).

IV. General discussion

1. Instrumental

1.1. Differences in specimen thickness calculations

Two different processes for specimen thickness calculations are discussed in this work for line scans A and B. The specimen thickness at line scans A and B is calculated once by free software as described in section III-3.4.3 and it is calculated in addition by commercial software of the Gatan company as described in section III-3.5.6. Both calculation processes are based on the log-ratio method to derive reduced specimen thickness values. The results obtained from the two different calculation processes are in contradiction to each other. Reduced specimen thicknesses derived by the Gatan software yield values of approximately one third of the values that are derived by free software.

In difference to the calculation by free software, the GMS EELS package of the Gatan company applies a power-law fit during the calculation of the total integrated intensity I from a low energy loss spectrum like discussed in the user guide [29]. Intensities at energy losses larger than energy losses of plasmon peaks are approximated by a power-law decrease in order to eliminate the influence of noise which dominates the low energy loss spectrum at high energy losses. Reduced thickness values of maximum 0.01 difference to values obtained in section III-3.4.1 are obtained by applying a similar fit for spectra evaluated by free software at line scans A and B. These differences are in the range of the given uncertainties for the resulting p values. Thus, the contradiction in p values between the two calculation processes can not be explained by the applied power-law fit in low energy loss spectra.

Another difference for the two calculation processes arises from the correction of plural scattering. The low energy loss spectra of line scans A and B are corrected for plural scattering by the Gatan software using the Fourier-Log deconvolution method which is discussed in literature like [22]. These spectra are not corrected during the evaluation by free software. But the influence of plural scattering on the energy loss spectra is small, because the resulting p values that are shown in tab.III-2 are already low, indicating a relative thin specimen. Therefore, the plural scattering correction in the low energy loss spectra should not be able to account for the occurring difference in reduced specimen thickness values between the two calculation processes.

The TEM specimen Co₃Ti₁₃ would be very thin at line scan positions A and B according to results based on the Gatan software. Note that these scan positions are not located next to a specimen edge. The visible specimen area in STEM images of nanocrystals A and B implies a distance of least 30 nm to the specimen hole. The results obtained by Gatan software yield specimen thickness values that are of equal thickness or even thinner than the embedded nanocrystals themselves like shown in fig.III-14. One could argue that the plateau which occurs in the integrated intensity profile at scan positions of nanocrystal A indicates a cut-off of the nanocrystal's shape at the specimen surface. This plateau can be recognized in fig.III-9.c and fig.III-9.d. Similar plateaus occur in all integrated intensity profiles for nanocrystals of the cobalt-titanium alloy. Thus, the plateaus could

also be related to a faceting of the nanocrystals shape rather to a cut-off of nanocrystals at the specimen surface. This faceting is already visible in the TEM BF images of fig.III-2. It appears clearly in the ADF image of fig.III-3.a and in HRTEM images that are shown in fig.III-18. Plateaus could not be observe in integrated intensity profiles of titanium oxide particles. In agreement with the shape observation that is discussed here, these TiO_2 particles also reveal a more spherical shape than nanocrystals of the cobalt-titanium alloy. Such difference in shape between TiO_2 particles and cobalt-titanium nanocrystals can be recognized again from ADF images and HAADF images in fig.III-3 for instance.

1.2. Contrast in SEM images

Areas displaying the amorphous matrix reveal a positive contrast to crystalline areas at acquired BSE images in the SEM like shown in fig.III-1. This contrast is unexpected because an amorphous matrix should yield a similar but still lower density than its crystalline counterpart of the same chemical composition. Therefore, the mean atomic number dependence of the contrast generated by BSE should lead to lower brightness values at the amorphous matrix compared to brightness values at the crystalline phase in the images.

A similar behavior can be observed in as-bought samples as discussed in section II-1. There are two areas of different chemical composition shown in the SEM image of fig.II-1. These areas are analyzed in a previous TEM study. Areas of 28 at.% titanium correspond to the $\text{Co}_{2.1}\text{Ti}_{0.9}$ Laves phase and areas of 21 at.% titanium correspond to a $\gamma\gamma'$ phase consisting of high temperature hexagonal cobalt and Co_3Ti . The contrast between these two different regions is also inverse to the expected contrast in BSE images.

Two effects are discussed here that could be responsible for the flipped contrast.

1.2.1. Variations of the oxygen concentration

Additional oxygen concentration in samples has a huge influence on the mean Z contrast in BSE images due to the small atomic number of the element oxygen compared to the elements titanium and cobalt. This is already shown in the HAADF image and in the HAADF profile of fig.III-16. HAADF images in TEM reveal a Z contrast similar to BSE images in SEM. Thus, a higher oxygen concentration at crystalline areas compared to amorphous areas could explain the observed contrast in the BSE images of as-deformed samples. The same argumentation can be applied to areas of the $\gamma\gamma'$ phases in comparison to areas of the $\text{Co}_{2.1}\text{Ti}_{0.9}$ Laves phase for as-bought samples.

Highly deformed structures can be observed for the as-deformed crystalline phase in the TEM. Therefore, crystalline areas should reveal a high density of interfaces in form of lattice defects, small angle boundaries and large angle boundaries. These interfaces could facilitate the diffusion of oxygen from the surface into the sample. In contrast to the roughly homogeneous plastic deformation of a crystalline material, the plastic deformation in amorphous materials is concentrated locally in shear bands. This difference in deformation behavior and in the density of defects could lead to a higher oxygen concentration at crystalline areas compared to the oxygen concentration at the amorphous matrix in the considered samples.

A similar argumentation can be applied to the as-bought material. Here the nanostructured $\gamma\gamma'$ phases must have high densities of crystalline boundaries which could lead to an increased diffusion of oxygen from the surface into the samples. Thus, a higher amount of oxygen is possible at regions of $\gamma\gamma'$ phases compared to the micrometer scaled regions of the $\text{Co}_{2.1}\text{Ti}_{0.9}$ Laves phase.

1.2.2. Magnetic contrast

The backscattering coefficient of BSE in the SEM can depend on magnetic fields near the specimen surface like mentioned in Reimer's and Kohl's book Transmission Electron Microscopy [24]. Since the amorphous cobalt-titanium matrix in the as-deformed samples and the $\text{Co}_{2.1}\text{Ti}_{0.9}$ Laves phase in the as-bought samples are ferromagnetic [40], an additional magnetic contrast could also be the reason for higher brightness values of these phases in BSE images.

2. Material science

2.1. Oxygen and surface layers

High concentrations of oxygen are not restricted to the cobalt oxide layer at the TEM specimen surface. A similar amount of oxygen is present at specimen edge areas 1 and 2 which are discussed in section III-3.5.6 even though they reveal different cobalt and titanium concentrations. Specimen area 1 is located at the very edge of the TEM specimen with a distance of approximately 2.5 nm from the edge. The low $c_{\text{Ti}}/c_{\text{Co}}$ ratio and the high oxygen concentration indicate that nearly only Co_3O_4 is present at this specimen area. Specimen area 2 is set at a distance of 6 nm from the edge. Here the $c_{\text{Ti}}/c_{\text{Co}}$ ratio is already similar to the value for the amorphous matrix but still a high oxygen concentration can be observed like mentioned above. Since most of the cobalt atoms are still bound in Co_3O_4 , the actual $c_{\text{Ti}}/c_{\text{Co}}$ ratio of the amorphous matrix must be much higher at position 2. Thus, one can conclude that TEM specimen Co3Ti.I3 reveals a layer of high amount of titanium beneath the cobalt oxide surface layer. This layer cancels the effect of a higher cobalt concentration at the specimen surface on the measured mean chemical compositions at the specimen.

If the simplification is applied that the whole amount of cobalt is bound in Co_3O_4 , then the remaining amount of oxygen yields a value of $32 \text{ at.}\% \pm 13 \text{ at.}\%$ or $32 \text{ at.}\% \pm 3 \text{ at.}\%$ for specimen area 1 or 2. Thus, the remaining amount of oxygen seems to be constant relative to the amount of titanium at these areas even though a large uncertainty in the resulting value is obtained at position 1 due to the small absolute titanium concentration. This relation do not hold for specimen position 3 where already a considerable amount of amorphous matrix should be present and where the amount of oxygen is reduced.

So the results of section III-3.5.6 show, in agreement with results of section III-3.5.2, that the amount of oxygen in the specimen depends on the amount of titanium. This dependency occurs at least in layers near the specimen surface. Since the oxygen is concentrated near the specimen surface, oxygen model 2 (see section II-5.3.2) is a more accurate model than oxygen model 1 for the TEM specimens.

2.2. Nanocrystals and oxides

Nanocrystals of the cobalt-titanium alloy nucleate inside the amorphous matrix which reveals the same mean c_{Ti}/c_{Co} ratio as the mean c_{Ti}/c_{Co} ratio at specimen positions next to the nanocrystals. Thus, the matrix corrected chemical composition calculations should lead to valid results like shown in section III-3.5.5 for nanocrystal A. Here similar values for a mean specimen thickness are obtained from electron low energy loss spectra (see section III-3.4.3) and from a recalculation based on the assumption that nanocrystal A is in the Co_2Ti Laves phase (see section III-3.5.5). The recalculated specimen thickness is compared to the obtained specimen thickness in tab.III-12 and in tab.III-14.

If one would assume the $Co_{2.1}Ti_{0.9}$ Laves phase for nanocrystal A, then the mean titanium and cobalt concentrations at line scan positions of the nanocrystal are already equal to the nominal concentrations. Thus, a specimen thickness of $t \lesssim 15$ nm could be estimated from the diameter of nanocrystal A. This value is smaller than the value of 22.6 nm ($\pm$ 2.0 nm ($-$) 3.9 nm which is obtained from electron low energy loss spectra.

In this work the presence of Co_3Ti nanocrystals (C), $Co_{2.1}Ti_{0.9}$ nanocrystals (VI) and Co_2Ti nanocrystals (A, IV, V and VII) is indicated by a chemical analysis based on EELS and it is confirmed by HRTEM. The nanocrystals are embedded in an amorphous cobalt-titanium matrix in regions that are clearly separated from crystalline remnants at as-deformed samples. Since embedded nanocrystals occur in the amorphous matrix of TEM specimens that are prepared by different methods, they are not artifacts of the TEM specimen preparation.

The presence of a cobalt oxide surface layer could be the reason why the titanium concentrations at line scan positions of the TiO_2 particles B, D (oxide) and VIII seems to be lower than the nominative concentration of TiO_2 . The element oxygen is concentrated not only at the TiO_2 particles, but also at the Co_3O_4 layer. So the actual c_{Ti}/c_{Co} ratios of the titanium oxide particles must be higher than the ones averaged over the specimen thickness which are shown in fig.III-14 and fig.III-15.

If the oxide particles form during the thinning process of the TEM specimen preparation, it is reasonable to assume the nucleation sites of TiO_2 particles in the titanium rich layer beneath the Co_3O_4 surface layer because of the high oxygen concentration and the low cobalt concentration in these layer. The slight increase in specimen thickness at TiO_2 particle B compared to its surrounding amorphous matrix supports the suggestion that TiO_2 particle B is located near a surface rather than at the center of the TEM specimen in thickness direction. This thickness increase can be seen from the mean specimen thickness values in tab.III-4 as well as in fig.III-10.c and fig.III-10.d. If the titanium oxide particles nucleate from the titanium rich layer and the specimen is still covered with cobalt oxide, then the titanium concentration in the remaining material surrounding the oxide particle in thickness direction must be decreased when compared to the mean value of specimen positions next to the oxide particle. Decreased mean c_{Ti}/c_{Co} values could be a reason for the failure of matrix corrected chemical composition calculations at oxide particles for specimen thickness values given in section III-3.4.3. These calculations are discussed in section III-3.5.5. Lower mean c_{Ti}/c_{Co} values of the amorphous matrix are equivalent to larger specimen thickness values as shown in fig.III-13 for oxide particle B.

Nanocrystals of the cobalt-titanium alloy are present in TEM specimen Co3Ti_I4 that is prepared by mechanical polishing followed by electrolytic polishing and they are present in TEM specimen Co3Ti_cross that is prepared by mechanical polishing followed by ion milling.

Thus, the nanocrystals form by dynamic crystallization during the HPT deformation.

Faceting of the nanocrystals could be caused by the low surface energy of low index planes.

TiO₂ particles reveal a more spherical shape than the nanocrystals of the cobalt-titanium alloy. They are either present already in the initial material or assumed to nucleate in the titanium rich layer near the TEM specimen surface. These oxide particles are rather artifacts of the sample preparation than oxide particles formed during HPT deformation.

2.3. Compositional variations of the amorphous matrix

Variations of the titanium and cobalt concentration at the amorphous matrix can be recognized from the c_{Ti}/c_{Co} profiles of fig.III-9 and fig.III-10. In addition most of the peak positions in a titanium curve correlate with a peak position in an oxygen curve for integrated intensity profiles. One possible explanation for this correlation could be the presence of the titanium and oxygen rich layer beneath the specimen surface.

The intensity in HAADF images is proportional to n_a and it is proportional to Z^α with $\alpha \simeq 1.6$. The dependency on the specimen thickness is implied in n_a . Thus the contrast variations in HAADF images depends on both, changes in n_a and changes in mean Z values. Lets assume a constant amount of titanium and cobalt at a specific specimen position. Then an increase of the amount of oxygen at this position would lead to a larger value of n_a but it would lead also to a smaller value of Z for instance. At the given chemical concentrations for the elements titanium cobalt and oxygen, the variations in n_a and in $Z^{1.6}$ are of the same order of magnitude and partially cancel each other. In order to relate chemical variations or variations in n_a to contrast variations in acquired HAADF images at the amorphous matrix, the contrast in HAADF images is calculated along EELS line scans. Therefore, n_a ratios and mean Z ratios are calculated from EELS data by eq.II-7 for each line scan position. The values are set relative to mean values for the amorphous matrix. Then a HAADF profile calculated from EELS data along a line scan can be compared to a HAADF profile that is deduced from an acquired image along the scan line.

Mean values for absolute atomic concentrations of all three elements must be known at the amorphous matrix for calculating HAADF profiles. The results of a chemical analysis by the Gatan EELS package that are displayed in tab.III-15 and results displayed in tab.III-8 can be used to estimate mean atomic concentrations at the amorphous matrix for each of the line scans A to D. In addition mean absolute atomic concentrations at the amorphous matrix can be calculated for line scan B from tab.III-7 like discussed at the end of section III-3.5.2. Then tab.III-8 is used again to estimate the mean concentrations at all line scans A to D.

IV. General discussion

Calculations based on the Gatan EELS package lead to mean concentrations of about 21 at.% titanium, 54 at.% cobalt and 25 at.% oxygen at the amorphous matrix of all line scans A to D. Calculations based on line scan B lead to mean concentrations of about 13 at.% titanium, 37 at.% cobalt and 50 at.% oxygen. Both results yield a similar c_{Ti}/c_{Co} value but different relative cobalt and oxygen concentrations. This difference in c_{O}/c_{Co} has an neglectable influence on the calculated HAADF profiles. The calculation of profiles shown in fig.IV–1 is based on line scan B.

Similar contrast variations along calculated and acquired HAADF profiles can be recognized at line scans A to D. The contrast variations are on a smaller length scale compared to variations related to embedded nanocrystals. Calculated and acquired HAADF profiles are compared for line scan A and line scan D in fig.IV–1. Contrast variations in the calculated HAADF profile of line scan D (see fig.IV–1.b) are reduced in amplitude when compared to the strong variations of the relative atomic numbers for the elements titanium and oxygen that are shown in fig.III–11.a.

It is shown that variations of chemical concentration or a variation in the number of atoms per specimen area can lead to contrast variations at the amorphous matrix in HAADF images. Thus, the observed contrast variations in the images indicate that these variations do indeed occur at the amorphous matrix. A change of specimen thickness and a change in number density lead both to changes in n_a .

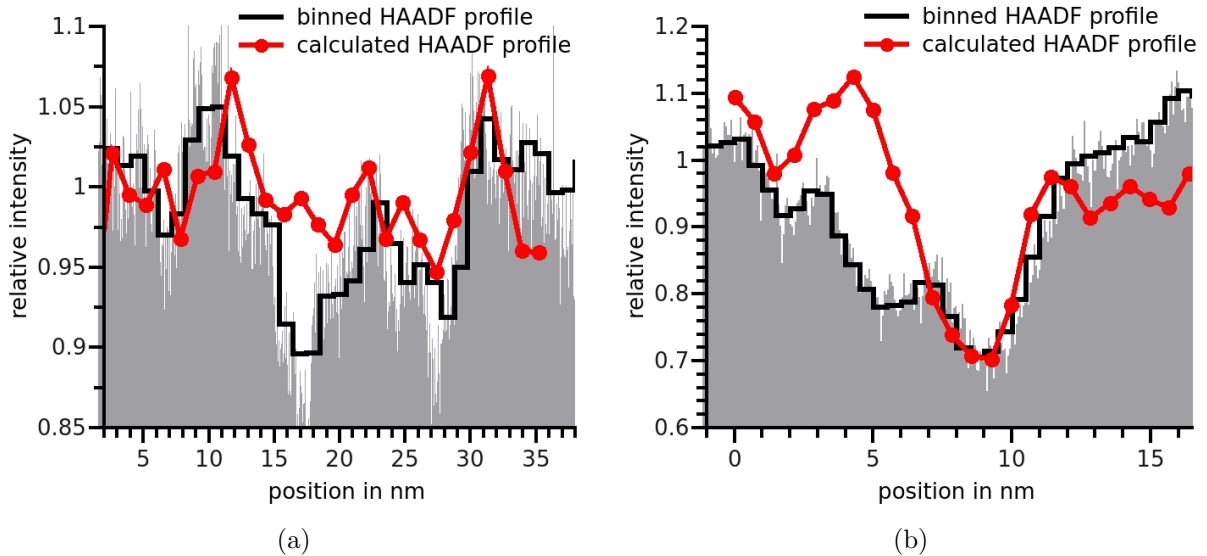


Figure IV–1.: Acquired HAADF profiles along EELS line scan A (a) and EELS line scan D (b). Binned profiles and calculated profiles are overlaid in the images. HAADF profiles are binned to approximately 1 pixel per nanometer (a) or 2 pixel per nanometer (b) in order to adjust the pixel resolution to the calculated HAADF profiles. The calculation is based on n_a values of titanium, cobalt and oxygen which are derived from EELS for each line scan position. The intensity values are set relative to a mean value of the amorphous matrix.

The considered contrast changes in HAADF images would correspond to differences in specimen thickness values between about 1 nm and 3 nm. This values would be in the range of the uncertainty of specimen thickness values given in tab.III-4. But the SD of a single thickness value is smaller than the uncertainty values given in the table. It has a value of about 1 nm for line scan A and a value of about 1.5 nm for line scans B to D. Therefore, changes in the specimen thickness should be recognizable along the EELS line scans. But the specimen thickness profiles do not correlate with integrated intensity profiles for high spatial variations in general like shown in fig.III-9, fig.III-10 and fig.III-11. This result suggests that changes in n_a are related to density changes in the amorphous matrix rather than to specimen thickness changes in general.

The discussed contrast variations in HAADF images are much weaker at specimen Co3Ti.I4 than at specimen Co3Ti.I3. These variations are overlayed by lower spatial frequency variations in HAADF images of specimen Co3Ti.I4.

In general, the precipitation of nanocrystals in the amorphous matrix during the HPT deformation requires diffusion processes and atomic rearrangements under a high hydrostatic pressure of 4 GPa. A chemical segregation by the formation of chemical domains with different c_{Ti}/c_{Co} ratios in the amorphous matrix during the HPT deformation could be a reason for dynamic crystallization of nanocrystals in phases of different chemical composition (polymorphous dynamic crystallization).

But instead of chemical changes or changes in n_a at the amorphous matrix itself, the changes could also be restricted to the near surface layers. The contrast variations in HAADF images are also present at positions of nanocrystals and similar variations can be recognized in oxygen rich areas at the specimen edges.

2.4. Effects of the EELS line scans

After an EELS line scan is acquired a negative contrast to the surrounding amorphous matrix can be recognized along the scan line in HAADF and ADF images. A second line scan is set right after the acquisition of a first line scan to study this effect. Therefore, the second line scan crosses the first line scan at a high angle. Both line scans are set near the specimen edge at amorphous regions because the effect seems to be stronger at thin specimen regions. An increase of the zero-loss peak and a drastic decrease of intensity in the whole electron high energy loss spectrum is observed along the second line scan at scan positions corresponding to the first line scan. Especially the loss of the core loss signals indicates that the acquisition of an EELS line scans leads to a local deepening in the amorphous matrix along the scan line.

V. Conclusions

- L1₂ long range ordered Co₃Ti can be made amorphous by the severe plastic deformation method of high pressure torsion. The amorphous cobalt-titanium phase has the same chemical composition as the crystalline phase revealing a titanium concentration of 24.08 at.% $\pm$ 0.12 at.% by EDX measurements in the SEM. Only the elements cobalt and titanium are considered for these measurements. The amorphous phase forms in bands during the deformation. Broader bands or larger amorphous regions occur at higher deformed regions near the circumference of HPT sample discs.
- A TEM analysis shows that nanocrystals are embedded homogeneously inside amorphous regions. This nanometer sized crystalline precipitates form dynamically in the amorphous phase of the cobalt-titanium alloy during the HPT deformation. Their volume fraction is smaller than 3 %. They are roughly of spherical shape revealing some faceting. The diameters of nanocrystals range from about 2 nm to 20 nm.
- EELS measurements of chemical compositions of nanocrystals indicate the presence of the L1₂ phase Co₃Ti, the C36 Laves phase Co_{2.1}Ti_{0.9} and the C15 Laves phase Co₂Ti.
- The analysis of HRTEM images supported by HRTEM image simulations confirms that nanocrystals of all three structural phases are embedded in the amorphous cobalt-titanium matrix. Therefore, it can be concluded that nanocrystals of different phases, composition and formed by polymorphous dynamic crystallization.
- In addition, TiO₂ nanoparticles are present in an electrolytic polished and ion milled TEM specimen and they are of spherical shape with similar diameters than the nanocrystals of the cobalt-titanium alloy.
- The TEM specimens are covered with a Co₃O₄ surface layer of about 3 nm $\pm$ 2 nm in thickness. This oxide surface layer is also made of nanocrystals with a mean lateral length of 4 nm $\pm$ 1 nm if their shape is approximated by squares. Amorphous areas reveal a layer of higher titanium concentration beneath the specimen surface.
- The Co₃O₄ surface layer reveals lattice fringe contrast in HRTEM images at specimen positions corresponding to the amorphous matrix.
- Electrolytic polished TEM specimen reveal a higher titanium concentration of 25.4 at.% $\pm$ 0.4 at.% when compared to the EDX measurements of the bulk material in the SEM at amorphous regions. This chemical composition is measured by EDX in the TEM and it is in agreement to EELS measurements within the uncertainty tolerance.
- Electrolytic polishing leads to the formation of a polishing layer. This layer can be removed by additional ion milling. A chemical analysis shows that the ion milled TEM specimen Co3Ti.I3 reveals more uniform concentrations than TEM specimen Co3Ti.I4 that is prepared by electrolytic polishing only. There especially the oxygen concentration exhibits higher variations for different specimen areas.

VI. Appendix

1. Scripts

1. Fiji scripts

1.a align_image_rows_on_maxima.ijm

```
1 macro "align_image_rows_on_maxima" {
2   setBatchMode("True");
3   //*****define function to find maximum + position per image row*****
4   function findmax(counterY,startX,endX) {
5       max=getResult("X"+startX,counterY);
6       for (j=startX+1; j<=endX; j++) {
7           value=getResult("X"+j,counterY);
8           if (value > max) {
9               max=value;
10              positionX=j;
11          }
12      }
13      return newArray(max,positionX);
14  }
15  //*****dialogs and region of interest*****
16  firstImageDirectory=File.openDialog("Select energy loss shifted image");
17  open(firstImageDirectory);
18  firstImage=getTitle();
19  w=getWidth();
20  h=getHeight();
21
22  Dialog.create("Intervall:");
23  Dialog.addNumber("Intervall: eV-start", 0);
24  Dialog.addNumber("Intervall: eV-end", w);
25  Dialog.show();
26  gx = Dialog.getNumber();
27  gw = Dialog.getNumber();
28  dummy=0;
29  toUnscaled(gx,dummy);
30  toUnscaled(gw,dummy);
31
32  makeRectangle(gx, 0, gw-gx+1, h); //export selected energy loss region
33  run("Image to Results");
34  run("Select None");
35  //*****first image row = reference position*****
36  y=0;
37  results=findmax(0,gx,gw);
38  xReference=results[1];
39  toScaled(results[1],y);
40  print("I="+results[0], " x="+results[1], " y="+y, " row="+0); //logfile
41  //*****loop for other image rows*****
42  for (i=1; i<=h-1; i++) {
43      y=i;
44      results=findmax(i,gx,gw);
45      makeRectangle(0, i, w, 1); //shift of grayscale values
46      run("Cut");
```

```

47     makeRectangle(xReference-results[1], i, w, 1);
48     run("Paste");
49     toScaled(results[1], y);
50     print("I="+results[0], " x="+results[1], " y="+y, " row="+i); //logfile
51 }
52 run("Select None");
53 setBatchMode("False");
54 }

```

1.b align_image_rows_on_slope-max.ijm

In contrast to script 1.a a different function is defined that finds the first maximum of the slope in a given interval. Here only the first parts of the script are displayed. The rest of the script is almost identical with script 1.a starting at the headline "first image row = reference position". The script shown below continues with line number 35 of the script 1.a after line number 42 by exchanging the function "findmax(...)" in line numbers 37 and 44 of script 2.a with the function "firstslopemax(...)".

```

1  macro "align_image_rows_on_slope-max" {
2  setBatchMode("True");
3  //****define function to find slope maximum + position per image row****
4  function firstslopemax(counterY, startX, endX) {
5      max=getResult("X"+startX, counterY);
6      newmax=getResult("X"+startX+1, counterY);
7      j=2;
8      do {
9          oldmax=max;
10         max=newmax;
11         newmax=getResult("X"+j+startX, counterY);
12         j=j+1;
13     } while (((j<=endX-2) &&
14         ((newmax - max) >= (max - oldmax))) || ((max - oldmax)<0));
15     return newArray(oldmax, startX+j-2);
16 }
17 //*****dialogs and region of interest*****
18 firstImageDirectory=File.openDialog("Select energy loss shifted image");
19 open(firstImageDirectory);
20 firstImage=getTitle();
21 w=getWidth();
22 h=getHeight();
23
24 Dialog.create("Intervall:");
25 Dialog.addNumber("Intervall: eV-start", 0);
26 Dialog.addNumber("Intervall: eV-end", w);
27 Dialog.show();
28 gx = Dialog.getNumber();
29 gw = Dialog.getNumber();
30 dummy=0;
31 toUnscaled(gx, dummy);
32 toUnscaled(gw, dummy);
33 //*****gaussian blure filter + export results*****
34 run("Select None");
35 run("Duplicate ...", "title=[gaussian-blur-image.tif]");
36 for (i=0; i<=h-1; i++) {
37     makeRectangle(0, i, w, 1);
38     run("Gaussian Blur...", "sigma=2");
39 }
40 makeRectangle(gx, 0, gw-gx+1, h); //export selected energy loss region
41 run("Image to Results");
42 selectWindow(firstImage);

```

1.c vertical-average.ijm

```

1 macro "vertical-average" {
2 // ***** Requires: open image *****
3 imagewidth=getWidth();
4 imageheight=getHeight();
5 for (n=1; n<=imagewidth; n++) {
6     makeRectangle(n-1, 0, 1, imageheight);
7     getStatistics(area, mean);
8     run("Set...", "value=mean");
9 }
10 run("Select None");
11 }

```

1.d set-0-per-row-ROI.ijm

```

1 macro "set-0-per-row-ROI" {
2 setBatchMode("True");
3 // ***** dialogs and region of interest *****
4 firstImageDirectory=File.openDialog("Select energy loss shifted image");
5 open(firstImageDirectory);
6 firstImage=getTitle();
7 w=getWidth();
8 h=getHeight();
9
10 Dialog.create("Zero set intervall:");
11 Dialog.addNumber("Intervall: eV-start", 0);
12 Dialog.addNumber("Intervall: eV-width", 1);
13 Dialog.show();
14 gx = Dialog.getNumber();
15 gw = Dialog.getNumber();
16 dummy=0;
17 toUnscaled(gx, dummy);
18 toUnscaled(gw, dummy);
19 // ***** loop through rows *****
20
21 for (r=0; r<h; r++) { //search for values < 0 in intervall
22     i=gx;
23     do {
24         i=i+1;
25     } while ((i<gx+gw) && (getPixel(i, r)>0))
26     if (getPixel(i, r)<=0) // set values to zero after first negative value
27     {
28         makeRectangle(i, r, gw+gx-i, 1);
29         run("Set...", "value=0");
30         run("Select None");
31     }
32 }
33 setBatchMode("False");

```

2. Mathematica scripts

2.a pvoigt-fit.nb

```

1  (*****first part: open image and plot spectra*****)
2  name1 = SystemDialogInput["FileOpen"];
3  Imageinput = Import[name1, "Data"];
4  dim = Dimensions[Imageinput];
5  min = 1; max = dim[[2]];
6  Manipulate[ListPlot[Imageinput[[n]], PlotRange -> {{0, 300}, {0, 6000}}],
7    {n, 1, dim[[1]], 1}]
8  (*****second part: fit functions to image rows*****)
9  DialogInput[Grid[{
10    {"min pixel value for Fit", InputField[Dynamic[min], Number]},
11    {"max pixel value for Fit", InputField[Dynamic[max], Number]},
12    {DefaultButton[]}}]];
13  Imageoutput = ConstantArray[0, {dim[[1]], dim[[2]]}];
14  f[y_] := y;
15  count = Array[f, max - min + 1, {min, max}];
16  Fitarray = ConstantArray[0, dim[[1]]]; (*stores fitted functions*)
17  Dataarray = ConstantArray[0, {dim[[1]], max - min + 1, 2}];
18  M = ConstantArray[0, {4, dim[[1]]}]; (*stores fitting parameters*)
19  DM = ConstantArray[0, {4, dim[[1]]}]; (*stores error values*)
20  (*****loop to fit function to every image row *****)
21  For[n = 1, n <= dim[[1]], n++,
22    data = {count, Imageinput[[n, min ;; max]]};
23    Peakintensity = Max[data[[2]]];
24    Peakposition = data[[1, Position[data, Peakintensity][[1, 2]]];
25    width = (max - min)/2;
26    fit = NonlinearModelFit[Transpose[data],
27      {I0*((1 - d1)*Exp[-(x - xc)^2/(2*w^2)]/Sqrt[2*\[Pi]] +
28        d1/(\[Pi]*((x - xc)^2/w^2 + 1))), 0 <= d1 <= 1},
29      {{I0, Peakintensity/(1/\[Pi] + 1/Sqrt[2*\[Pi]])}, {xc, Peakposition}},
30      {w, width}, {d1, 0.5}}, x, Method -> NMinimize];
31    Imageoutput[[n]] = Array[fit, dim[[2]]];
32    Fitarray[[n]] = fit[x];
33    Dataarray[[n]] = Transpose[data];
34    Print[n];
35    Print[fit["ParameterTable"]]; (*print parameter values and errors*)
36  (*****assign parameter values and error values *****)
37  parameters = fit["BestFitParameters"];
38  errorparameters = fit["ParameterErrors"];
39  {DM[[1, n]], DM[[2, n]], DM[[3, n]], DM[[4, n]]} = errorparameters;
40  {M[[1, n]], M[[2, n]], M[[3, n]], M[[4, n]]} = {I0, xc, w, d1}
41    /.parameters;
42  ]
43  (*****plot fitted region of functions and data and save as image*****)
44  Manipulate[Show[ListPlot[Dataarray[[n]], Plot[Fitarray[[n]],
45    {x, min, max}, PlotStyle -> Red]], {n, 1, dim[[1]], 1}]
46  name2 = SystemDialogInput["FileSave"];
47  Export[name2, Image[Imageoutput, "Real32"], "BitDepth" -> 32];
48  (*****third part: plot region of interest *****)
49  Plotregion = {{100,300},{0,3000}}; (*{{x-min, x-max},{I-min, I-max}}*)
50  Manipulate[Show[ListPlot[Imageinput[[n]], PlotRange -> Plotregion],
51    Plot[Fitarray[[n]], {x, 0, dim[[2]]}, PlotRange -> Plotregion,
52    PlotStyle -> Red]], {n, 1, dim[[1]], 1}]

```



```

53 | (*****fourth part: average fitting parameters *****)
54 | exeptionrows = {0}; (*initiate vector to exclude image rows*)
55 | exeptionrows = {4, 11, 12, 18, 28}; (*example for excluded image rows*)
56 | errorregion = {150, 187}; (*example for custom error region*)
57 | If[Det[DiagonalMatrix[exeptionrows]] == 0, { (*exclusion/no exclusion*)
58 |   Mpointer[i_] := M[[i, All]];
59 |   DMpointer[i_] := DM[[i, All]];},
60 | { (*else*)
61 |   exeptions = ConstantArray[0, {Dimensions[exeptionrows][[1]], 1}];
62 |   (*****loop: row -> column vector*****)
63 |   For[i = 1, i <= Dimensions[exeptionrows][[1]], i++,
64 |     exeptions[[i, 1]] = exeptionrows[[i]];
65 |   ]
66 |   Mpointer[i_] := Delete[M[[i, All]], exeptions];
67 |   DMpointer[i_] := Delete[DM[[i, All]], exeptions];
68 |   }];
69 | columns = Dimensions[DMpointer[1]][[1]]; (*number of rows (spectra)*)
70 | averageparameters = ConstantArray[0, Dimensions[M][[1]]];
71 | averageerrors = ConstantArray[0, Dimensions[M][[1]]];
72 | (*****loop: calculate parameters*****)
73 | For[i = 1, i <= Dimensions[M][[1]], i++,
74 |   averageparameters[[i]] = Mean[Mpointer[i]];
75 |   averageerrors[[i]] = Sqrt[Mean[DMpointer[i]^2]/columns];
76 | ];
77 | meansquareerror = Sum[Sum[(Imageoutput[[n, x]] - Imageinput[[n, x]]]^2,
78 |   {x, min, max}], {n, 1, columns}]/((max - min + 1)*columns);
79 | meansquareerror2 = Sum[Sum[(Imageoutput[[n, x]] - Imageinput[[n, x]]]^2,
80 |   {x, errorregion[[1]], errorregion[[2]]}], {n, 1, columns}]
81 | /((errorregion[[2]] - errorregion[[1]] + 1)*columns);
82 | Print["Averaged fit parameters:\n{I0, xc, w}"] (*print results*)
83 | Print[averageparameters]
84 | Print["\nPropagated errors:\n{dI0, dxc, dw}"]
85 | Print[averageerrors]
86 | Print["\nRoot mean square error - for fitted intervals:"]
87 | Print[Sqrt[meansquareerror]]
88 | Print["\nRoot mean square error - for custom intervals:"]
89 | Print[Sqrt[meansquareerror2]]

```

2.b pvoigt-fit-predef-1.nb

This script is based on the previous script 2.a. Therefore, just the modified rows of the script are shown here. The scripts can be compared with respect to the line numbers in front of each row. In this script the starting values for the fitting parameters are taken from a first run so that the fitting process leads to stable results for all image rows.

```

18 | M = ConstantArray[0, {3, dim[[1]]}]; (*stores fitting parameters*)
19 | DM = ConstantArray[0, {3, dim[[1]]}]; (*stores error values*)

23 | d=0.14; (*fixed value of Lorentzian fraction in Pseudo-Voigt function*)
24 |
25 |
26 | fit = NonlinearModelFit[Transpose[data],
27 |   {I0*((1 - d)*Exp[-(x - xc)^2/(2*w^2)]/Sqrt[2*\[Pi]] +
28 |     d/(\[Pi]*((x - xc)^2/w^2 + 1)))},
29 |   {{I0, 198017}, {xc, 204.97}, {w, 6.54882}}, x, (*starting values*)
30 |   Method -> LevenbergMarquardt];

39 | {DM[[1, n]], DM[[2, n]], DM[[3, n]]} = errorparameters;
40 | {M[[1, n]], M[[2, n]], M[[3, n]]} = {I0, xc, w}
41 | /.parameters;

```

2.c **pvoigt-fit_predef-2.nb**

This script is also based on the script 2.a. The modified rows of the script compared to 2.a are shown here. The scripts can be compared with respect to the line numbers in front of each row. In this script the starting values for the fitting parameters are taken from a first run so that the fitting process leads to stable results for all image rows.

```

18 M = ConstantArray[0, {2, dim[[1]]}]; (*stores fitting parameters*)
19 DM = ConstantArray[0, {2, dim[[1]]}]; (*stores error values*)

23 d=0.14; (*fixed value of Lorentzian fraction in Pseudo-Voigt function*)
24 I0 = 425014; (*fixed scaling parameter for the function values*)
25
26 fit = NonlinearModelFit[Transpose[data],
27   {I0*((1 - d)*Exp[-(x - xc)^2/(2*w^2)]/Sqrt[2*\[Pi]] +
28     d/(\[Pi]*((x - xc)^2/w^2 + 1)))},
29   {{xc, 204.97}, {w, 6.54882}}, x, (*starting values*)
30   Method -> LevenbergMarquardt];

39 {DM[[1, n]], DM[[2, n]]} = errorparameters;
40 {M[[1, n]], M[[2, n]]} = {xc, w}
41 /.parameters;

```

2.d **gaussian-fit.nb**

The script for the gaussian fit has the same structure as the script 2.a for the Pseudo-Voigt fit. Here the modified rows in comparison to script 2.a are shown. The scripts can be compared with respect to the line numbers in front of each row. The starting values for the fitting parameters are taken from a first run so that the fitting error is reduced.

```

18 M = ConstantArray[0, {3, dim[[1]]}]; (*stores fitting parameters*)
19 DM = ConstantArray[0, {3, dim[[1]]}]; (*stores error values*)

23
24
25
26 fit = NonlinearModelFit[Transpose[data],
27   {I0*Exp[-(x - xc)^2/(2*w^2)]/(w*Sqrt[2*\[Pi]])},
28   {{I0, 6.11621*10^8}, {xc, 147}, {w, 15}}, x, (*starting values*)
29   Method -> LevenbergMarquardt];
30

39 {DM[[1, n]], DM[[2, n]], DM[[3, n]]} = errorparameters;
40 {M[[1, n]], M[[2, n]], M[[3, n]]} = {I0, xc, w}
41 /.parameters;

```

2.e **gaussian-fit_predef-1.nb**

For this gaussian fits the intensity scaling parameter I_0 is fixed. The script is also based on script 2.a and the modified rows are shown. The scripts can be compared with respect to the line numbers in front of each row. The starting values for the fitting parameters are taken from a first run.

```

18 M = ConstantArray[0, {2, dim[[1]]}]; (*stores fitting parameters*)
19 DM = ConstantArray[0, {2, dim[[1]]}]; (*stores error values*)

23
24 I0 = 5.68047*10^10; (*fixed scaling parameter for the function values*)
25
26 fit = NonlinearModelFit[Transpose[data],
27   {I0*Exp[-(x - xc)^2/(2*w^2)]/(w*Sqrt[2*\[Pi]])},

```

```

28     {{xc, 120}, {w, 18}}, x, (*starting values*)
29     Method -> LevenbergMarquardt];
30
31
32
33
34
35
36
37
38
39     {DM[[1, n]], DM[[2, n]]} = errorparameters;
40     {M[[1, n]], M[[2, n]]} = {xc, w}
41     /.parameters;

```

3. DigitalMicrograph scripts

3.a fourier-ratio_deconvolution.s

```

1  image allspectra, lowlossspectra, smoothimage
2  GetThreeImages("select highloss and lowloss and smoothimage (0-loss)",
3    allspectra, lowlossspectra, smoothimage) //open image dialog
4
5  number xsize, ysize
6  getSize(allspectra, xsize, ysize)
7  image newspectra=allspectra
8  newspectra=0
9
10 for(number i=0; i<ysize; i++) //loop for image rows (spectra)
11 {
12   image onespectrum=allspectra[i, 0, i+1, xsize] //extract row
13   image onelowlossspectrum=lowlossspectra[i, 0, i+1, xsize]
14   image onesmoothimage=smoothimage[i, 0, i+1, xsize]
15
16   newspectra[i, 0, i+1, xsize]=realIFFT(realfft(onespectrum)*
17     realfft(onesmoothimage)/realfft(onelowlossspectrum)) //deconvolve
18 }
19 showimage(newspectra)

```

3.b fourier-ratio_deconvolution_Gaussian-profile.s

```

1  image allspectra, lowlossspectra, lowslossprofile
2  GetThreeImages("select highloss and lowloss and lowslossprofile -withROI",
3    allspectra, lowlossspectra, lowslossprofile) //open image dialog
4
5  number xsize, ysize
6  getSize(allspectra, xsize, ysize)
7  image newspectra=allspectra
8  newspectra=0
9  image smoothimage=Function_Gaussian_Fit(lowslossprofile, xsize) //Gaussian
10
11 for(number i=0; i<ysize; i++) //loop for image rows (spectra)
12 {
13   image onespectrum=allspectra[i, 0, i+1, xsize] //extract row
14   image onelowlossspectrum=lowlossspectra[i, 0, i+1, xsize]
15   newspectra[i, 0, i+1, xsize]=realIFFT(realfft(onespectrum)*
16     realfft(smoothimage)/realfft(onelowlossspectrum)) //deconvolve
17 }
18 showimage(newspectra)

```

2. List of acronyms

ADF annular dark field

ASTEM Austrian Scanning Transmission Electron Microscope

bcc body centered cubic

BF bright field

BSE backscattered electron

dhcp double hexagonal close packed

DM dual modulation

EDX energy dispersive X-ray

EELS electron energy loss spectroscopy

fcc face centered cubic

FFT Fast Fourier transformation

FWHM full width half maximum

GMS Gatan Microscopy Suite

HAADF high angle annular dark field

HRTEM high resolution transmission electron microscopy

HTP high pressure torsion

IFFT inverse Fast Fourier transformation

NCEM National Center for Electron Microscopy

PIPS Precision Ion Polishing System

ROI region of interest

RPM rotations per minute

SADP selected area diffraction pattern

SE secondary electrons

SD standard deviation

SPD severe plastic deformation

SEM scanning electron microscope

TEM transmission electron microscope/microscopy

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