



universität
wien

MASTERARBEIT

Titel der Masterarbeit

On the Systems
Ta-Co-B and Nb-Co-B

Verfasserin

Julia Wind, Bakk.rer.nat.

angestrebter akademischer Grad

Master of Science (MSc)

Wien, 2012

Studienkennzahl lt. Studienblatt: A 066 862

Studienrichtung lt. Studienblatt: Chemie

Betreuerin / Betreuer: Univ.-Prof. Dr. Peter Franz Rogl

Für meine Mama

Acknowledgements

First of all I want to thank Prof. Rogl for his guidance and constant support during the whole research work.

I thank all my colleagues in the working group for their great help with all kind of practical as well as theoretical aspects concerning my research work, especially Anrdriy Grytsiv for all the interesting discussions.

Thanks to Gunther Schölhammer for the realization of DFT calculations.

I thank Dr. Jiri Bursik from the *Academy of Sciences of the Czech Republic* for his support concerning the TEM measurements and evaluation of the results.

Furthermore I thank Stephan Puchegger for his support with SEM and EPMA measurements and Christoph Eisenmenger-Sittner (Vienna University of Technology) for his support with hardness measurements.

I also want to thank Prof. Michor (Vienna University of Technology) for his support in the numerous attempts to get a suitable TaCo₂B single crystal, which unfortunately did not work out in the end.

Special thanks I want to express towards my friends and my family.

Abstract

Constitution of the ternary systems Nb-Co-B and Ta-Co-B was studied, employing optical and electron microscopy, X-ray powder, single crystal diffraction and electron probe microanalysis. Ternary phase equilibria were determined within an isothermal section at 1100°C. For the Co-rich part ($\geq 50\text{at}\%\text{Co}$) of the system, a liquidus surface projection and a corresponding Schulz-Scheil reaction scheme were constructed in combination with data for primary crystallization from as cast samples determined by SEM and EPMA measurements.

$\{\text{Nb,Ta}\}\text{CoB}$ with NbCoB-type exhibits a high temperature modification (ZrAlNi-type, $a=0.5953\text{ nm}$, $c=0.3248\text{ nm}$; $a=0.5926\text{ nm}$, $c=0.3247\text{ nm}$ for Nb and Ta respectively), which was only present in as cast alloys, but found to be stabilized by the addition of Fe to annealing temperatures of 1400°C. $\text{Ta}_3\text{Co}_4\text{B}_7$ ($a=0.3189\text{ nm}$, $b=1.8333\text{ nm}$, $c=0.8881\text{ nm}$) was proven to be isotypic with $\text{Nb}_3\text{Co}_4\text{B}_7$.

$\{\text{Nb,Ta}\}\text{Co}_2\text{B}$ was found to adopt a unique monoclinic structure type (space group $P2_1/c$; $a = 0.9190\text{ nm}$, $b = 0.64263\text{ nm}$, $c = 0.63144\text{ nm}$; $\beta = 109.954^\circ$, for Nb) very close to an orthorhombic setting (Cmce , $a = 0.63162\text{ nm}$, $b = 1.72810\text{ nm}$, $c = 0.64270\text{ nm}$, for Nb). Substitution of Co by Ni stabilizes the orthorhombic modification with Re_3B -type (Cmcm) although no homologue compound in the Ni-system was found. The crystallographic relations among the structure types of Re_3B and pseudo-orthorhombic as well as $\{\text{Nb,Ta}\}\text{Co}_2\text{B}$ were defined in terms of a Bärnighausen scheme. DFT calculations revealed very close stabilities for the three competing structure types. Detailed transmission electron microscopy (TEM) for $\text{Nb}(\text{Co,Fe})\text{B}$, $\{\text{Nb,Ta}\}\text{Co}_2\text{B}$, $\{\text{Nb,Ta}\}(\text{Co,Ni})_2\text{B}$ and $\text{Ta}_3\text{Co}_4\text{B}_7$ confirmed lattice parameters and crystal symmetry. Vickers hardness was measured for $\{\text{Nb,Ta}\}\text{Co}_2\text{B}$, $\{\text{Nb,Ta}\}(\text{Co,Ni})_2\text{B}$ and $\{\text{Nb,Ta}\}_{2-x}\text{Co}_{21+x}\text{B}_6$ revealing the highest value of hardness of $HV=17.6\pm 0.9\text{ GPa}$ for TaCo_2B .

Kurzfassung

Der Aufbau der beiden ternären Systeme Nb-Co-B und Ta-Co-B wurde mittels verschiedener experimenteller Methoden untersucht (Licht- bzw. Elektronenmikroskopie, Röntgenpulveranalyse, Einkristallstrukturanalyse, EPMA). Die Phasengleichgewichte wurden in Form eines isothermen Schnittes bei 1100°C bestimmt. Für den Co-reichen Teil des Systems ($\geq 50\text{at\%Co}$) wurde in Kombination mit Daten zur Primärkristallisation von Proben im Gusszustand (SEM, EPMA) eine Liquidus-Projektion sowie ein zugehöriges Schultze-Scheil-Diagramm erstellt.

Die Verbindung $\{\text{Nb,Ta}\}\text{CoB}$ mit NbCoB-Typ, weist eine Hochtemperaturmodifikation mit ZrNiAl-Typ ($a=0.5953\text{ nm}$, $c=0.3248\text{ nm}$; $a=0.5926\text{ nm}$, $c=0.3247\text{ nm}$ für Nb bzw. Ta) auf, die nur in Gussproben vorzufinden war, aber durch Zugabe von Fe auf Glühtemperaturen von 1400°C stabilisiert wurde. Weiters wurde gezeigt, dass die bereits bekannte Verbindung $\text{Ta}_3\text{Co}_4\text{B}_7$ ($a=0.3189\text{ nm}$, $b=1.8333\text{ nm}$, $c=0.8881\text{ nm}$) isotyp mit $\text{Nb}_3\text{Co}_4\text{B}_7$ ist.

Die Verbindungen $\{\text{Nb,Ta}\}\text{Co}_2\text{B}$ kristallisieren monoklin ($P2_1/c$; $a = 0.9190\text{ nm}$, $b = 0.64263\text{ nm}$, $c = 0.63144\text{ nm}$; $\beta = 109.954^\circ$, für Nb), jedoch nahe einer orthorhombischen Aufstellung (Cmce , $a = 0.63162\text{ nm}$, $b = 1.72810\text{ nm}$, $c = 0.64270\text{ nm}$, für Nb). Substitution von Co durch Ni stabilisiert die orthorhombische Modifikation mit Re_3B -Typ (Cmcm), obwohl keine homologe Verbindung im zugehörigen Ni-System bekannt ist. Die kristallographischen Zusammenhänge zwischen dem Re_3B -Typ, der pseudo-orthorhombischen als auch der monoklinen Aufstellung von $\{\text{Nb,Ta}\}\text{Co}_2\text{B}$ wurden in Form eines Bärnighausen Schemas dargestellt. DFT Berechnungen zeigen sehr ähnliche Stabilitäten für die drei betrachteten Strukturtypen. Gitterparameter und Kristallsymmetrien der Verbindungen Nb(Co,Fe)B, $\{\text{Nb,Ta}\}\text{Co}_2\text{B}$, $\{\text{Nb,Ta}\}(\text{Co,Ni})_2\text{B}$ und $\text{Ta}_3\text{Co}_4\text{B}_7$ wurden mittels detaillierter Untersuchungen am Transmissionselektronenmikroskop bestätigt.

Für die Verbindungen $\{\text{Nb,Ta}\}\text{Co}_2\text{B}$, $\{\text{Nb,Ta}\}(\text{Co,Ni})_2\text{B}$ und $\{\text{Nb,Ta}\}_{2-x}\text{Co}_{21+x}\text{B}_6$ wurden Vickers Härte Messungen durchgeführt. Hierbei zeigte TaCo₂B mit $HV=17.6\pm 0.9\text{ GPa}$ den höchsten Wert.

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1 Introduction

Interest in suitable metal binders for hard refractory materials such as TaB₂ has led to the early discovery of two ternary borides with unknown crystal structure, TaCoB₂ and “cubic TaCo₅B₂” within the claimed “quasi-binary” section Co - TaB₂ [1961Lav]. From a detailed investigation of the Co-rich corner of the ternary system (> 50 at.% Co) in terms of an isothermal section at 800°C as well as of a liquidus surface, Stadelmaier and Hofer [1964Sta] concluded that “TaCo₅B₂” is in fact consistent with the cubic Cr₂₃C₆ type structure with an approximate formula Ta₂Co₂₁B₆. The compound TaCoB₂ was confirmed and a further compound TaCo₂B with unknown structure was reported. Furthermore, the tie line structure did not provide hints for a quasi-binary section TaB₂ – Co but revealed a two-phase equilibrium between (Co) and the TaCo₂B phase [1964Sta]. All these features were also found for the homologous system Nb-Co-B [1966Sta]. Whereas the liquidus projection for the system Ta-Co-B indicates, that TaCo₂B melts congruently [1964Sta], homologous NbCo₂B is covered by a field of primary crystallisation of NbB [1966Sta]. Interestingly the investigation of the entire isothermal section Nb-Co-B at 800°C by Kuzma [1968Kuz1] did not reveal the NbCo₂B phase, but instead showed a two-phase equilibrium (Co) + NbCoB, and furthermore confirmed Nb₂Co₂₁B₆, NbCoB₂ and reported a new compound tentatively labelled as “Nb₂Co₃B₅”. The crystal structure of NbCoB, a topological combination of structural units of the ZrNiAl and TiNiSi types, was (erroneously) claimed by Krypiyakevich et al. [1971Kry] to correspond to the phase labelled as NbCo₂B by [1966Sta]. TaCoB was discovered to be isotypic with the NbCoB-type [1973Kuz], whereas NbCoB₂ was defined as a unique structure type [1976Kuz] for which TaCoB₂ was proven to be an isotypic representative [1978Ste]. In a reinvestigation of the isothermal sections Nb-Co-B and Ta-Co-B at 800°C, Kuzma et al. [1979Kuz] re-labelled the Nb₂Co₃B₅ phase as NbCo₂B₃ and introduced a new compound Nb₃Co₅B₂ in equilibrium with (Co). Consequently the new equilibrium interferes with the tie line (Co) + NbCoB as stated earlier [1968Kuz]: in the new version NbCoB is now connected by tie lines to Nb₃Co₅B₂ and NbCo₂. Phase relations for Ta-Co-B are reported as practically identical with those of the Nb-Co-B system: Nb₃Co₅B₂ and Ta₃Co₅B₂ were both said by Kuzma et al. [1979Kuz] to be isotypic and isostructural with the Ti₃Co₅B₂ type and these compounds were furthermore supposed to replace NbCo₂B and TaCo₂B of Stadelmaier and Hofer [1964Sta] and of Stadelmaier and Schöbl [1966Sta], respectively. At 800°C so-called tau-phases Nb₂Co₂₁B₆ and Ta₂Co₂₁B₆ were listed as stoichiometric compounds without a significant homogeneous range [1979Kuz]. However, at 1100°C a small homogeneous phase field was determined for the tau-phase from lattice parameter and EMPA analyses, extending from TaCo₂₂B₆ to Ta₂Co₂₁B₆ [1979Ste1]. A slightly

hyperstoichiometric composition $\text{Ta}_{2.18}\text{Co}_{20.82}\text{B}_6$ was derived by Stadelmaier et al. [1989Sta] from X-ray single crystal intensity data ($R_F=0.063$) on a crystal dissolved by (HCl+10%HF) out of a eutectic matrix 6.5Ta74.9Co18.6B. $\text{Nb}_2\text{Co}_{21}\text{B}_6$ is a ferromagnet below $T_C = 512$ K with a saturation moment of $0.76 \mu_B$ per Co-atom at 77 K [1981Jor]. A structure determination for the “ $\text{Nb}_2\text{Co}_3\text{B}_5$ ” or “ NbCo_2B_3 ” phase finally yielded the proper formula $\text{Nb}_3\text{Co}_4\text{B}_7$ [1986Kuz]. In a review article by Kuzma and Chaban the phase “ $\text{Ta}_2\text{Co}_3\text{B}_5$ ” or “ TaCo_2B_3 ” was assumed to be $\text{Ta}_3\text{Co}_4\text{B}_7$ isostructural with $\text{Nb}_3\text{Co}_4\text{B}_7$, however, no further details were given [1990Kuz].

Although with all this information phase relations in both systems Nb-Co-B and Ta-Co-B seem to be profoundly established, controversies still prevail: (i) Sprenger [1977Spr] noted that X-ray powder diagrams of TaCoB did not match those he obtained for the phase at TaCo_2B and (ii) a reinvestigation of the Ta-Co-B system at 1100°C by Steurer [1979Ste2] did not yield any hints for the existence of $\text{Ta}_3\text{Co}_5\text{B}_2$ with $\text{Ti}_3\text{Co}_5\text{B}_2$ type, but prompted a novel, unique structure type for isotypic $\{\text{Nb,Ta}\}\text{Co}_2\text{B}$, (iii) the investigation of Steurer [1979Ste2] revealed high temperature modifications for $\{\text{Nb,Ta}\}\text{CoB}$ with ZrNiAl-type, and furthermore (iv) the tie line $\text{TaCoB} + \tau$ [1979Kuz, 1990Kuz] contradicts the tie line $\text{Co}_2\text{B} + \text{TaCo}_2\text{B}$ [1964Sta, 1979Ste2].

In view of these inconsistencies and as a structure determination on poor-quality single crystals of $\{\text{Nb,Ta}\}\text{Co}_2\text{B}$ [1979Ste2] was only of rather preliminary nature, the present work attempts to provide information on (a) the Ta(Nb)-Co-B phase relations at 1100°C (based on the re-evaluation of existing data by Oksana Romaniv), (b) the liquidus surfaces and invariant reactions in the melting-crystallization regions of the Co-rich part of the systems, (c) details on the crystal structures pertinent to the systems and (d) a check on possible isotypic compounds and/or solid solutions in the $\{\text{Nb,Ta}\}\text{-}\{\text{Fe,Co,Ni}\}\text{-B}$ systems.

2 Theoretical Background

The following chapter is summarized from standard literature and lecture notes, especially [2007Mas], [2009Bla], [2009Ric], [2010Rog].

2.1 X-Ray Diffraction

2.1.1 The Generation of X-rays

X-rays are electromagnetic radiation of wavelengths of 0.01-1 nm and energies corresponding to the energy loss by electronic transitions of inner orbitals. They are generated by collision of highly accelerated electrons with a metal target.

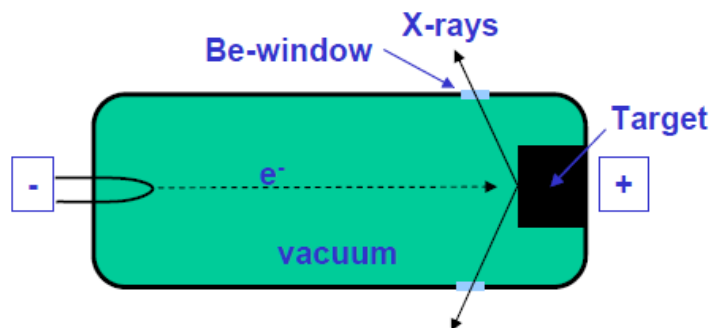


Fig. 2.1: X-ray tube, schematic [2010Ric].

In X-ray tubes (see Fig. 2.1), electrons are emitted by the cathode, usually a heated tungsten filament, and accelerated in an electric field of 20-60 kV towards the anode. The impact of the electrons on the target material yields a lot of thermal energy (cooling necessary) and X-ray photons, giving the typical X-ray spectrum, shown in Fig. 2.2.

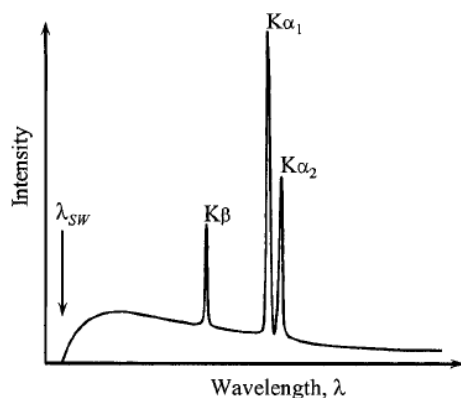


Fig. 2.2: X-ray spectrum [2005PEC].

The radiation emitted consists of a continuous range of wavelengths, the so-called “Bremsstrahlung”, arising from the electrons’ kinetic energy, depending on the accelerating voltage, and some sharp peaks at defined wavelengths, the characteristic X-rays that result from the transition of electrons of outer orbitals to inner shells, from which an electron was ejected by an incident electron. The emitted characteristic radiation is of defined wavelengths

and typical for the target material in use (i.e. Cu, Fe, Mo). The transition from the 2p (3p) to the 1s orbital gives K_α (K_β) radiation, due to different spin states in 2p, K_α further splits into $K_{\alpha 1}$ and $K_{\alpha 2}$.

2.1.2 Diffraction

Diffraction can be observed when the distances between the scattering objects are in the same order of magnitude as the wavelength of the incident wave, as it is the case for the interatomic distances in crystals and X-rays. The incident waves are scattered from electrons, or more precisely from the electron density, periodically distributed in the crystal lattice.

W.H. and W.L. Bragg proposed, that the waves can be considered as if they were reflected off the atomic planes (hkl), spaced by the distance d as shown in Fig. 2.3.

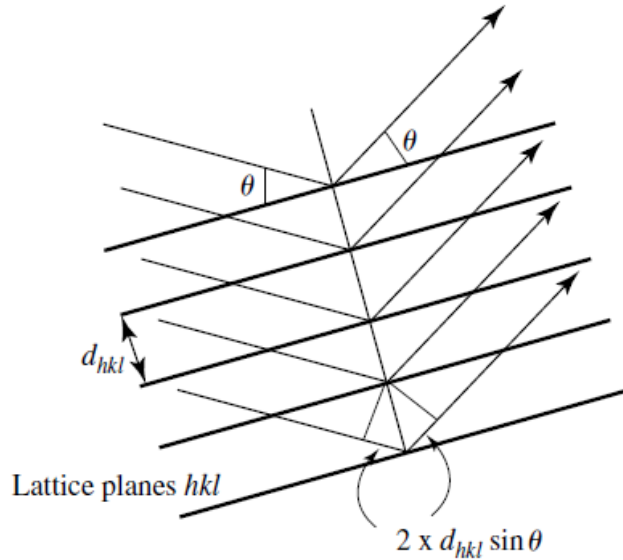


Fig. 2.3: Diffraction of X-rays from crystal lattice planes illustrating Bragg's law [2009Bla].

The Bragg equation gives the geometric condition for diffraction to occur, depending on the wavelength λ , the incident and reflection angle θ and the distance d between the lattice planes:

$$2d \sin \theta = n\lambda \quad (2.1)$$

2.1.2.1 The Intensity of Diffracted X-Rays

The atomic scattering factor f_j describes the scattering of one single atom as a function of $\sin \theta / \lambda$. The scattering power is proportional to the number Z of electrons and decreases with increasing diffraction angle.

The structure factor describes the scattering from the complete unit cell and is the sum the atomic scattering terms f_j of all N atoms in the unit cell with their atomic coordinates x_i , y_i , z_i , multiplied by a phase factor that considers the phase difference between waves scattered from atoms on different atomic planes with same Miller indices (hkl) :

$$F(hkl) = \sum_{j=1}^N f_j \exp[2\pi i(hx_j + ky_j + lz_j)] \quad (2.2)$$

The intensity of the diffracted X-rays with the index hkl is proportional to the squared structure factors $F(hkl)$, with some additional correction factors described below:

$$I = F(hkl)^2 H A L P T \quad (2.3)$$

When the X-ray beam travels through a sample it is partially absorbed, thus the total diffracted intensity must be corrected by the **absorption factor A**, dependent i.e. on sample thickness and crystal shape (important in SC measurement). The **Lorentz and the Polarization factor** are usually combined to a joint geometrical correction factor

$$LP = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \quad (2.4)$$

dependent on the diffraction angle θ . The **multiplicity factor H** considers the increased intensity of symmetrically equivalent crystal faces hkl.

The temperature factor B

$$T = e^{-2B \frac{\sin^2 \theta}{\lambda}} \quad (2.5)$$

corrects the thermal motion of the atoms in the lattice and is sometimes included in the structure factor. B is a function of the temperature and proportional to the mean square displacement of the atom.

2.1.2.2 The symmetry of the diffraction pattern

The symmetry of the obtained diffraction pattern is closely related to the symmetry of the unit cell. In absence of anomalous dispersion the X-ray patterns are always centrosymmetric (conf. eq.(2.2)). This is known as Friedel's law. Thus in the diffraction pattern only 11 Laue classes can be directly observed, that are the 32 point groups (230 space groups) with the addition of an inversion center (neglecting cell centering and replacing all translational elements by pure rotation and reflection respectively).

2.1.2.3 Systematic absences

The presence of translational symmetry leads to the systematic extinction of some combinations of Miller indices due to symmetrical contributions in eq.(2.2). Each type of unit cell centering as well as glide planes and screw axes have an associated pattern of systematic absences and can thus be identified. Systematic absences for the centering of unit cells are listed in Tab. 2.1. Although analysis of systematic absences narrows possibilities for the choice of the appropriate space groups only a few space groups can be uniquely determined and further considerations are necessary.

Tab. 2.1: Systematic absences for centered unit cells [2009Bla].

Centring	Points equivalent to 0,0,0	Condition for observed intensity	Fraction of observed data
<i>P</i>	none	none	1
<i>A</i>	0, 1/2, 1/2	$k + l = 2n$	1/2
<i>B</i>	1/2, 0, 1/2	$h + l = 2n$	1/2
<i>C</i>	1/2, 1/2, 0	$h + k = 2n$	1/2
<i>I</i>	1/2, 1/2, 1/2	$h + k + l = 2n$	1/2
<i>F</i>	0, 1/2, 1/2 and 1/2, 0, 1/2 and 1/2, 1/2, 0	h, k, l all even or all odd	1/4
<i>R</i>	1/3, 2/3, 2/3 and 2/3, 1/3, 1/3	$-h + k + l = 3n$	1/3

2.1.2.4 Statistical analysis

Further information can be obtained by the statistical analysis of the distribution of intensities. Based on a number of assumptions the distribution of normalized amplitudes, the so-called E-values ($|E|^2=1$) can be calculated. This distribution, the so-called Wilson-plot, is different for centric and acentric structures and thus indicate the probable absence or presence of inversion symmetry.

2.1.3 Phase Problem

The electron density ρ_{xyz} in a unit cell with volume V at a point xyz is given by

$$\rho_{xyz} = \frac{1}{V} \sum_{hkl} F(hkl) \exp[-2\pi i(hx + ky + lz)] \quad (2.6)$$

$F(hkl)$ is the Fourier transform of ρ_{xyz} , the structure factors are the Fourier coefficients for the Fourier synthesis of the electron density.

X-Ray measurements yield intensities, proportional to the squared structure factor, and thus only information about the amplitude of the Fourier coefficients. This loss of information on the phases is known as the *phase problem* and the central problem in the solution of structures.

If a structural model already exists (correct positions for about 50% of atoms in the asymmetric unit), theoretical structure factors F_c can be calculated. The obtained, calculated phase information is now combined with observed F_o and gives a new (improved) structural model.

To obtain a suitable structural model and hence to solve the phase problem several techniques are used, the most important being Patterson synthesis and direct methods.

2.1.3.1 Patterson Method

The Patterson method is mainly used to locate the approximate positions of some (heavy) atoms in the structure. By using the squared structure factors, the unknown phases are omitted, giving a real expression for the Patterson function

$$P(uvw) = \frac{1}{V} \sum_{hkl} |F(hkl)|^2 \cos[2\pi(hu + kv + lw)] \quad (2.7)$$

The peaks (maxima) in the Patterson function correspond to the vectors between pairs of atoms in the structure, including “self-vectors” between similar atoms giving a maximum at the origin. For n atoms in the unit cell, $n^2 - n$ peaks can be observed in the vector-density distribution, the so-called Patterson map, all being twice as broad as the peaks in the electron density distribution $\rho(xyz)$. Thus the Patterson method can only be used for unit cells with fewer atoms or for the location of strongly scattering atoms to construct a partial structure model that can be completed by differential Fourier synthesis.

2.1.3.2 Direct methods

Direct methods estimate phases directly by mathematical methods from measured intensities and relationships among the structure factors without prior knowledge about the crystal structure itself. Amplitude and phase of the structure factor are not independent, but related via the electron density distribution. Constraints on the electron density distribution (i.e. $\rho(x,y,z) \geq 0$) impose corresponding constraints on the structure factor. As amplitudes are known from intensity measurements, these constraints apply mostly on the phases.

For calculations unitary structure factors U and normalized structure factors E are used to reduce the dependence on atomic scattering factors, thermal motion as well as the effect of space group symmetry on the observed intensities.

The impossibility of a negative electron density gives rise to the *Karle-Hauptmann* inequality:

$$\begin{vmatrix} U_0 & U_{\bar{h}_1} & U_{\bar{h}_2} & \cdots & U_{\bar{h}_n} \\ U_{h_1} & U_0 & U_{h_1-h_2} & & U_{h_1-h_n} \\ U_{h_2} & U_{h_2-h_1} & U_0 & & U_{h_2-h_n} \\ \vdots & & & \ddots & \vdots \\ U_{h_n} & U_{h_n-h_1} & U_{h_n-h_2} & \cdots & U_0 \end{vmatrix} \geq 0 \quad (2.8)$$

In a special case for $n = 3$, the determinant yields the *Harker-Kasper* inequality for a crystal containing only a center of symmetry:

$$U^2(hkl) \leq \frac{1}{2}(1 + U(2h2k2l)) \quad (2.9)$$

If $|F(hkl)|$ and $|F(2h2k2l)|$ are both strong, then the sign of $F(2h2k2l)$ is *likely* to be positive.

A general determinant of order three gives a special relation between phases of triplets of reflections $h, k, h-k$. For a centro-symmetric structure, calculating the determinant yields

$$1 - |U_h|^2 - |U_k|^2 - |U_{h-k}|^2 + 2U_h U_k U_{h-k} \geq 0 \quad (2.10)$$

which, if all moduli are fixed, depends only on the sign of the product $2U_h U_k U_{h-k}$. Given sufficiently *large moduli*, the sign of this product consequently has to be positive:

$$s(h)s(k)s(h-k) = + \quad (2.11)$$

For non-centro-symmetric structures, the inequality puts a restriction on the allowed phase values:

$$\phi_h + \phi_k + \phi_{h-k} \approx 0 \pmod{2\pi} \quad (2.12)$$

All these equations require large values of U 's to provide phase information.

2.1.4 Powder Diffraction

X-ray powder diffraction is a powerful method for phase identification. Moreover it is used for lattice parameter and structure determination, refinement of structural models, texture analysis, investigation of grain size etc. In a powder experiment a collection of randomly orientated polycrystallites is exposed to the beam, each of them giving its own diffraction pattern. A comparison between single crystal and powder diffraction is shown in Fig. 2.4.

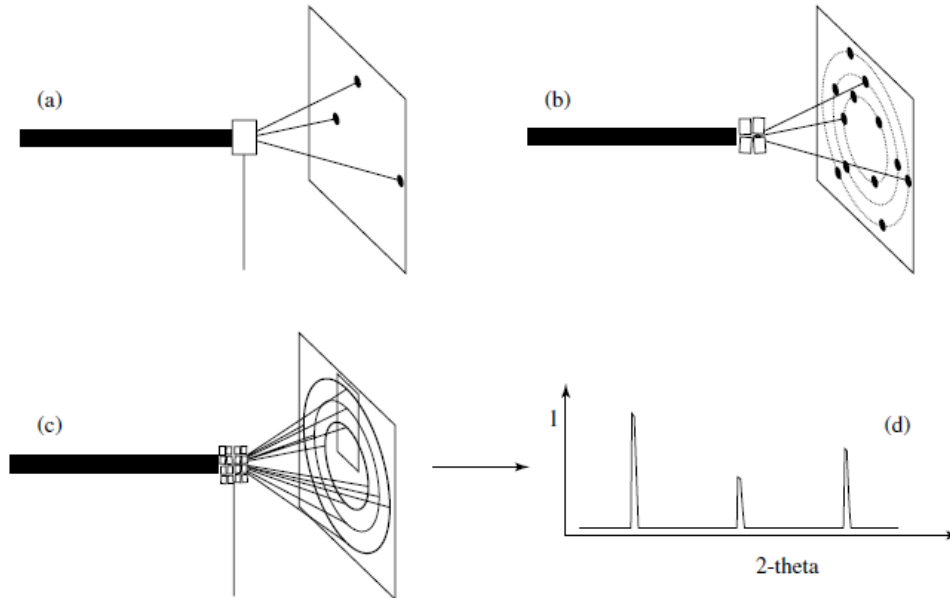


Fig. 2.4: a) Diffraction from an oriented single crystal. b) Diffraction from a collection of 4 crystals at different orientations with respect to the incident beam. c) Diffraction from a polycrystalline material. d) Resulting I versus 2θ plot obtained by scanning across the outlined rectangle of c).

2.1.4.1 Guinier Technique

The Guinier technique uses monochromated and focused $K_{\alpha 1}$ radiation. As detection system for the scattered X-rays an image plate is used: Incident X-rays produce Eu^{3+} and trapped electrons in color centers in a layer of BaFBr:Eu^{2+} in an organic binder – a two-dimensional image of the intensity is stored. In the scanning step, a laser is used to stimulate emission from the trapped electrons; this signal is detected by a photomultiplier. The image plate is erased by the exposure with white light.

2.1.4.2 The Rietveld Method

The main steps in evaluating a powder pattern are the comparison with theoretical structures (calculated; from literature) and the further refinement of this structural model. For the latter, the Rietveld method is used. Step by step experimental, structural and profile related parameters can be refined, making a least square fit of the theoretically calculated and the observed powder pattern.

Structure determination from powder data is difficult and thus usually done with single crystal analysis.

2.2 Scanning Electron Microscopy and EPMA

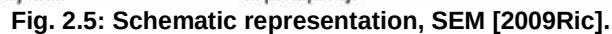
In Scanning Electron Microscopy a focused high energy electron beam is scanned in a rectangular raster over the sample.

The electrons are produced by thermal emission of the cathode (W or LaB_6), accelerated at a voltage of 15-40 kV towards the sample and focused by a series of electromagnetic lenses to a spot size of less than $1\mu\text{m}$. A schematic representation of a scanning electron microscope is given in Fig. 2.5.

Interaction of the electron beam with the sample surface and near-surface material (interaction volume) causes different effects: backscattered electrons, secondary electrons, auger electrons, continuous Bremsstrahlung, characteristic X-rays, fluorescence X-rays and absorbed electrons (sample current).

Backscattered electrons (BSE) are high energy electrons ($>50\text{eV}$) that are ejected from the sample after multiple elastic and inelastic scattering with the atoms in the sample surface region. The BSE give a contrast due to the average atomic number, more specific, due to the backscatter coefficient that increases with increasing atomic number. A larger average atomic number yields a brighter BSE image.

Secondary electrons have lower energies ($<50\text{eV}$) and are along the path of the beam electrons by ionization of specimen atoms. Because of their low energy, they leave the



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and detector around a focusing circle are necessary. This technique is more expensive and time consuming, but provides higher resolution and the possibility to measure light elements down to Be.

2.3 Differential Thermal Analysis

All reactions and phase transitions are connected with the exchange of heat. In DTA (Differential Thermal Analysis) the sample and a reference material, placed in separated crucibles, are heated up at specified heating rates (temperature program); the temperature difference $\Delta T = T_R - T_S$ between sample and reference, and thus the thermal effect taking place in the sample, is measured.

Reactions involving liquids generally lead to a bigger amount of heat exchanged, thus eutectic reactions show bigger effects than peritectic and transition reactions. Solid state reactions show small, often diffuse effects; slow diffusion in the solid state makes determination of exact temperatures difficult.

3 Literature Review

3.1 The Binary Boundary Systems

To construct the phase relations in the {Nb,Ta}-Co-B systems, the binary boundary systems described below were used. Fig. 3.1-Fig. 3.5 present the revised phase diagrams. Invariant reactions and congruent melting points are summarized in Tab. 3.1-Tab. 3.5. A listing of the crystallographic information of all stable and metastable phases pertinent to the systems Nb-Co-B and Ta-Co-B is presented in Appendix Tab. 1.

3.1.1 The Binary Co-B System

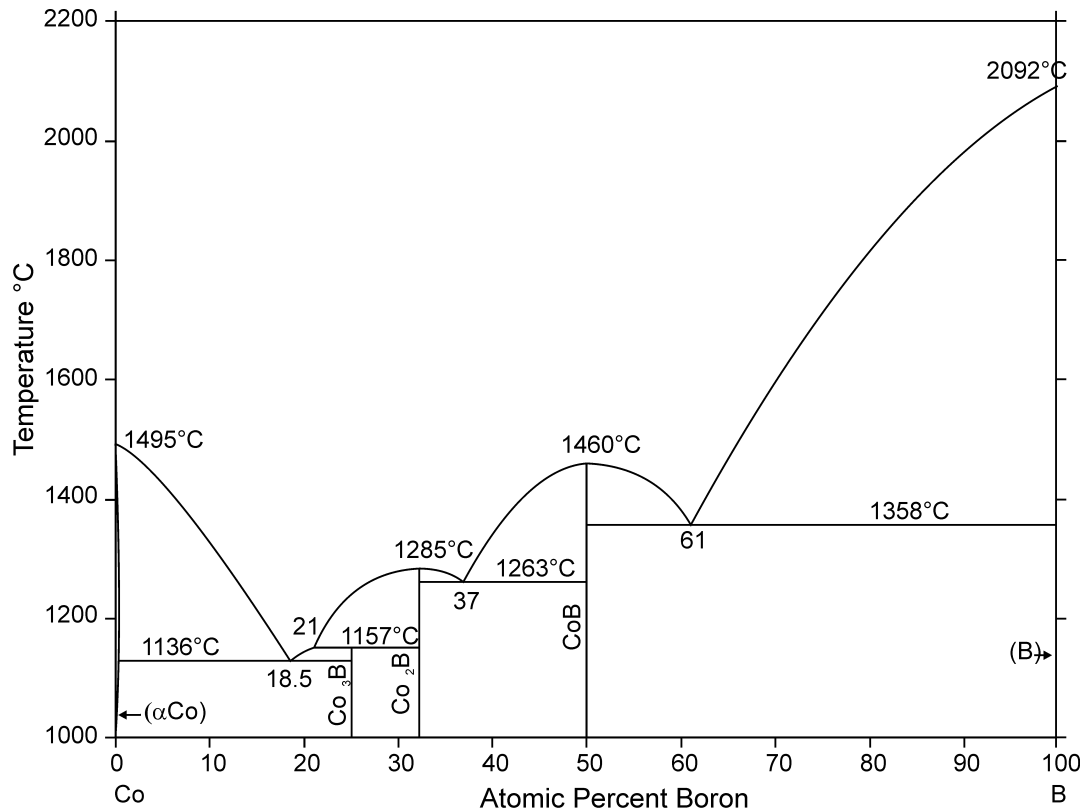


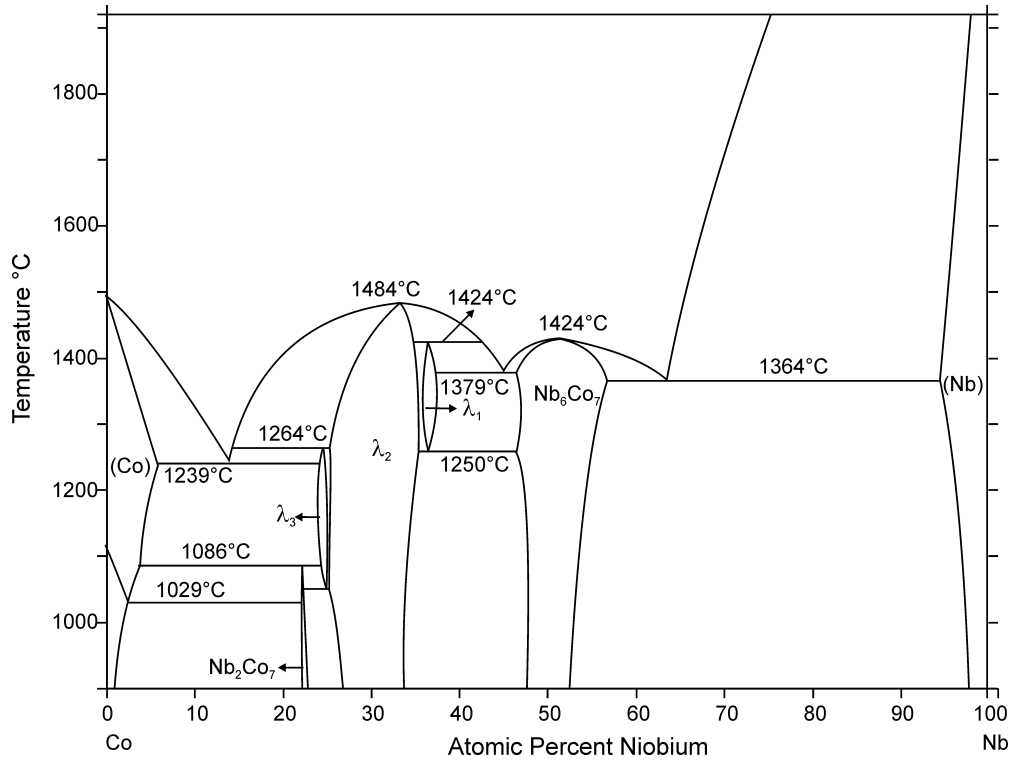
Fig. 3.1: The Co-B binary system [2000Oka, 2002Du].

Phase equilibria in the system Co-B have been summarized by Okamoto [2000Oka] and are essentially based on the experimental data published by Schöbel and Stadelmaier [1966Sch]. Using these data together with re-measured temperatures for the invariant reactions, a thermodynamic modelling has been performed by Du et al. [2002Du]. A more recent microstructural characterization of as-cast Co-B alloys is due to Faria et al. [2006Far]. Furthermore a eutectoid decomposition reaction at 845°C was derived from EMF data for Co₃B: $\text{Co}_3\text{B} \leftrightarrow (\text{Co}) + \text{Co}_2\text{B}$ [1976Omo]. The revised phase diagram is presented in Fig. 3.1

Tab. 3.1: Invariant reactions and congruent melting points in the Co-B system.

Reaction	T/°C	at% B	Reference
$\text{Co}_3\text{B} \leftrightarrow \text{Co} + \text{Co}_2\text{B}$	845	25	[1976Omo]
$\text{I} \leftrightarrow \text{Co} + \text{Co}_3\text{B}$	1136±2	18.5	[2002Du]
$\text{I} + \text{Co}_2\text{B} \leftrightarrow \text{Co}_3\text{B}$	1157±2	21	[2002Du]
$\text{I} \leftrightarrow \text{Co}_2\text{B} + \text{CoB}$	1263±2	37	[2002Du]
$\text{I} \leftrightarrow \text{CoB} + \text{B}$	1358±2	61	[2002Du]
$\text{I} \leftrightarrow \text{Co}_2\text{B}$	~1285	33.3	[2002Du]
$\text{I} \leftrightarrow \text{CoB}$	1460±5	50	[2000Oka]

3.1.2 The Binary Nb-Co System

**Fig. 3.2: The binary Nb-Co system [2000Oka, 2008Ste].**

The Nb-Co system in the version of [2000Oka, 2008Ste] is presented in Fig. 3.2.

Tab. 3.2: Invariant reactions and congruent melting points in the Nb-Co system.

Reaction	T/°C	at% Nb	Reference
$\lambda_3 \leftrightarrow \text{Nb}_2\text{Co}_7 + \lambda_2$	1040±40	25	[2008Ste]
$\text{Co} + \lambda_3 \leftrightarrow \text{Nb}_2\text{Co}_7$	1086±2	22	[2008Ste]
$\text{I} \leftrightarrow \text{Co} + \lambda_3$	1239±2	14	[2008Ste]
$\lambda_1 \leftrightarrow \lambda_2 + \text{Nb}_6\text{Co}_7$	1250±20	36	[2008Ste]
$\text{I} + \lambda_2 \leftrightarrow \lambda_3$	1264±2	25	[2008Ste]
$\text{I} \leftrightarrow \text{Nb}_6\text{Co}_7 + \text{Nb}$	1364	63.3	[2000Oka]
$\text{I} \leftrightarrow \lambda_1 + \text{Nb}_6\text{Co}_7$	1379±2	46	[2008Ste]
$\lambda_2 + \text{I} \leftrightarrow \lambda_1$	1424±4	36	[2008Ste]
$\text{I} \leftrightarrow \text{Nb}_6\text{Co}_7$	1424	51	[2008Ste]
$\text{I} \leftrightarrow \lambda_2$	1484	33.3	[2008Ste]

3.1.3 The Binary Nb-B System

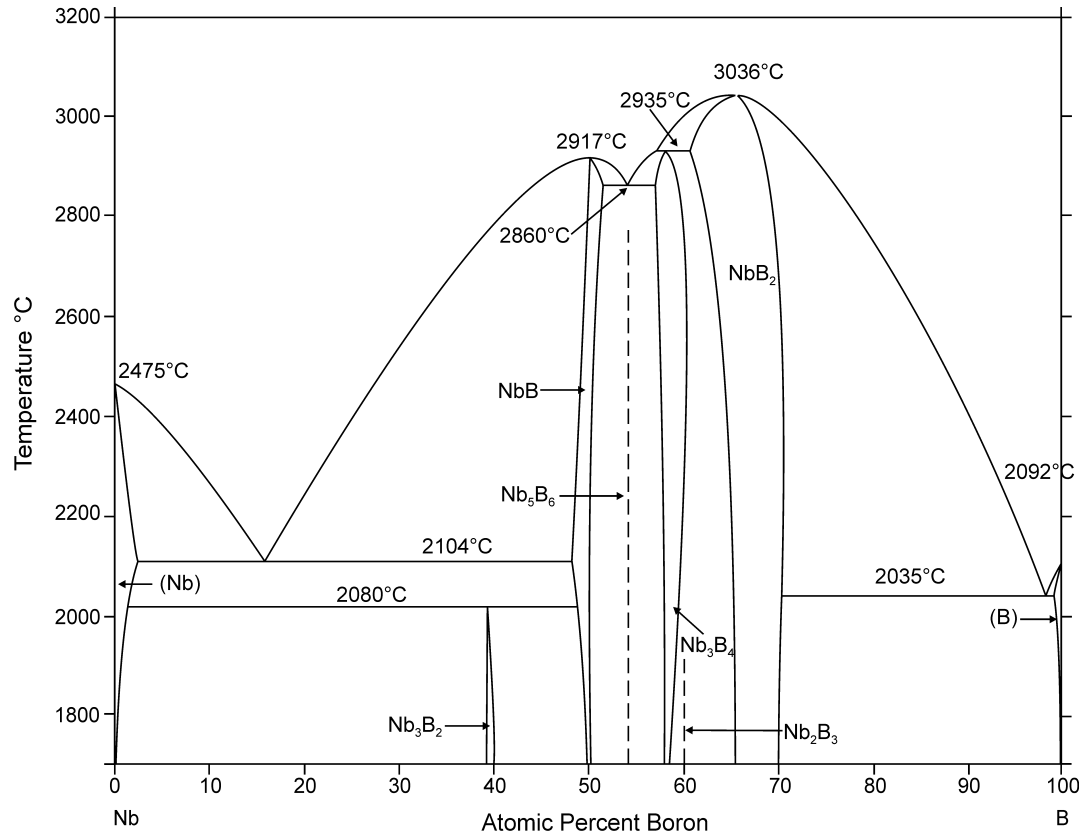


Fig. 3.3: The Nb-B binary system [1998Rog, 2005Nun, 2007Pec, 2008Tan].

The binary Nb-B system is in the version of [1998Rog, 2005Nun, 2007Pec, 2008Tan]. An unsolved puzzle is the existence of Nb₂B₃, reported by [1991Oka] from Cu-flux experiments, but not yet confirmed in bulk samples. The phase diagram is presented in Fig. 3.3.

Tab. 3.3: Invariant reactions and congruent melting points in the Nb-B system.

Reaction	T/°C	at% B	Reference
$\text{L} \leftrightarrow \text{NbB}_2 + \text{B}$	2035±20	98	[1969Rud]
$\text{Nb} + \text{NbB} \leftrightarrow \text{Nb}_3\text{B}_2$	2080±40	40	[1969Rud]
$\text{L} \leftrightarrow \text{Nb} + \text{NbB}$	2104±5	16	[2002Bor]
$\text{L} \leftrightarrow \text{NbB} + \text{Nb}_3\text{B}_4$	2860±15	54	[1969Rud]
$\text{L} + \text{Nb}_3\text{B}_4 \leftrightarrow \text{Nb}_5\text{B}_6$	2897	52	[2007Pec]
$\text{L} \leftrightarrow \text{NbB}$	2917±10	50	[1969Rud]
$\text{L} + \text{NbB}_2 \leftrightarrow \text{Nb}_3\text{B}_4$	2935±12	58	[1969Rud]
$\text{L} \leftrightarrow \text{NbB}_2$	3036±15	66	[1969Rud]

3.1.4 The Binary Ta-Co System

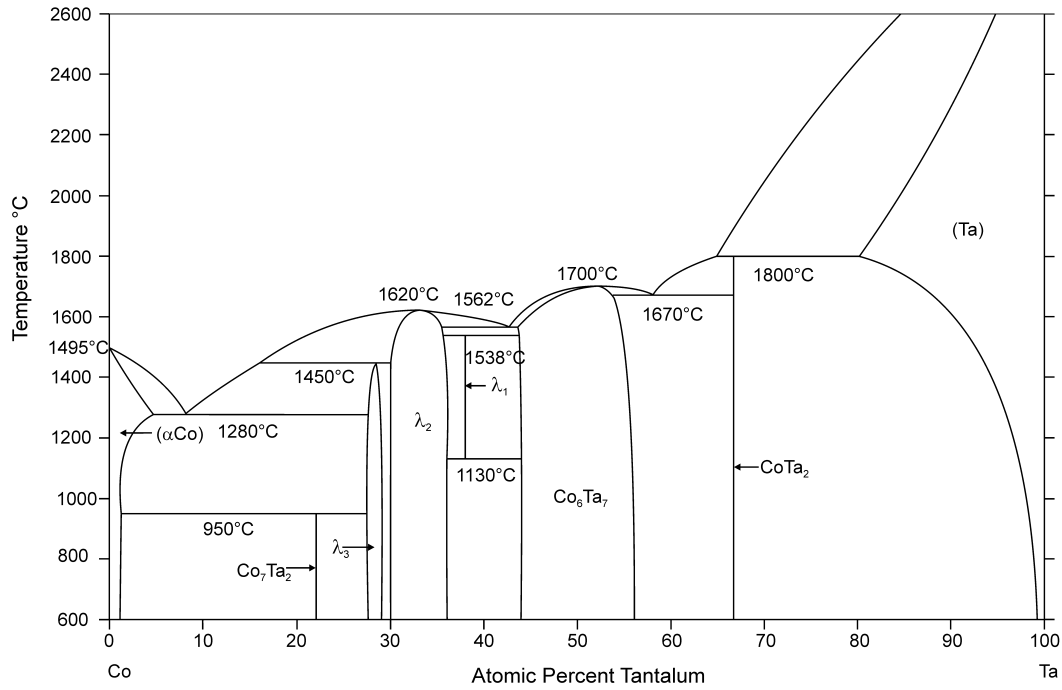


Fig. 3.4: The binary Ta-Co system [2000Oka, 2002Kum].

The Ta-Co system was accepted in the version of Okamoto [2000Oka], considering a later review by Kumar et al. [2002Kum], see Fig. 3.4.

Tab. 3.4: Invariant reactions and congruent melting points in the Ta-Co system.

Reaction	T/°C	at% Ta	Reference
$\text{Co} \leftrightarrow \varepsilon\text{-Co} + \text{Ta}_2\text{Co}_7$	409		[2002Kum]
$\text{Co} + \lambda_3 \leftrightarrow \text{Ta}_2\text{Co}_7$	950	22	[2002Kum]
$\lambda_1 + \lambda_2 + \text{Ta}_6\text{Co}_7$	1129	39	[2002Kum]
$\text{L} \leftrightarrow \text{Co} + \lambda_3$	1278	12	[2002Kum]
$\text{L} + \lambda_2 \leftrightarrow \lambda_3$	1450	27	[2002Kum]
$\lambda_2 + \text{Ta}_6\text{Co}_7 \leftrightarrow \lambda_1$	1540	39	[2002Kum]
$\text{L} \leftrightarrow \lambda_2 + \text{Ta}_6\text{Co}_7$	1577	42	[2002Kum]
$\text{L} \leftrightarrow \lambda_2$	1620	33	[2002Kum]
$\text{L} \leftrightarrow \text{Ta}_6\text{Co}_7 + \text{Ta}_2\text{Co}$	1627	58	[2002Kum]
$\text{L} \leftrightarrow \text{Ta}_6\text{Co}_7$	1650	50	[2002Kum]
$\text{L} + \text{Ta} \leftrightarrow \text{Ta}_2\text{Co}$	1800	66.7	[2002Kum]

3.1.5 The Binary Ta-B System

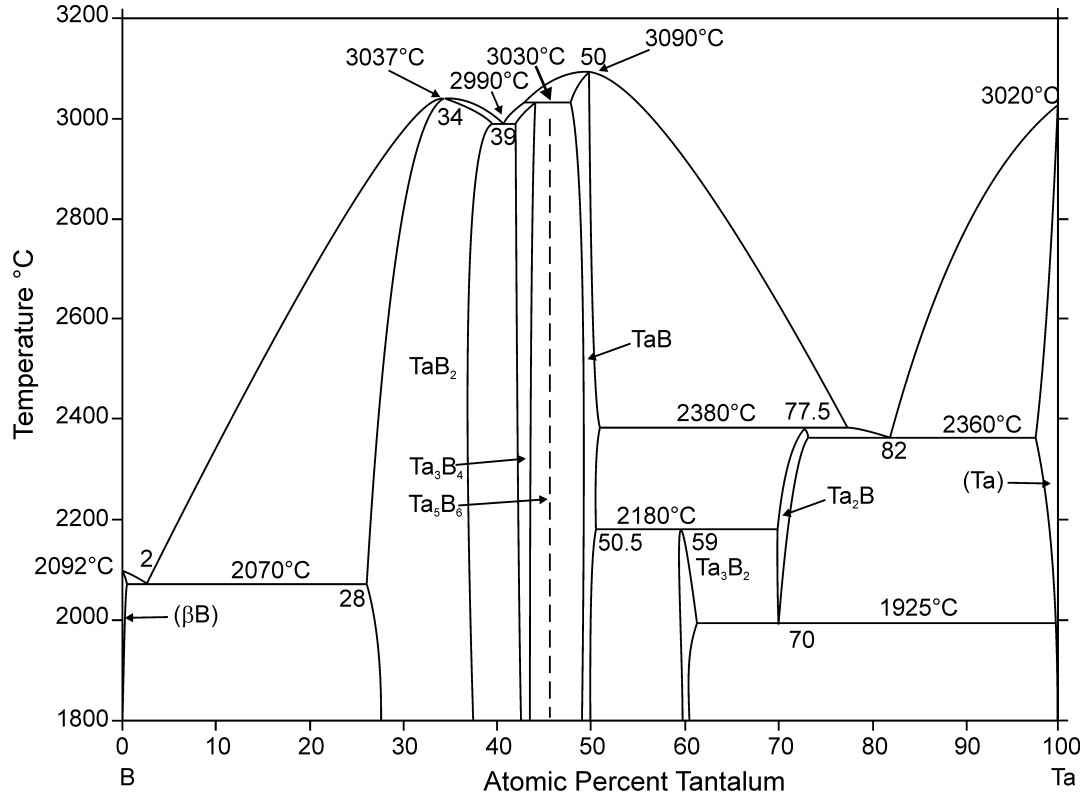


Fig. 3.5: The binary Ta-B system [1992Rog, 2008Cha].

Ta-B is used according to Chad et al. [2008Cha], who unfortunately missed the well-established existence of Ta₅B₆ [1990Oka, 1992Rog]. The phase diagram is presented in Fig. 3.5.

Tab. 3.5: Invariant reactions and congruent melting points in the Ta-B system.

Reaction	T/°C	at% Ta	Reference
Ta ₂ B ↔ Ta ₃ B ₂ + (Ta)	1925 ± 25	70	[2006Cha]
L ↔ (B) + TaB ₂	2070	2	[1990Oka]
TaB + Ta ₂ B ↔ Ta ₃ B ₂	2180 ± 20	59	[1990Oka]
L ↔ Ta ₂ B + (Ta)	2360	18	[2006Cha]
L + TaB ↔ Ta ₂ B	2380	22.5	[2006Cha]
L ↔ TaB ₂ + Ta ₃ B ₄	2990 ± 20	39	[1990Oka]
L + TaB ↔ Ta ₃ B ₄	3030 ± 30	43	[1990Oka]
L ↔ TaB ₂	3037 ± 20	34	[1990Oka]
L ↔ TaB	3090 ± 15	50	[1990Oka]

3.2 The Ternary Systems Ta-Co-B and Nb-Co-B

3.2.1 Isothermal Sections at 800°C

The development in the ternary systems was already discussed in the introduction. Fig.3.6 shows the currently accepted isothermal sections at 800°C by [1990Kuz].

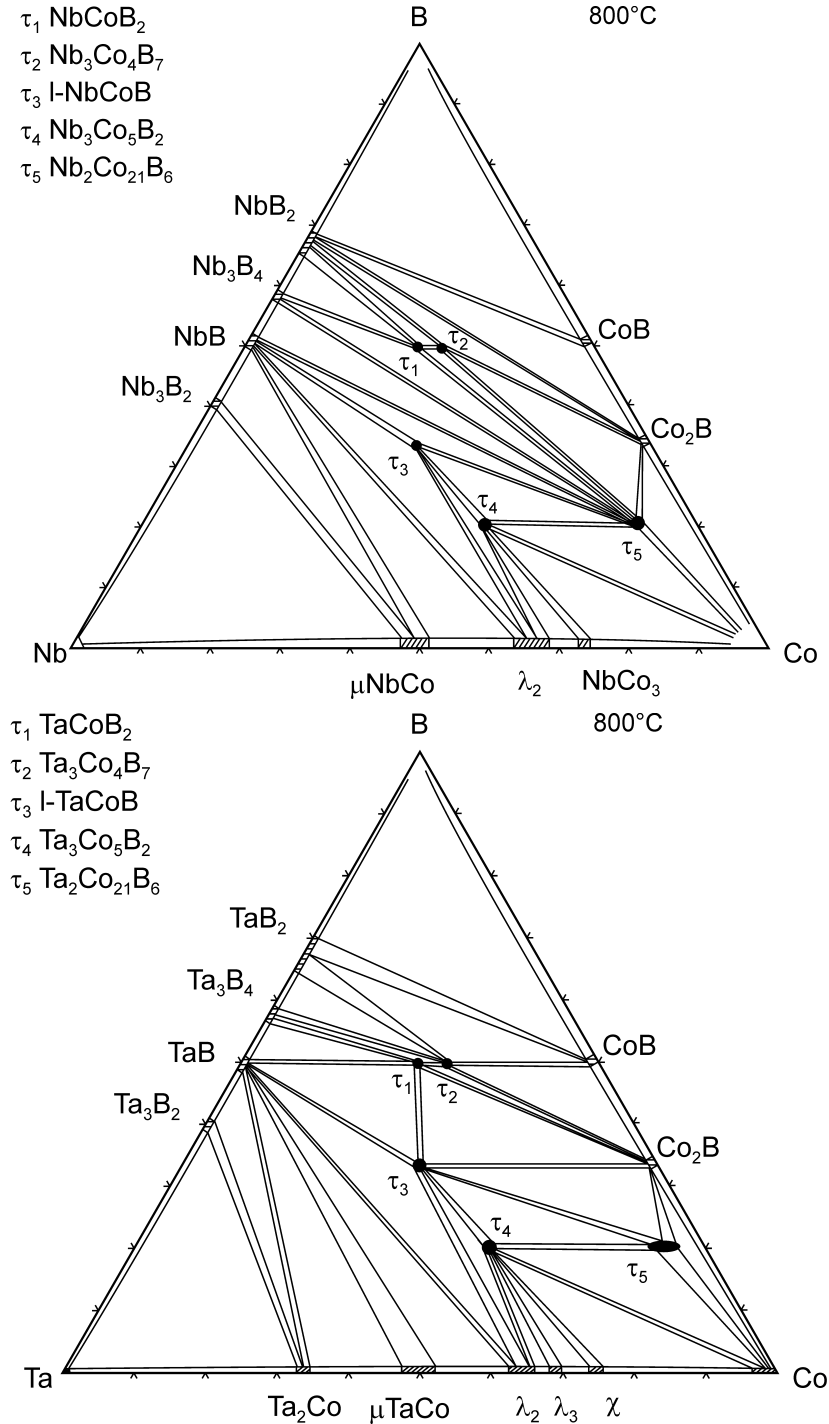


Fig.3.6: Currently accepted isothermal sections at 800°C [1990Kuz].

3.2.2 The Liquidus Projections

As already mentioned above, liquidus surface projections for the Co-rich part of the {Nb,Ta}-Co-B systems were published by [1964Sta] and [1966Sta] respectively. It has to be noted that Stadelmaier et. al were not able to quench Co_3B in their alloys and Co_3B was thus not included in their diagrams.

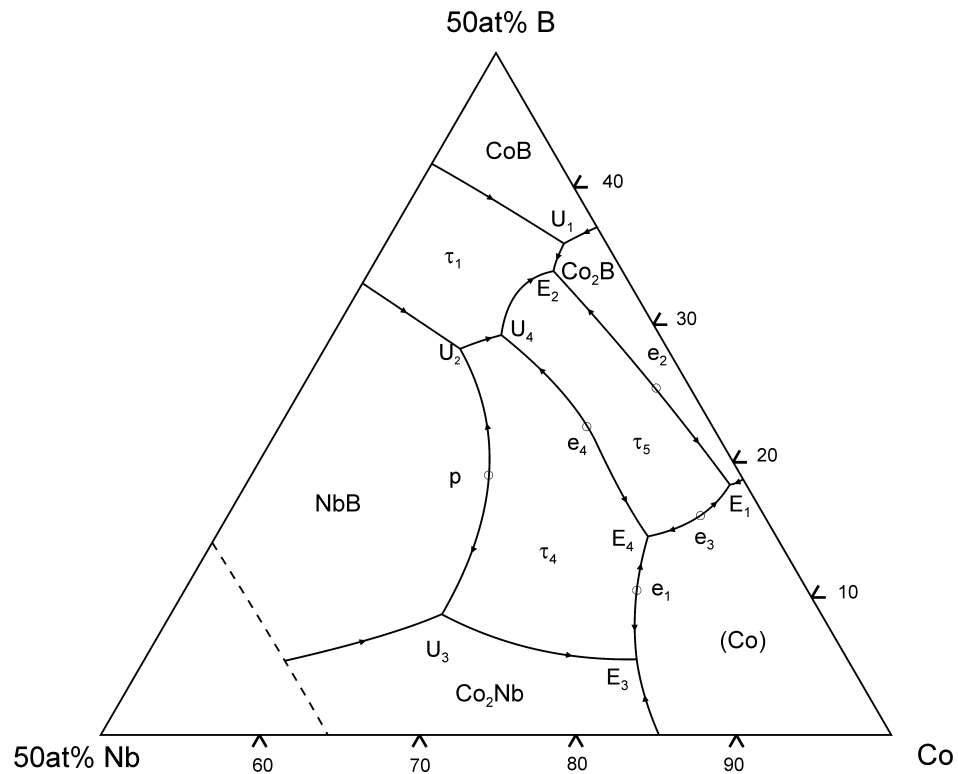


Fig.3.7a: Currently accepted liquidus projections of the Nb-Co-B system as published by Stadelmaier and Schöbl [1966Sta].

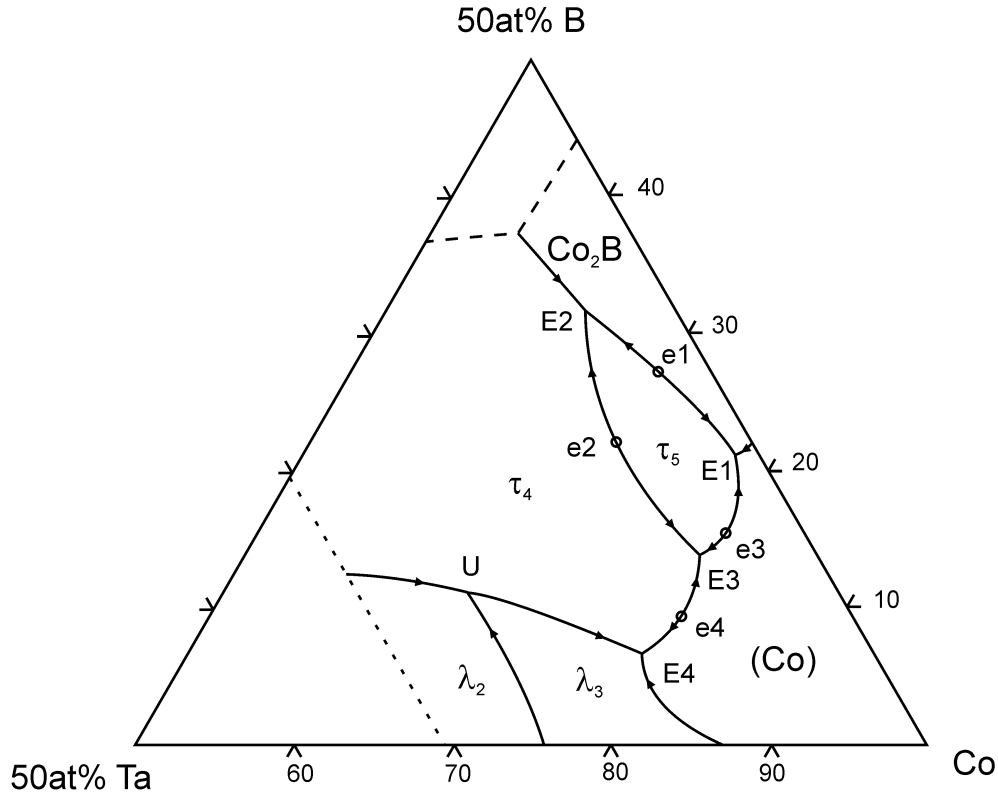


Fig.3.7: Currently accepted liquidus projection of the Ta-Co-B system as published by Stadelmaier and Hofer [1964Sta].

Invariant reactions proposed by [1964Sta] and [1966Sta] are summarized in Tab 3.6, A listing of the crystallographic information of all stable and metastable phases pertinent to the systems Nb-Co-B and Ta-Co-B is presented in Appendix Tab. 1.

Tab 3.6: Invariant reactions in the Co-rich part of the Nb-Co-B and Ta-Co-B as proposed by Stadelmaier and Hofer [1964Sta] and Stadelmaier and Schöbl respectively.

Nb-Co-B	Ta-Co-B
E ₁ L↔Co ₂ B+ Nb ₂ Co ₂₁ B ₆ +(Co)	E ₁ L↔Co ₂ B+ Ta ₂ Co ₂₁ B ₆ +(Co)
E ₂ L↔Co ₂ B+NbCo ₂ B+Nb ₂ Co ₂₁ B ₆	E ₂ L↔Co ₂ B+TaCo ₂ B+Ta ₂ Co ₂₁ B ₆
E ₃ L↔NbCo ₂ B+Co+λ ₂	E ₃ L↔TaCo ₂ B+ Ta ₂ Co ₂₁ B ₆ +(Co)
E ₄ L↔ Nb ₂ Co ₂₁ B ₆ +NbCo ₂ B+(Co)	E ₄ L↔TaCo ₂ B+(Co)+λ ₃
U ₁ L+CoB↔Co ₂ B+NbCoB ₂	U ₁ L+λ ₂ ↔TaCo ₂ B+λ ₃
U ₂ L+NbB↔NbCoB ₂ +NbCo ₂ B	
U ₃ L+NbB↔λ ₂ +NbCo ₂ B	
U ₄ L+NbCo ₂ B↔NbCoB ₂ + Nb ₂ Co ₂₁ B ₆	

4 Experimental

4.1 Sample Preparation and Characterization Methods

Starting materials were 99.9 mass% pure elemental powders of Nb, Ta, Fe, Co, Ni, 98 mass% pure 300 mesh fine amorphous powder of boron as well as 99.8 mass% pure Nb, Ta-foil, 99.9 % Fe, Co, Ni, Nb, Ta rods and pieces of 99.8 mass% pure crystallized boron. Alloys were prepared in two ways. Part of the alloys, each of a weight of 2 grams, was prepared by reaction sintering of powder blends, which were cold compacted in steel dies without lubricants. The tablets were then placed on a BN-substrate in a W-crucible and slowly heated (48 hrs) in a high vacuum furnace of 3×10^{-4} Pa with a W-sheet metal heater to 1050 or to 1400°C and kept at this temperature for 100 hrs. Slow heating was essential to prevent violent self-heating via exothermic reactions. After this first reaction the samples were ground in a WC-Co mortar to a grain-size $< 40 \mu\text{m}$, re-compacted and quickly heated to 1400°C. At this temperature the alloys were kept up to 3 days and finally radiation quenched to room temperature by cutting the power to the W-heater. A part of the samples were reintroduced into the high-vacuum furnace heated quickly to 1400°C from which they were slowly cooled to 1100°C (for 3 days) and kept at 1100°C up to 7 days, prior to radiation quenching.



Fig. 4.1: Arc furnace.

A second set of samples was prepared by arc melting metal ingots (Fe, Co, Ni) and boron pieces wrapped in the proper amount of Nb/Ta foil under Ti-gettered 6N-argon with a nonconsumable tungsten electrode on a water-cooled copper plate (see Fig. 4.1). The alloys were remelted at least three times in order to achieve complete fusion and homogeneity. Mass-losses were checked to be below 0.5%. After melting, heat treatment in a high vacuum furnace was applied as described above.

X-ray powder diffraction (XPD) data from alloys were collected employing Guinier-Huber image plate systems with $\text{Cu-K}\alpha_1$ and $\text{Fe-K}\alpha_1$ radiation ($8^\circ < 2\theta < 100^\circ$) (see Fig. 4.2) or a D5000 diffractometer equipped with an energy dispersive SOLX detector. Precise lattice parameters were calculated by least-squares fits to the indexed θ -values employing Ge as internal standard ($a_{\text{Ge}} = 0.5657906 \text{ nm}$).

Quantitative Rietveld refinements of the X-ray powder diffraction data were performed with the FULLPROF program [2001Roi], with the use of its internal tables for scattering lengths and atomic form factors.

Single crystals of $(\text{Nb,Ta})(\text{Co,Ni})_2\text{B}$ were mechanically isolated from crushed alloys with off-stoichiometric nominal compositions slightly richer in Co/Ni, $\{\text{Nb,Ta}\}_{22}\text{Co}_{53}\text{B}_{25}$, $\{\text{Nb,Ta}\}_{22}\text{Co}_{38}\text{Ni}_{15}\text{B}_{25}$, $\text{Nb}_{22}\text{Co}_{38}\text{Ni}_{15}\text{B}_{25}$, heated and slowly cooled from a temperature slightly below the peritectic melting to assure good crystallization conditions. Inspection on an AXS-GADDS texture goniometer assured high crystal



Fig. 4.2: Fe-Guinier.

quality, unit cell dimensions and Laue symmetry of the specimens prior to X-ray intensity data collection on a four-circle Nonius Kappa diffractometer equipped with a CCD area detector employing graphite monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.071073 \text{ nm}$). Orientation matrix and unit cell parameters were derived using the program DENZO [1998Non]. No special absorption corrections were necessary because of the rather regular crystal shape and small dimensions of the investigated specimens. The structures were refined with the aid of the SHELXL-97 program [1997She].



Fig. 4.3: Cutting machine.

The as cast and annealed samples were cut (see Fig. 4.3), polished using standard procedures and were examined by optical metallography and scanning electron microscopy (SEM). Compositions were determined via Electron Probe Micro-Analyses (EPMA) on a Carl Zeiss Supra V equipped with a Link EDX system operated at 20 kV and 60 μA .

A Philips CM12 STEM transmission electron microscope (TEM) was used with an EDX analyzer and Phoenix software to corroborate unit cell, symmetry and formation of superstructures. TEM investigations were performed on particles (0.1–2 μm), which were obtained by mechanically crunching alloy pieces under ethanol and transferring the particles on a thin holey carbon film supported by a copper grid (see Fig. 4.4a). Alternatively samples for TEM were prepared in a form of

thin lamellas (lateral dimensions about 10x8 micron, see Fig. 4.4b) perpendicular to the polished facet of material fragments using a focused ion beam (FIB) technique in a TESCAN LYRA 3 XMU FEG/SEMxFIB scanning electron microscope.

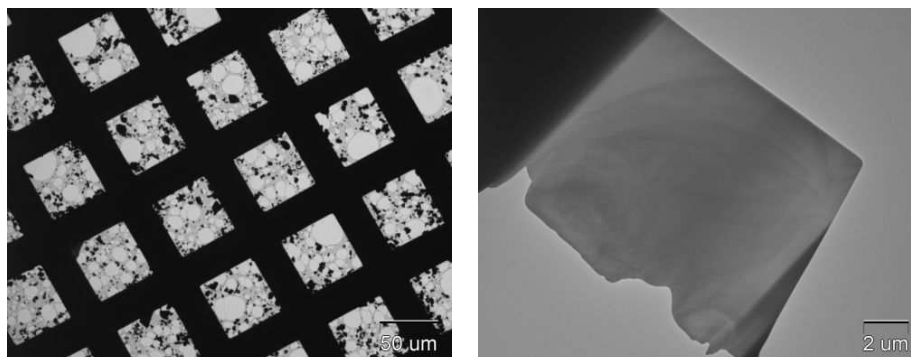


Fig. 4.4: TEM samples (a) powder on a Cu-grid, (b) lamellar.

Vicker's hardness measurements were performed on a Anton Paar Microhardness Tester Microduromat 4000 (MD 4000) employing loads of 0.49, 0.98, 1.72, 1.96 N (50, 100, 175, 200 ponds respectively) and a loading time of 10 s (referred to as HV). For all the indentation data the hardness HV was calculated via equation, $HV = 2F \sin 136^\circ / l^2 = 1.854 F / l^2$, with the diagonal length $2l$ of the indent and F the indentation load. The accuracy for these measurements is about 5%.

Thermal analyses were performed in a calibrated Netzsch STA 409 PG/4/G Luxx Differential Scanning Calorimeter (DSC) employing a heating rate of 5 K/min in Al_2O_3 crucibles under a stream of 6N argon. Prior to DTA (differential thermal analysis), the alloys were annealed at 1100°C for 200 hrs.

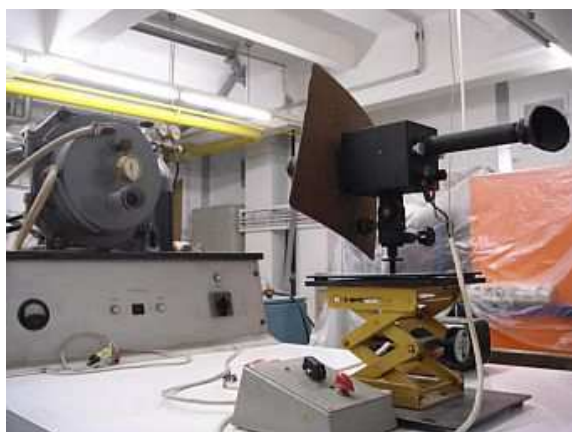


Fig. 4.5: Pirani furnace with optical pyrometer.

The green bodies (with a lateral hole directly pressed into the sample) were then slowly heated on BN in high vacuum (see above) to a final sintering temperature of 1400°C during 12 hours. Phase condition was checked by XPD prior to the measurements. In the

Melting points of the specimens for temperatures above 1400°C were determined using the Pirani-Altherthum technique based on the black body principle [1923Pir]. For this technique sample specimens was prepared from powder blends, which were directly compacted in form of the final Pirani shape in steel dies using a small amount of acetone as densification aid.

Pirani furnace the cuboid-like sample of a length of about 3 cm and a cross section of about 5x3 mm (see Fig. 4.6) is mounted to contact two water-cooled Cu-electrodes.

The sample is directly heated under a protective atmosphere of 6N Ar-gas passing an electric current through it. With an optical pyrometer the hole is focused and the melting behavior and temperature is observed simultaneously. For reproducibility of the acquired data each measurement is repeated several times. Therefore about four Pirani samples of each composition were prepared.



Fig. 4.6: Pirani sample.

Prior to the measurements a precise micro-pyrometer calibration curve for the temperature region from 1100°C to 1600°C was established, comparing the theoretical and the experimentally observed melting temperatures of pure solid or sintered pieces of Fe (sintered), Co (rod), Ni (sintered) and Ti (rod). The defined linear regression fit is presented in Fig. 4.7.

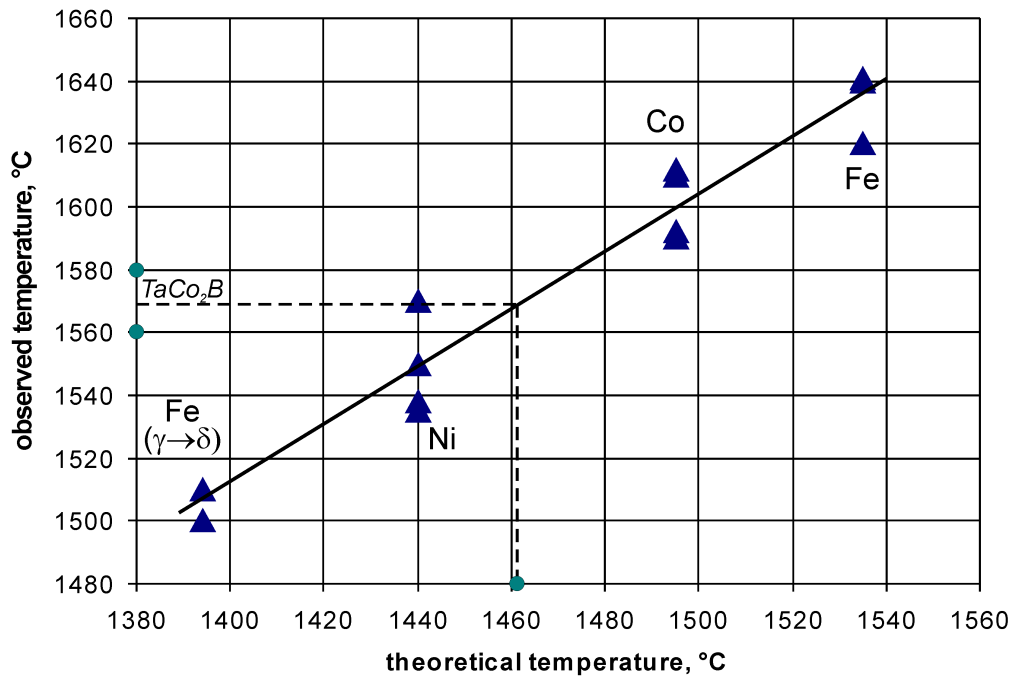


Fig. 4.7: Calibration curve of micro-optical pyrometer.

4.2 First-principles Calculations

By Gunther Schöllhammer

Structure optimizations, total-energy computations, and electronic structure calculations were performed with the Vienna ab-initio simulation package (VASP) [1993Kre, 1994Kre, 1996Kre,]. The Kohn-Sham equations of density functional theory [1964Hoh, 1965Koh] with periodic boundary conditions were solved within a plane wave basis set of electron-ion interactions described by the projector augmented wave method [1994Blo, 1999Kre]. Exchange correlations were treated within the generalized gradient approximation of Perdew and Wang, PW91, (see reference [1996Per] and the references therein). A cutoff energy of 500 eV was chosen for the plane wave basis set. Reciprocal space sampling was performed using suitably large Monkhorst-Pack k meshes [1976Mon]. Reciprocal space integration was performed by the first-order Methfessel-Paxton method [1989Met] with a broadening parameter of 0.2 eV. Optimization of structural parameters has been achieved by minimization of atomic forces and stress tensors applying the conjugate gradient technique.

5 Results and Discussion

5.1 Phase Relations in the Systems Ta-Co-B and Nb-Co-B

5.1.1 The System Ta-Co-B

Phase relations at 1100°C, as derived by X-ray analyses of about 25 ternary alloys, are summarized in Fig. 5.1 and Tab. 5.1 and establish the formation of five ternary compounds τ_1 to τ_5 for which crystallographic details are presented in Appendix Tab. 1. The crystal structures of τ_1 -TaCoB₂, τ_3 -TaCoB and τ_5 -Ta_{2-x}Co_{21+x}B₆ have been confirmed. τ_2 -Ta₃Co₄B₇ indeed crystallizes with the Nb₃Co₄B₇-type (see below) as supposed by Kuzma and Chaban [1990Kuz]. There is no doubt on the formation of the compound τ_4 -TaCo₂B with a unique structure (see section below). However, there was no indication for the presence of a phase Ta₃Co₅B₂ as reported by Kuzma et al. [1979Kuz]: X-ray patterns of samples quenched at various temperatures in the range from 800 to 1400°C at this composition were collected and all were completely indexed and refined on the basis of a three-phase structure τ_4 -TaCo₂B+ τ_3 -TaCoB+ λ_2 -TaCo₂. Long term anneal for 1500 h at 800°C did not change the equilibrium and no traces of Ta₃Co₅B₂ appeared. Although we note a similarity in the X-ray powder intensities between τ_4 -TaCo₂B and Ta₃Co₅B₂, we failed to index and refine the powder patterns of the sample with composition Ta₃Co₅B₂ on the basis of the Ti₃Co₅B₂-type structure. We thus may safely assume that “Ta₃Co₅B₂” does not exist and phase equilibria rather cover the compound τ_4 -TaCo₂B instead. TaCoB with the NbCoB-type at low temperatures exhibits a high temperature modification ZrNiAl-type structure (see below), which can be obtained from as cast alloys but which on annealing at temperatures of 1550°C or smaller decomposes to the low-temperature form. Except for τ_5 -Ta_{2-x}Co_{21+x}B₆ no significant homogeneity regions were observed for the ternary compounds and mutual solid solubilities of cobalt and tantalum borides were found to be very small (less than about 1 at.%). The homogeneity region for τ_5 was found to extend from Ta_{0.97}Co_{22.03}B₆ (a=1.0505 nm) to Ta_{2.48}Co_{20.52}B₆ (a=1.0576 nm) for alloys in as cast condition, that includes the region reported by Steurer et. al. [1979Ste1] (a=1.0515-1.0562 nm for 0≤x≤1) for alloys annealed at 1100°C as well as SC data from Stadelmaier et.al. [1989Sta] (a=1.0552 nm for Ta_{2.18}Co_{20.82}B₆).

Besides the fact that Ta₃Co₅B₂ does not exist and is represented by the novel phase τ_4 -TaCo₂B instead, phase relations among the ternary compounds at 1100°C reveal significant differences with the isothermal section at 800°C published by Kuzma and Chaban [1990Kuz]. Main differences concern the tie lines (this work, 1100°C, see Fig. 5.1,

[1990Kuz] see Fig.3.6): (i) τ_1 -TaCoB₂ + TaB₂ at 1100°C contradicts the tie line τ_2 -Ta₃Co₄B₇ + Ta₃B₄ at 800°C, (ii) τ_2 -Ta₃Co₄B₇ + τ_3 -TaCoB at 1100°C contradicts the tie line τ_1 -TaCoB₂ + Co₂B, (iii) Ta₅B₆ + τ_1 -TaCoB₂ appears as an additional tie-line, and (iv) τ_4 -TaCo₂B + Co₂B at 1100°C contradicts the tie line τ_3 -TaCoB + τ_5 -Ta_{2-x}Co_{21+x}B₆. Some of these differences may arise from solid state four-phase reactions connecting the crossing tie lines at a temperature somewhere within the region from 800 to 1100°C. Corresponding reactions are included in the Scheil reaction scheme derived for the Co-rich part of the Ta-Co-B system (>50 at.% Co; see Fig. 5.26).

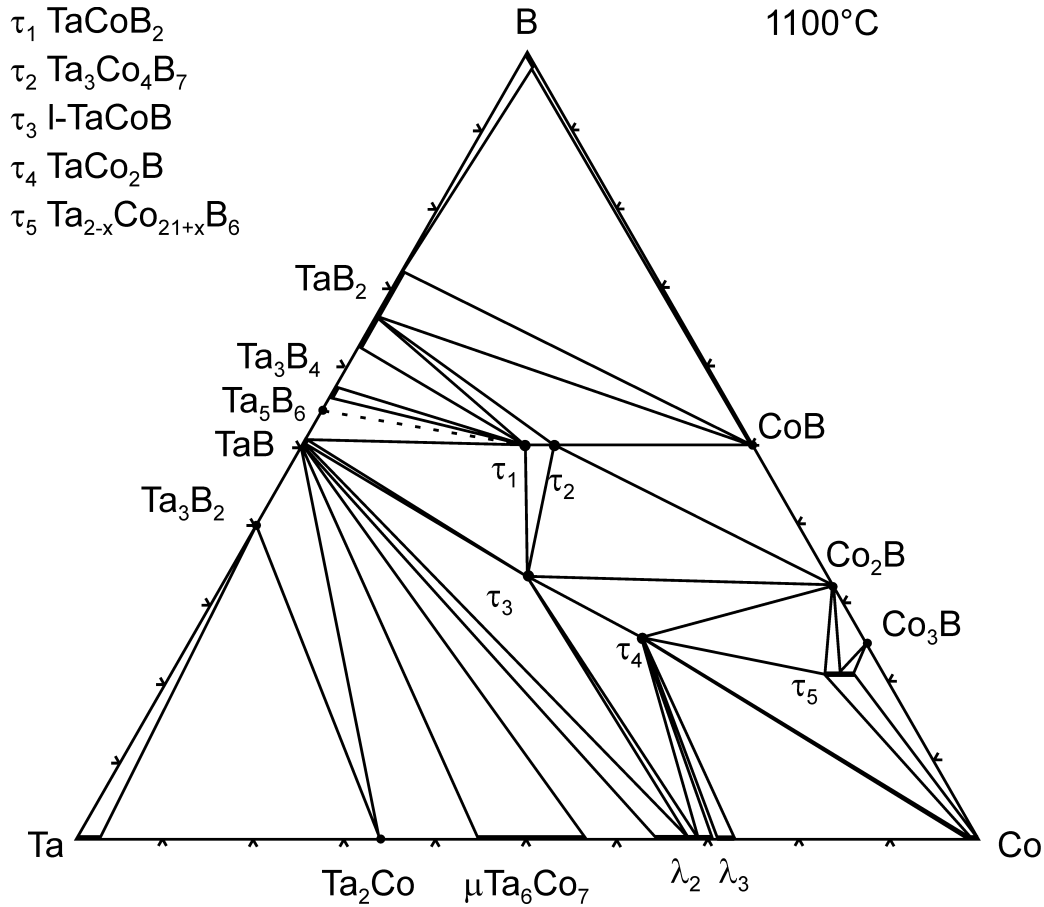


Fig. 5.1: The system Ta-Co-B at 1100°C.

Tab. 5.1: Phase relations in the system Ta-Co-B at 1100°C.

Three Phase Field	Nominal sample composition			X-ray phase analysis	Lattice Parameters/nm			
	Ta	Co	B		a	b	c	β
Ta ₃ B ₄ +TaB ₂ + τ_1	33	10	57.6	TaB ₂	0.3097	0.3097	0.3227	-
				Ta ₃ B ₄	0.3129	0.3285	1.4005	-
				τ_1	0.6002	0.3109	0.8187	-
TaB+ τ_1 + τ_3	35	25	40	TaB	0.3278	0.8666	0.3154	-
				τ_1	0.6000	0.3109	0.8184	-
				τ_3	0.3252	1.7053	0.5909	-
τ_2 + τ_3 +Co ₂ B	22.5	37.5	40	Co ₂ B	0.5016	0.5016	0.4220	-
				τ_2	0.3189	1.8356	0.8880	-
				τ_3	0.3255	1.7049	0.5907	-
τ_3 + τ_4 + λ_2	28.3	56.7	15	λ_2	0.6728	0.6728	0.6728	-
				τ_3	small quantities			-
				τ_4	0.9149	0.6412	0.6291	109.891°
τ_4 + τ_5 +Co ₂ B	12.5	60	27.5	Co ₂ B	0.5017	0.5017	0.4221	-
				τ_4	0.9154	0.6415	0.6289	109.922°
				τ_5	1.0559	1.5587	1.5587	-
Ta+Ta ₃ B ₂ +Ta ₂ Co	66.7	13.3	20	Ta	0.3310	0.3310	0.3310	-
				Ta ₃ B ₂	0.6176	0.6176	0.3284	-
				Ta ₂ Co	0.6116	0.6116	0.4969	-
TaB+Ta ₂ Co+Ta ₇ Co ₆	55	25	20	TaB	0.3281	0.8673	0.3157	-
				Ta ₂ Co	0.6123	0.6123	0.4961	-
				Ta ₇ Co ₆	0.4804	0.4804	2.6467	-
τ_4 +Co+ λ_3	20	65	15	(Co)	lost			-
				λ_3	0.6721	0.6721	0.6721	-
				τ_4	0.9152	0.6413	0.6292	-
τ_4 + λ_2 + λ_3	26.7	53.3	20	λ_2	0.4733	0.4733	1.5426	-
				λ_3	0.6686	0.6686	0.6686	-
				τ_4	0.9153	0.6413	0.6290	109.917°
Co ₃ B+Co+ τ_5	2.5	78.5	19	ϵ -(Co)	0.2508	0.2508	0.4083	-
				Co ₃ B	0.5266	0.6630	0.4411	-
				τ_5	1.0526	1.0526	1.0526	-

5.1.2 The System Nb-Co-B

Thirteen ternary alloys were selected in order to check on the phase relations in critical parts of the diagram. According to the X-ray phase analyses we were able to derive the phase relations for the Nb-Co-B system in the isothermal section at 1100°C as shown in Fig. 5.2 and Tab. 5.2: Phase relations in the system Nb-Co-B at 1100°C confirming the compounds τ_1 -NbCoB₂, τ_2 -Nb₃Co₄B₇, τ_3 -NbCoB and τ_5 -Nb_{2-x}Co_{21+x}B₆ (for crystallographic details see Appendix Tab. 1).

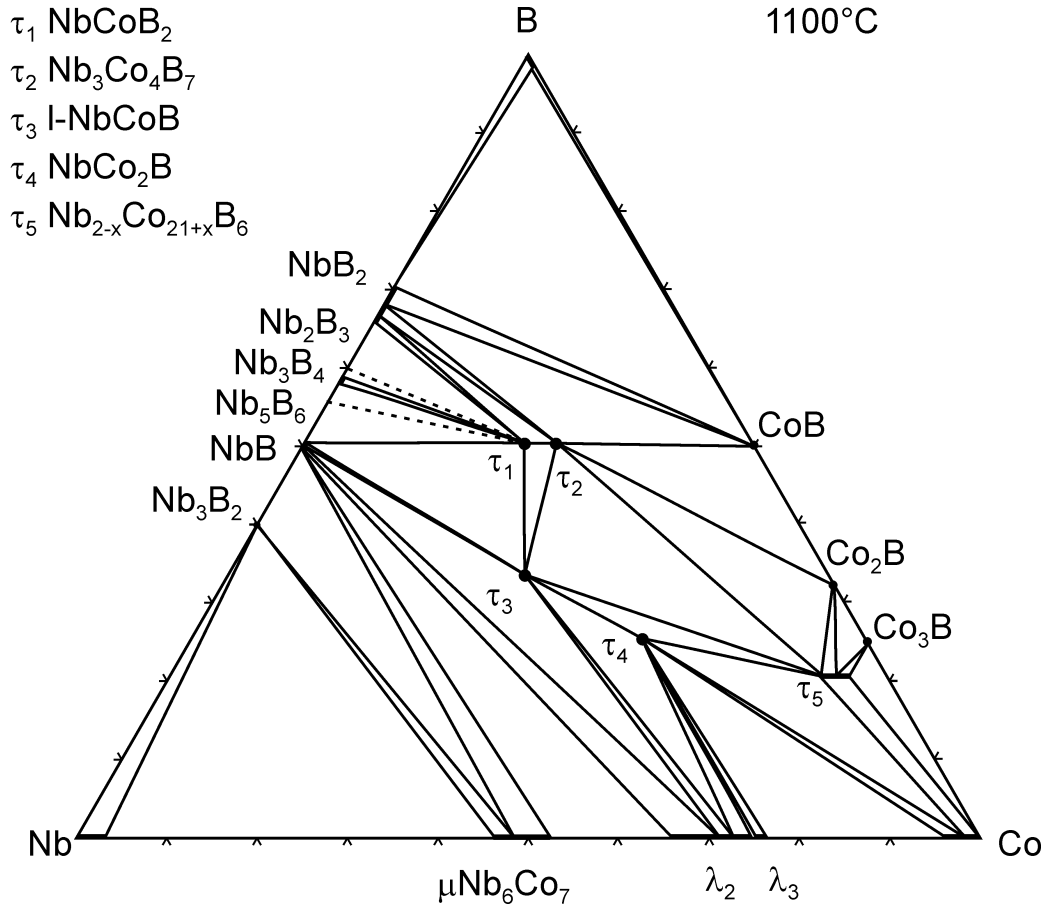


Fig. 5.2: The system Nb-Co-B at 1100°C.

The situation concerning the compound “Nb₃Co₅B₂” turned out to be exactly alike “Ta₃Co₅B₂”: X-ray patterns did not deliver any hints for the formation of a Ti₃Co₅B₂ type structure not even at long term annealing for 1500 h at 800°C. Rietveld refinements of the specimen (NbCo₂)_{0.8}B_{0.2} solely reveal a three-phase structure τ_4 -NbCo₂B+I- τ_3 -NbCoB+ λ_2 -NbCo₂ and confirm the formation of the compound τ_4 -NbCo₂B isostructural with the Ta-homologue TaCo₂B. Similarly to TaCoB also τ_3 -NbCoB exhibits a high temperature modification with the ZrNiAl-type structure (see below), which can be obtained from as cast alloys but which on annealing at temperatures of 1550°C or smaller transfers to the low-temperature form.

Tab. 5.2: Phase relations in the system Nb-Co-B at 1100°C

Three Phase Field	Nominal sample composition			X-ray phase analysis	Lattice Parameters/nm			
	Nb	Co	B		a	b	c	β
NbB+ λ_2 + τ_3	33.3	33.3	33.4	NbB	0.3295	0.8709	0.3164	
				λ_2	0.6768	0.6768	0.6768	
				τ_3	0.3263	1.7109	0.5935	
λ_2 + τ_3 + τ_4	28.3	56.7	15	λ_2	0.6731	0.6731	0.6731	
				τ_3	0.3264	1.7134	0.5937	
				τ_4	0.9182	0.6422	0.6314	109.981°
τ_1 + τ_2 + τ_3	27.5	27.5	45	τ_1	0.6013	0.3122	0.8207	
				τ_2	0.3196	1.8412	0.8909	
				τ_3	0.3261	1.7113	0.5937	
τ_2 + τ_3 + τ_5	17.5	52.5	30	τ_2	0.3193	1.8411	0.8903	
				τ_3	0.3262	1.7103	0.5929	
				τ_5	1.0568	1.0568	1.0568	
(Co)+ τ_4 + τ_5	8	77.5	14.5	(Co)	0.3737	0.3737	0.3737	
				τ_4	small quantities			
				τ_5	1.0579	1.0579	1.0579	
Co ₂ B+Co ₃ B+ τ_5	2.5	73.5	24	Co ₂ B	0.5013	0.5013	0.4218	
				Co ₃ B	0.5203	0.6655	0.4395	
				τ_5	1.0539	1.0539	1.0539	
Co ₂ B+ τ_2 + τ_5	10	54	36	Co ₂ B	0.5014	0.5014	0.4218	
				τ_2	0.3195	1.8400	0.8903	
				τ_5	1.0558	1.0558	1.0558	

A comparison of the isothermal sections between the two systems Ta-Co-B and Nb-Co-B documents the thermodynamic, chemical and structural analogy. The essential difference only concerns the tie lines τ_4 -TaCo₂B + Co₂B and τ_3 -TaCoB + Co₂B in contrast to τ_2 -Nb₃Co₄B₇ + τ_5 -Nb_{2-x}Co_{21+x}B₆ and τ_3 -NbCoB + τ_5 -Nb_{2-x}Co_{21+x}B₆. These virtual contradictions may essentially be part of a series of four-phase equilibria (solid state transition reactions): τ_3 -MCoB + Co₂B $\Leftrightarrow$ τ_4 -MCo₂B + τ_2 -M₃Co₄B₇, τ_4 -MCo₂B + Co₂B $\Leftrightarrow$ τ_2 -M₃Co₄B₇ + τ_5 -M₂Co₂₁B₆ and τ_2 -M₃Co₄B₇ + τ_4 -MCo₂B $\Leftrightarrow$ τ_3 -MCoB + τ_5 -M₂Co₂₁B₆.

A comparison with the isothermal section at 800°C published by Kuzma and Chaban [1990Kuz] reveals some essential differences. The tie-line at 1100°C, τ_1 -NbCoB₂ + τ_3 -NbCoB contradicts the equilibria reported at 800°C: τ_5 -Nb₂Co₂₁B₆ + NbB and τ_5 -Nb₂Co₂₁B₆ + Nb₃B₄. A further difference exists for the tie-line at 1100°C, τ_2 -Nb₃Co₄B₇ + CoB, which stays in contrast to Co₂B + NbB₂ reported at 800°C [1990Kuz]. Some of these differences may arise from solid-state four-phase reactions connecting the crossing tie-lines at a temperature somewhere within the region from 800 to 1100°C. A reasonable proposal for these reactions is included in the Scheil reaction scheme derived for the Co-rich part of the Nb-Co-B system (>50 at.% Co, see Fig. 5.29).

5.2 Structural Chemistry

5.2.1 The Crystal Structures of h-NbCoB and h-TaCoB and Solid Solutions $\{\text{Nb,Ta}\}(\text{Fe}_x\text{Co}_{1-x})\text{B}$

X-ray powder patterns of as cast alloys NbCoB and TaCoB revealed, besides some amounts of TaB (CrB-type), a new powder pattern, which was completely indexed on a hexagonal unit cell close to that established for the homologous ternary compounds $\{\text{Nb,Ta}\}\text{FeB}$ [1967Kuz, 1971Kuz, 1990Kuz]. Rietveld refinements of the X-ray intensities, absence of systematic extinctions, and size of unit cells confirm isotypism with the structure type of ZrNiAl, an ordered superstructure of the Fe_2P -type (see Fig. 5.3). Crystallographic information is compiled in Tab. 5.3.

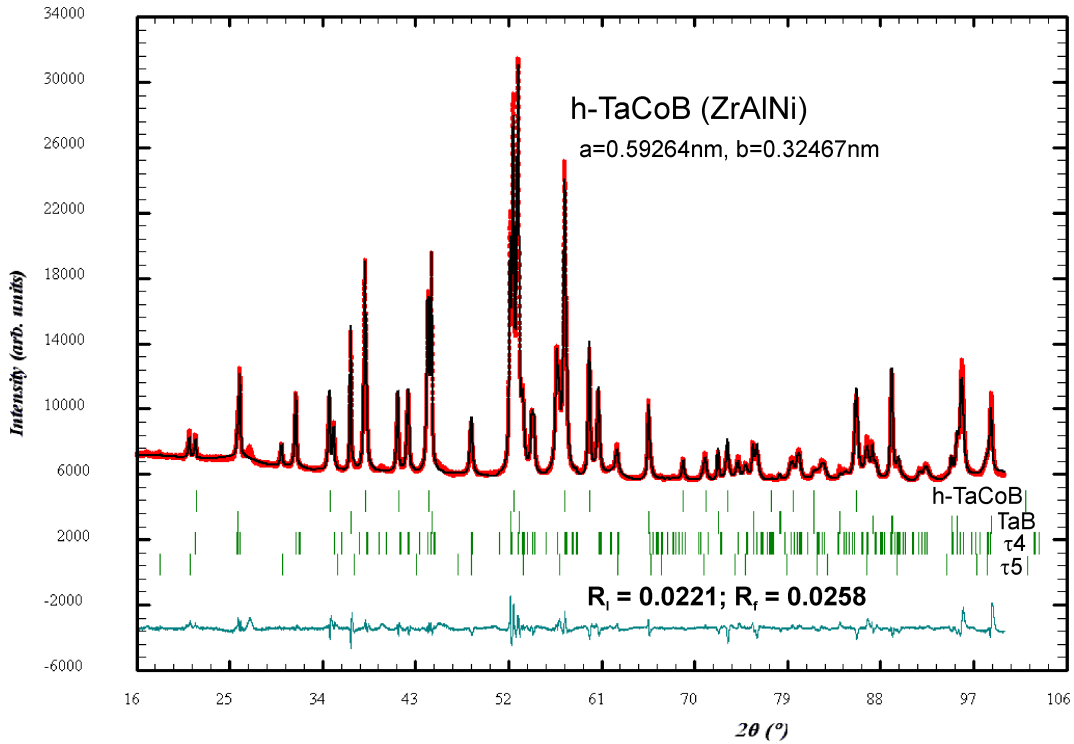


Fig. 5.3: Rietveld refinement of as cast alloy $\text{Ta}_{27}\text{Co}_{43}\text{B}_{30}$, revealing the majority phase h-TaCoB with ZrAlNi-type.

Tab. 5.3: Results of X-ray powder Rietveld refinement for h-{Nb,Ta}CoB with ZrNiAl-type (FeK α radiation). Biso fixed in refinement (B:0.7; Co: 0.5, Ta:0.3)

<i>Compound</i>	<i>h-NbCoB</i>	<i>h-TaCoB</i>
Sample composition	NbCoB	Ta ₂₇ Co ₄₃ B ₃₀
Heat treatment	as cast	as cast
Structure type	ZrNiAl	ZrNiAl
Space group	P $\bar{6}$ 2m (189)	P $\bar{6}$ 2m (189)
2 θ range (degrees)	8 $\leq$ 2 θ $\leq$ 100	8 $\leq$ 2 θ $\leq$ 100
a (nm), Guinier	0.59527(5)	0.59264(1)
c (nm), Guinier	0.32478(4)	0.32467(5)
Reflections in refinement	21	21
Number of variables	42	47
$R_F = \sum F_o - F_c / \sum F_o$	0.0976	0.0258
$R_I = \sum I_o - I_c / \sum I_o$	0.0747	0.0221
$R_{wp} = [\sum w_i y_{oi} - y_{ci} ^2 / \sum w_i y_{oi} ^2]^{1/2}$	0.194	0.0886
$R_p = \sum y_{oi} - y_{ci} / \sum y_{oi} $	0.232	0.0928
$R_e = [(N - P + C) / (\sum w_i y_{oi}^2)]^{1/2}$	0.0424	0.0474
$\chi^2 = (R_{wp} / R_e)^2$	21.0	3.50
M1 in 3f (x,0,0)	0.5937(1)	0.5869(1)
Co1 in 3g (x,0,1/2)	0.2525(4)	0.2422(4)
B1 in 1a (0,0,0)	-	-
B2 in 2d (1/3,2/3,1/2)	-	-

The small and rather insignificant variation of the lattice parameters in samples near the stoichiometric composition indicates the absence of ternary homogeneity regions for both phases. Annealing at temperatures below 1550°C, however, reduced the amount of the new phase and yielded increasing amounts of the NbCoB-type low-temperature modification. This behaviour suggests that the novel high temperature compounds h-NbCoB and h-TaCoB are only stable in a small temperature region below melting. The close structural chemical relationship among the ZrNiAl-type (high temperature form) and the NbCoB-type (low-temperature form) was outlined in detail by Krypiyakevich et al. [1971Kry]. A three-dimensional representation of the high- and low-temperature structure type is shown in Fig. 5.4.

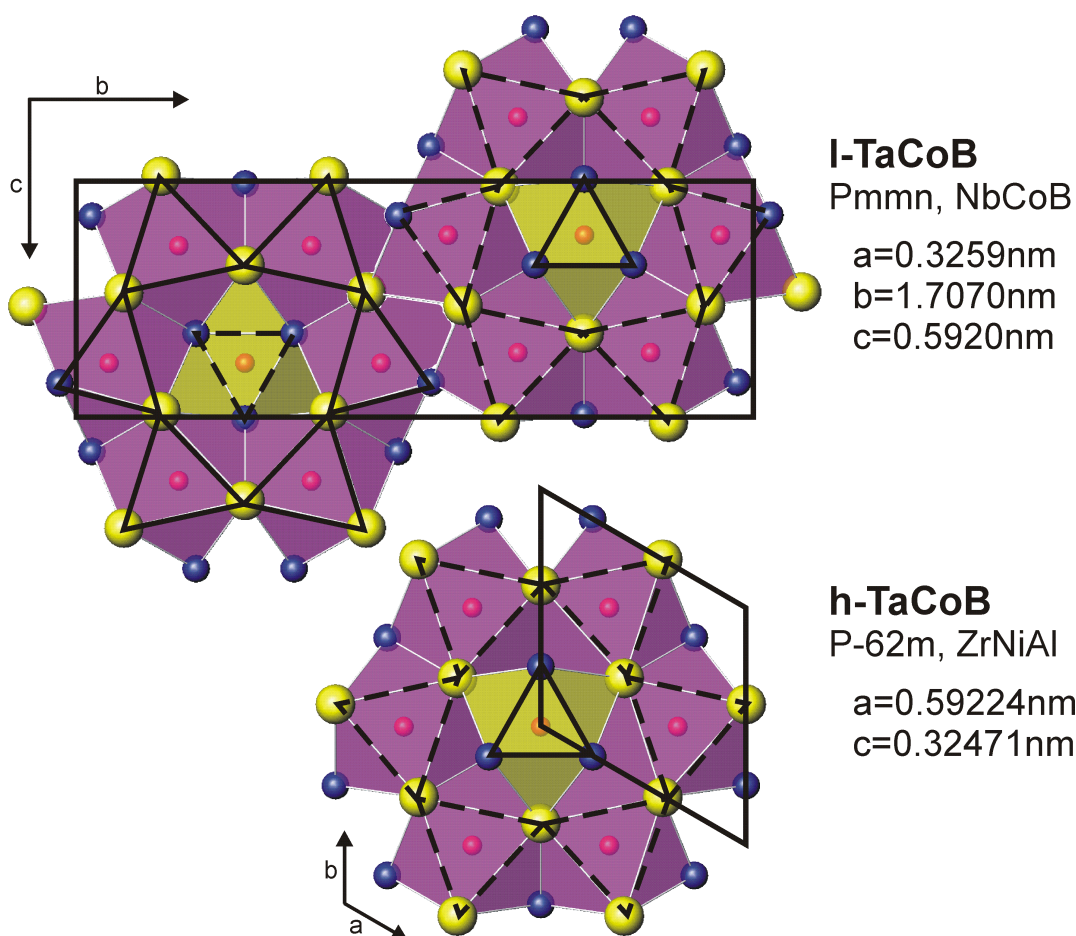


Fig. 5.4: Comparison of the crystal structures of h-TaCoB (ZrNiAl-type) and I-TaCoB (NbCoB-type).

Although the structures of high- and low-temperature form are closely related, the slow transformation process and a small but significant jump in the volume per atom indicates a major remodeling of the structures on transformation suggesting a first order transition in consistency with the fact that no direct crystallographic group-subgroup relation exists.

The lattice parameters of the high temperature modifications nicely fit to the almost linear lattice parameter dependence as a function of Fe/Co exchange in samples $\{\text{Nb,Ta}\}\text{Fe}_{1-x}\text{Co}_x\text{B}$ annealed at 1400°C for 100 hrs (see Fig. 5.6, Fig. 5.5, Tab. 5.4). The solid solution extends in both cases to a limit at $x=0.67$, above which the ZrNiAl-type phase is only present in as cast samples. It should be noted, that the present data for h- $\{\text{Nb,Ta}\}\text{CoB}$ are in fine agreement with those obtained by [1979Ste2] from X-ray films. The limit of the solid solution $\{\text{Nb,Ta}\}\text{Fe}_{1-x}\text{Co}_x\text{B}$ on alloys annealed at 1400°C was reported to be close to $x=0.9$ [1979Ste2]. Crystal symmetry and the Nb/(Fe,Co) metal ordering has been confirmed by X-ray structure analysis of a single crystal of $\text{NbCo}_{0.78}\text{Fe}_{0.22}\text{B}$ (see Appendix Tab. 2).

Tab. 5.4a: Lattice Parameters for NbFe_{1-x}Co_xB

x, Fe	a			c		
	[1979Ste2]	[1967Kuz]	This Work	[1979Ste2]	[1967Kuz]	This Work
1.00	0.5943		0.5953	0.3240		0.3248
0.85	0.5956			0.3237		
0.80	0.5960			0.3235		
0.75			0.5965			0.3238
0.70	0.5966			0.3235		
0.67			0.5968			0.3236
0.60			0.5971			0.3236
0.50			0.5976			0.3232
0.25			0.5989			0.3222
0.10	0.5995					
0.00	0.6001	0.6015	0.6008	0.3216	0.3222	0.3209

Tab. 5.4b: Lattice Parameters for TaFe_{1-x}Co_xB

x, Fe	a			c		
	[1979Ste2]	[1967Kuz]	This Work	[1979Ste2]	[1967Kuz]	This Work
1.00	0.5924		0.5922	0.3244		0.3247
0.90	0.5933			0.3239		
0.80	0.5938			0.3235		
0.75			0.5942			0.3231
0.70	0.5939			0.3232		
0.67			0.5946			0.3232
0.60	0.5943		0.5949	0.3230		0.3230
0.50	0.5947		0.5952	0.3223		0.3226
0.40	0.5950			0.3221		
0.30	0.5960			0.3210		
0.25			0.5970			0.3215
0.20	0.5962			0.3208		
0.10	0.5968			0.3204		
0.00	0.5977	0.5984	0.5986	0.3200	0.3195	0.3199

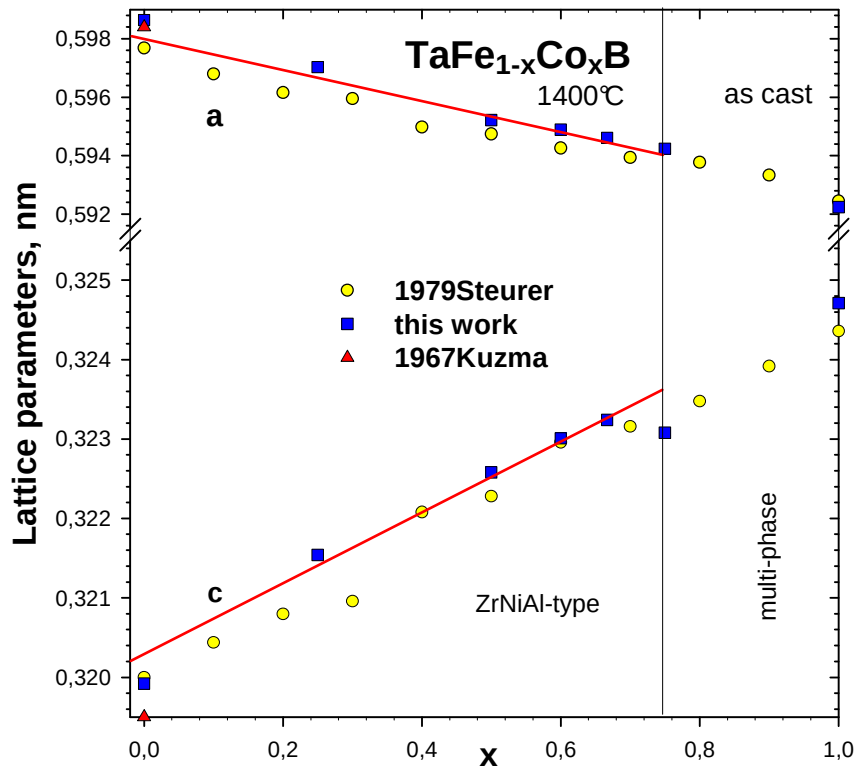
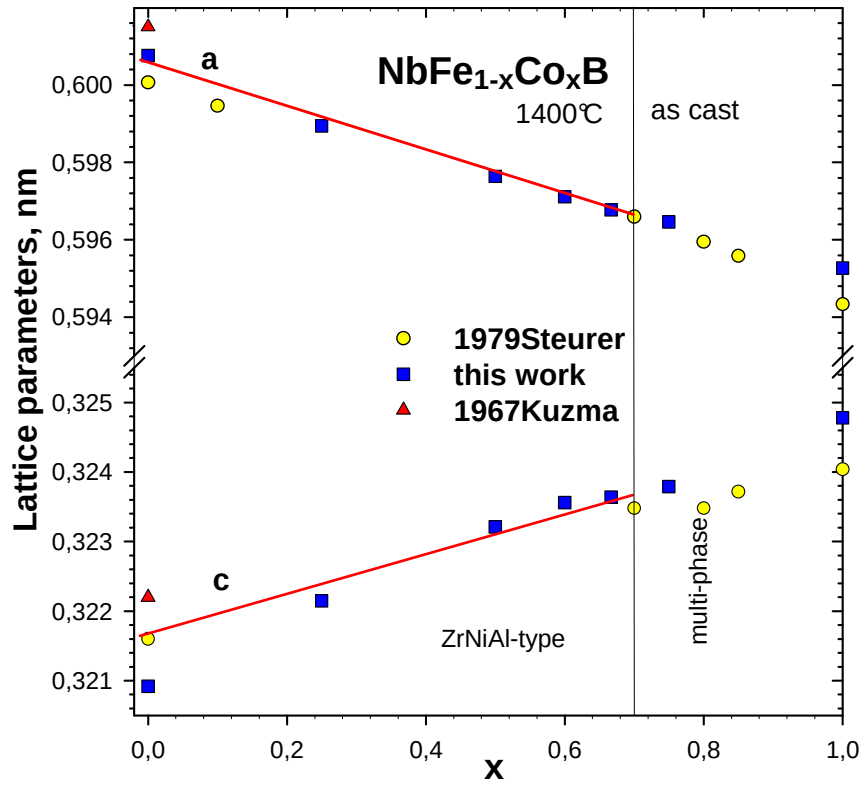


Fig. 5.5: Lattice-parameters versus iron content x in the alloy systems a) NbFe_{1-x}Co_xB b) TaFe_{1-x}Co_xB.

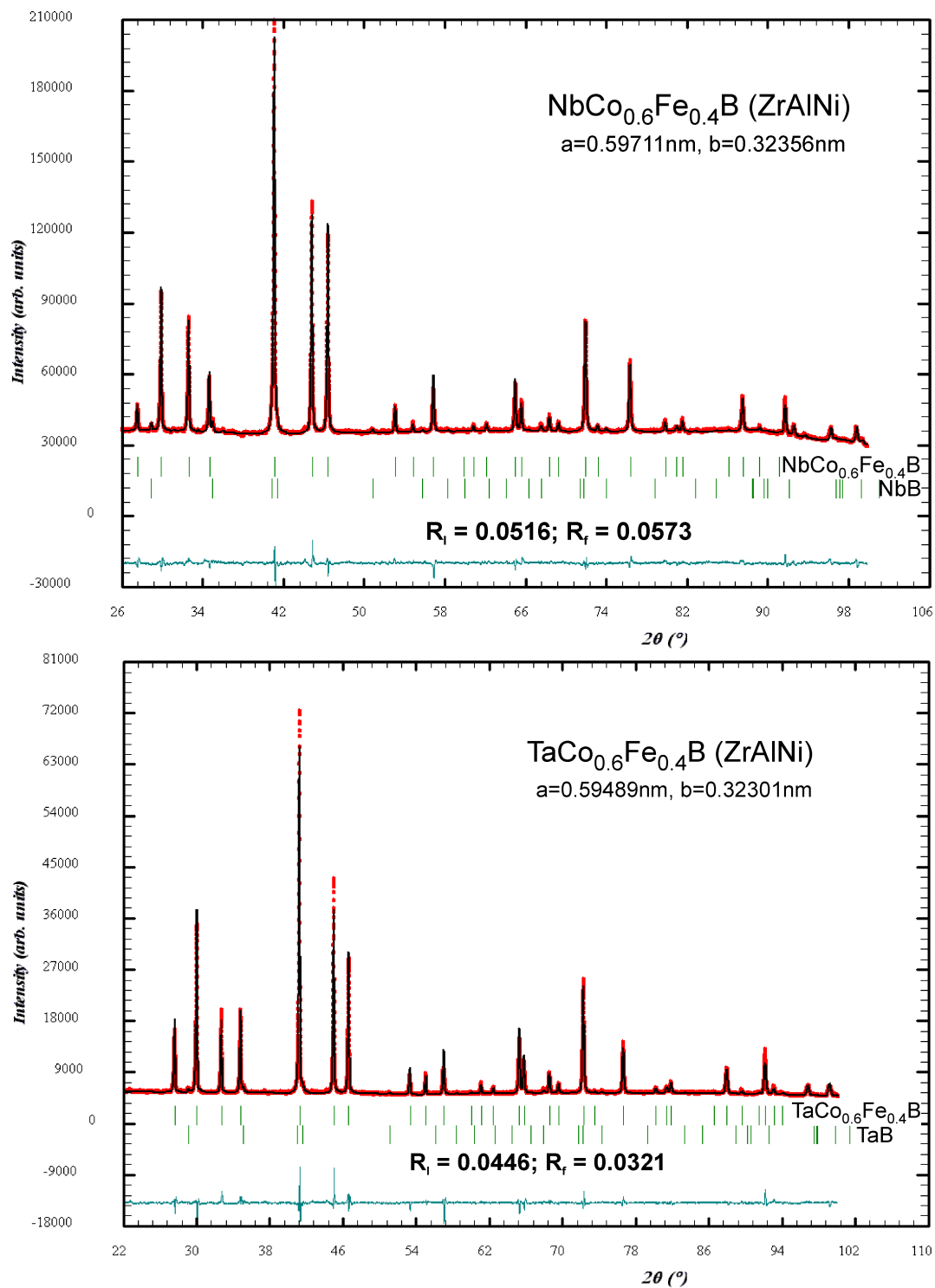


Fig. 5.6: Rietveld refinement of the alloys a) NbCo_{0.6}Fe_{0.4}B b) TaCo_{0.6}Fe_{0.4}B, both with ZrNiAl-type.

5.2.2 The Crystal Structure of NbCo₂B and TaCo₂B

Indexation of the single crystal X-ray diffraction data of NbCo₂B prompted several options for the unit cell at almost equal standard deviations: (i) a C-centered orthorhombic cell ($a = 0.63162(3)$ nm, $b = 1.72810(7)$ nm, $c = 0.64270(3)$ nm), and (ii) a triclinic cell with two angles practically equal to 90° ($a = 0.63144(2)$ nm, $b = 1.72771(6)$ nm, $c = 0.64263(2)$ nm; $\alpha = 90.0008(23)^\circ$, $\beta = 89.9984(20)^\circ$, $\gamma = 89.8607(23)^\circ$). The orthorhombic unit-cell, neglecting the deviation in angles from 90°, exhibits extinctions compatible with *Cmce* (#64) as the highest symmetric space group type. A solution of the structure employing direct methods yields seven independent atom positions for which interatomic distances agree with the sum of the respective atom radii. Refinement of the occupancy of Nb and Co positions gave no indication of a significant deviation from full positional occupation, thus in the refinement of the final structural model full occupation was assumed. The composition was confirmed by EPMA-measurements, giving a Co:Nb ratio of 2:1. Problems arose in inserting anisotropic temperature factors at the Co1 position in 16g. Thus an isotropic temperature factor was applied for this atom, finally refining the structure to $R_{F2}=0.0409$ with residual electron densities smaller than $\pm 4.8 \text{ e}^-/1000 \text{ nm}^3$ (see Appendix Tab. 3). However, a closer look on the X-ray powder pattern (Fe-K α_1) of the polycrystalline material shows splitting of peaks already occurring at 2θ values of 54° that cannot be described using the obtained orthorhombic structural model (see Fig. 5.7). The deviation in γ from 90°, although less than 0.14°, seems to be significant.

Subsequent examination of the corresponding primitive monoclinic unit-cell ($a = 0.9190(6)$ nm, $b = 0.64263(2)$ nm, $c = 0.63144(2)$ nm; $\beta = 109.954(6)^\circ$) led to a solution in space group $P2_1/c$ (#14), a subgroup of *Cmce*. Details on the cell transformations are given in Fig. 5.10 and Fig. 5.11. Eight independent atom positions were found, all, as in the orthorhombic setting, fully occupied. With isotropic temperature factors for boron atoms but anisotropic atom displacement parameters (ADP's) for the metal atoms refinement finally converged to $R_{F2}=0.0313$ and residual electron densities smaller than $2.8 \text{ e}^-/1000 \text{ nm}^3$. The monoclinic structure model was able to satisfactorily explain the splitting of the reflections and their relative intensity in the X-ray powder spectra and thus confirmed the structure solution (see Fig. 5.8).

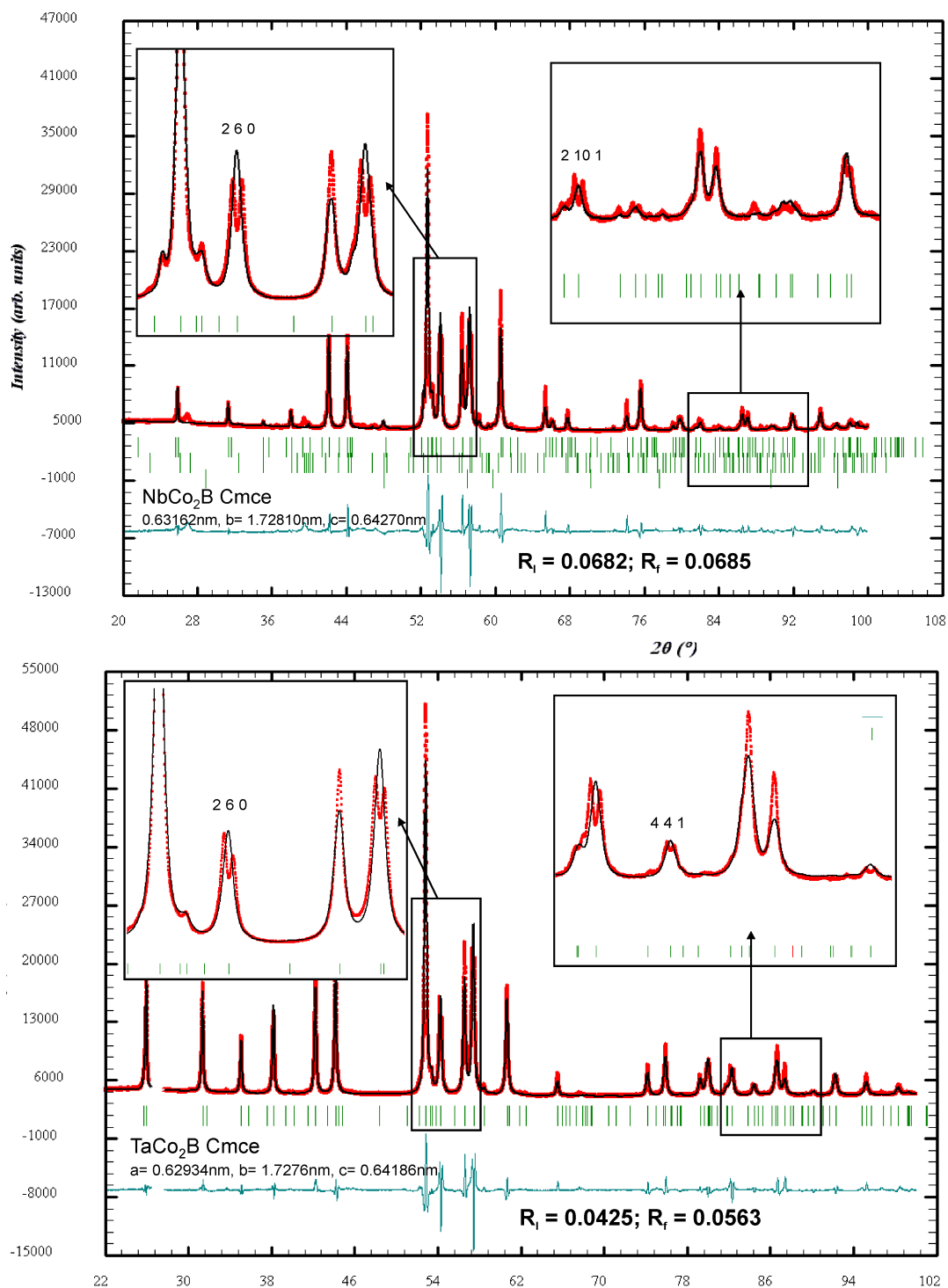


Fig. 5.7: Rietveld refinement for the specimens a)NbCo₂B and b)TaCo₂B, both in orthorhombic setting.

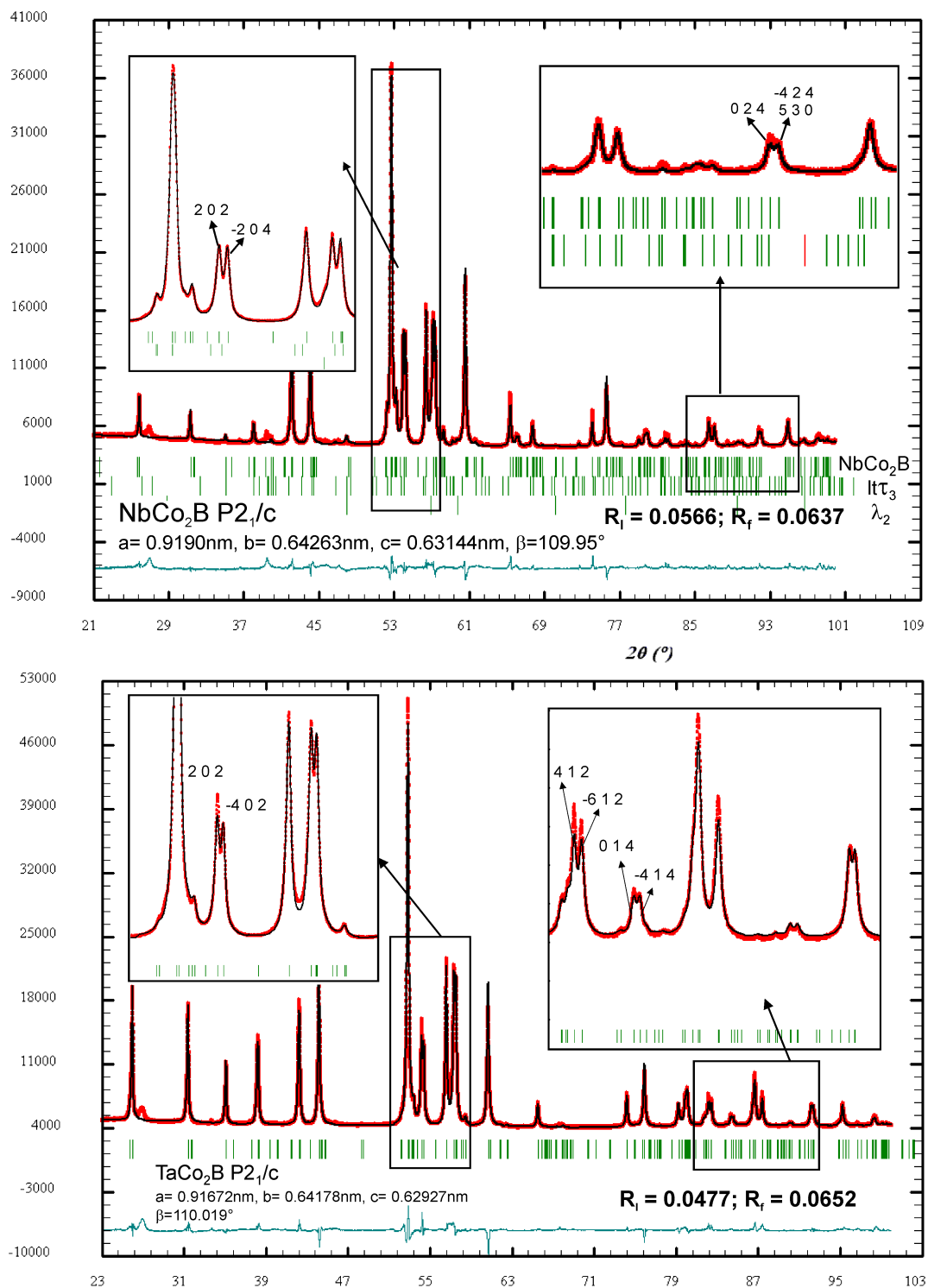


Fig. 5.8: Rietveld refinement for the specimens a)NbCo₂B and b)TaCo₂B, monoclinic setting.

A check on missing symmetry via the program PLATON interestingly suggested the above-mentioned orthorhombic solution in space group *Cmce* indicating only marginal deviations of the atom positions from the higher symmetry locations. In this context we

need to mention, that a solution for the triclinic unit cell in space group $P\bar{1}$ was attempted as well, but no significantly lower residual factor was obtained ($R_{F2}=0.0277$) and X-ray peak profiles do not justify the lower symmetry. Results of the final refinement for monoclinic $NbCo_2B$ are summarized in Appendix Tab. 4 revealing ADP's consistent with the atom mass and bonding in the structure. A search for the structure type (Pearson symbol: mP32) in Pearson's Crystal Data [2011Vil] prompted no results suggesting the $NbCo_2B$ -type to be a unique structure type. A three-dimensional representation of the crystal structure of $NbCo_2B$ is shown in Fig. 5.9.

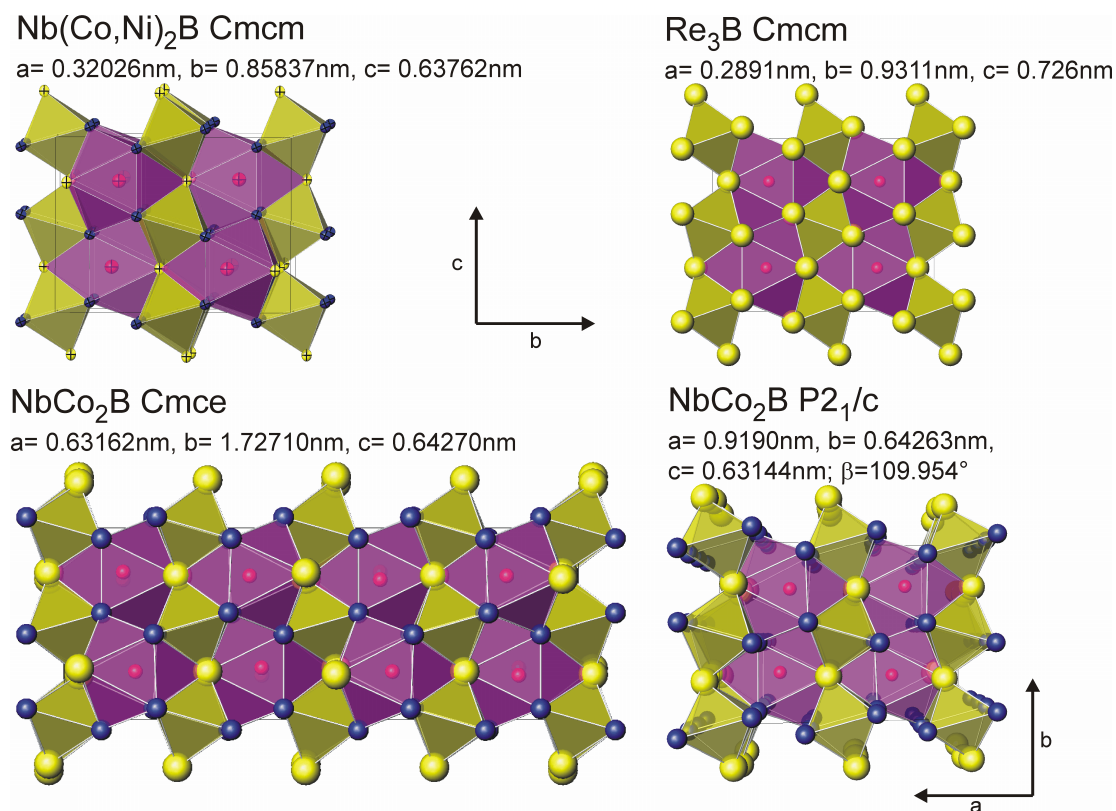


Fig. 5.9: The crystal structures of $\{Nb,Ta\}Co_2B$ (forced orthorhombic and monoclinic), $\{Nb,Ta\}(Co_{1-x}Ni_x)_2B$ and Re_3B in three-dimensional view. Small red atoms (B) are at the centres of tetrakaidekahedra, shown in violet (dark); octahedra (empty) are drawn with yellow colour (bright). Nb-atoms are in yellow, Co-atoms in blue.

Analyses of the interatomic distances, presented in Appendix Tab. 4b, reveal isolated boron atoms each coordinated by nine metal atoms in the form of a Nb_3Co_6 tetrakaidecahedron. Isolated boron atoms in tetrakaidecahedral metal coordination are consistent with the low boron to metal ratio ($B : M = 1 : 3$) as a typical feature of structure types at low boron contents [1991Rog]. The space between the Nb_3Co_6 tetrakaidecahedra is completely filled by octahedra Nb_2Co_4 . These octahedra are all empty as rather small distances from the center (Cn) of the octahedron to the metal ligands, $d_{Cn-Co} = 0.2155\text{ nm}$, and particularly $d_{Cn-Nb} = 0.1792\text{ nm}$, exclude the incorporation of any interstitial element

(B,C,N,O). The combination of tetrakaidecahedra and octahedra is found in a series of structure types adopted by borides such as the Re_3B -type (ordered version: MgCuAl_2 -type) and its shift-structure variant the Mo_2IrB_2 -type [1978Rog]. A comparison of the structural architecture of the Re_3B - with the NbCo_2B -type documents the close relationship particularly if we use the pseudo-orthorhombic setting for NbCo_2B : ($a_{\text{orth-NbCo}_2\text{B}} = 2a_{\text{Re}_3\text{B}}$, $b_{\text{orth-NbCo}_2\text{B}} = 2b_{\text{Re}_3\text{B}}$, $c_{\text{orth-NbCo}_2\text{B}} = c_{\text{Re}_3\text{B}}$). Thereby the ordered distribution of the Nb and Co atoms corresponds to the two Re positions in Re_3B (space group $Cmcm$, 8f and 4c sites, respectively). Thus the structural arrangement of the NbCo_2B -type can be conceived as a superstructure of the Re_3B -type or of its ternary ordered version the MgCuAl_2 -type. The superstructure, although not visible in the X-ray powder pattern but still obvious in SC data, only results from slight displacements of atomic positions. Details on the structural relation between the monoclinic and orthorhombic unit cell of NbCo_2B and the Re_3B cell are shown in Fig. 5.10 and Fig. 5.11 including also the transformation matrix for the orthorhombic to monoclinic cell conversion of NbCo_2B .

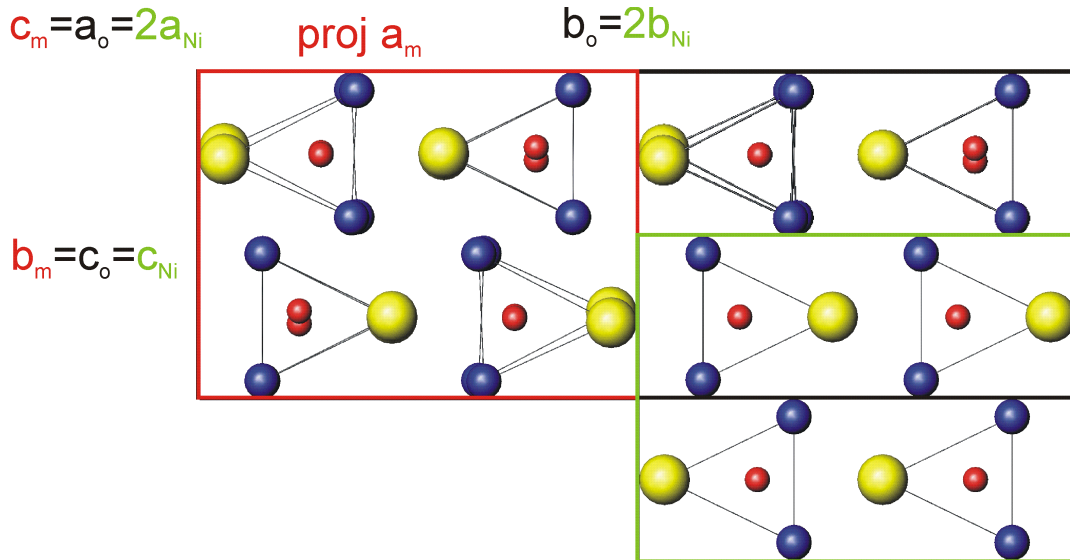


Fig. 5.10: Projection of the crystal structure of NbCo_2B along a_o or c_m . The deviation of atoms from the high symmetry positions in the Re_3B -type (unit cell outlined in green) is clearly visible.

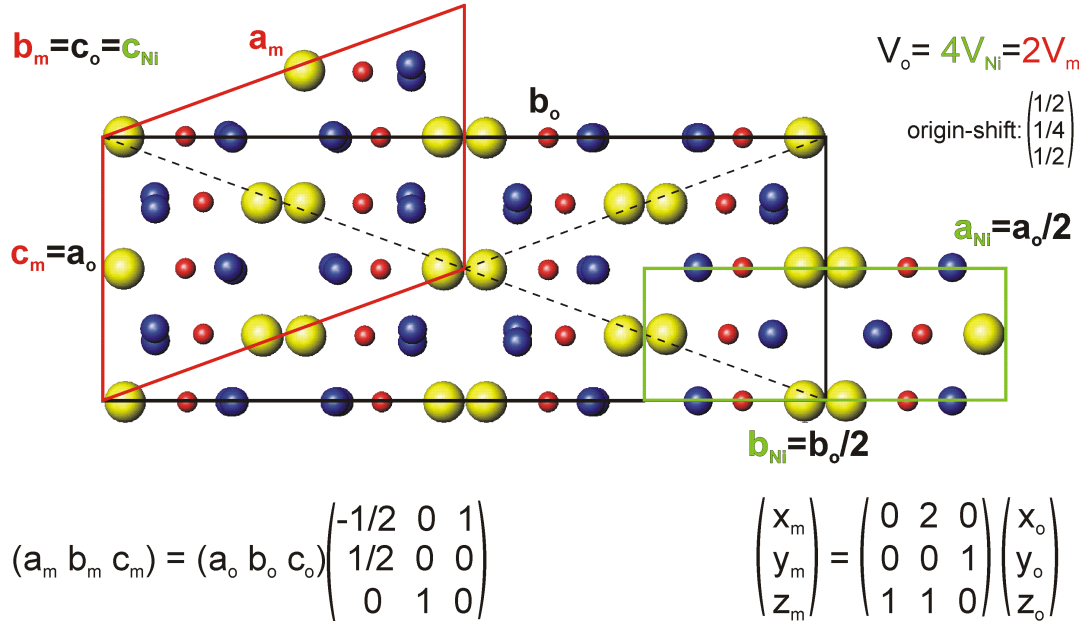


Fig. 5.11: Structural relations among the orthorhombic (unit cell outlined in black) and the monoclinic (unit cell outlined in red) setting of NbCo₂B as seen in projection along c_o (orthorhombic) or b_m (monoclinic). The unit cell of orthorhombic Re₃B-type is outlined in green (with origin shifted). The transformation matrices orthorhombic to monoclinic are given for the unit cell vectors as well as for the atom positions.

Single crystals of TaCo₂B showed practically identical behaviour with respect to the pseudo-orthorhombic lattice but monoclinic symmetry. Structure refinement with isotropic temperature factors for B atoms but anisotropic ADP's for the metal atoms finally converged to $R_{F2}=0.0420$ and residual electron densities smaller than $7.76e^-/1000 \text{ nm}^3$. X-ray powder diffraction intensities collected from a polycrystalline sample are in good agreement with the intensities calculated from the structural model taken from the single crystal. Monoclinic indexation of the powder spectrum confirms the isotypism with the structure type of NbCo₂B. Crystallographic data of the single crystal refinement of TaCo₂B are summarized in Appendix Tab. 3 and Appendix Tab. 4. Interatomic distances and coordination figures essentially correspond to the Nb-homologue, reflecting the close sizes of Nb and Ta atoms.

Although a general review on the crystal chemistry, bonding and properties of Re₃B-type intermetallics [2006Pöt] covered more than 100 representatives and about 60 ternary or quaternary compounds, where the octahedral voids are filled by carbon or nitrogen atoms [1982Rog, 1994Wit], it did not indicate any monoclinic distortion variants. Here it should be noted that a first structure determination for Pd₆P (Pd₃P_{1-x}, x~0.5) based on X-ray powder diffraction data indicated a monoclinic cell (a=0.2837 nm, b=0.9441 nm, c=0.7695 nm, β=90.20°, space group C2/c, R_B=0.058), which is close to orthorhombic symmetry and a structure model has been derived, essentially consistent with a P-defect Re₃B-type [1974And]. A detailed neutron diffraction study [1981And], however, prompted P/vacancy

ordering in a larger monoclinic cell ($a=0.56740$ nm, $b=0.94409$ nm, $c=0.82100$ nm, $\beta=110.414^\circ$, space group $P2_1/c$, $R_B=0.038$), which sustains the stoichiometry Pd_6P and adopts the same space group symmetry as TaCo_2B . Although the two structures, Pd_6P and TaCo_2B , indeed show similar structural features, which are outlined in Fig. 5.12, the relation between the crystallographic axes is not straightforward:

$$a_{\text{Pd}_6\text{P}} = 0.56740 \text{ nm} \rightarrow 0.62934 \text{ nm} = c_{\text{TaCo}_2\text{B}}$$

$$b_{\text{Pd}_6\text{P}} = 0.94409 \text{ nm} \rightarrow 0.86138 \text{ nm} = \text{proj } a_{\text{TaCo}_2\text{B}} = a_{\text{TaCo}_2\text{B}} \sin(180^\circ - \beta)$$

$$c_{\text{Pd}_6\text{P}} = 0.82100 \text{ nm} \rightarrow 0.68314 \text{ nm} = b_{\text{TaCo}_2\text{B}} / \sin(180^\circ - \beta); b_{\text{TaCo}_2\text{B}} = \text{proj } c_{\text{Pd}_6\text{P}}$$

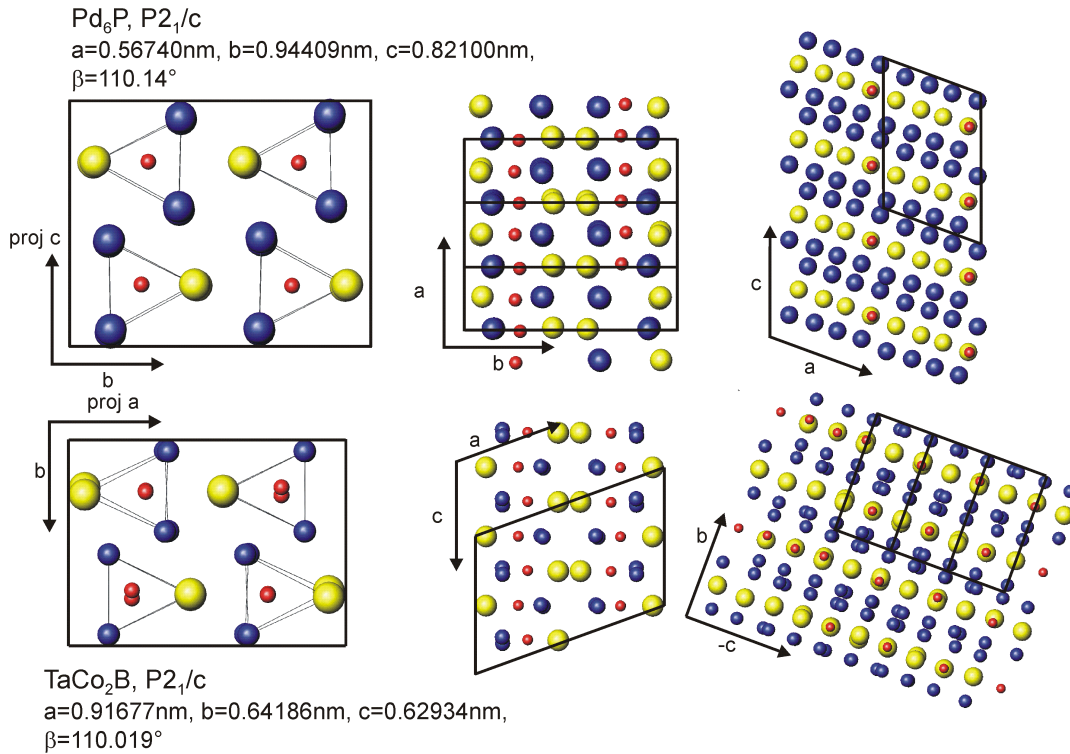


Fig. 5.12: Comparison of the crystal structures of Pd_6P (Pd_6P -type) and TaCo_2B (NbCo_2B -type). For better comparability, Pd atoms are colored blue and yellow, P atoms red.

5.2.3 The Crystal Structure of $\text{Ta}(\text{Co},\text{Ni})_2\text{B}$ and $\text{Nb}(\text{Co},\text{Ni})_2\text{B}$ and the Solid Solutions $\{\text{Nb},\text{Ta}\}(\text{Co}_{1-x}\text{Ni}_x)_2\text{B}$

With respect to earlier information [1967Sob] on a so-called Z-phase " $\text{Nb}_5\text{Ni}_{11}\text{B}_4 \approx \text{NbNi}_2\text{B}$ " we studied the solution behaviour of Ni in $\text{Nb}(\text{Ta})\text{Co}_2\text{B}$. Steurer [1979Ste2] mentioned that already small substitutions of Co by Ni lead to the stabilization of an orthorhombic structure, which yields X-ray intensities corresponding to a derivative structure of the NbCo_2B type. Inspection of two single crystals selected from samples with initial composition $\{\text{Nb},\text{Ta}\}_{22}\text{Co}_{38}\text{Ni}_{15}\text{B}_{25}$ in both cases indeed revealed an orthorhombic unit cell ($a=0.32026(2)$ nm, $b=0.85837(4)$ nm, $c=0.63762(3)$ nm) with deviations in angles from 90°

in a corresponding triclinic cell choice being less than 0.003°. The crystals showed orthorhombic Laue symmetry *mmm* with systematic extinctions compatible with space group *Cmcm* (# 63). Direct methods led to three independent atomic positions, T1 (T = Nb or Ta) in 4c, B1 in 4c and a mixed position of Co+Ni in 8f. The Co/Ni ratio was taken from EPMA-data, in good agreement with the initial sample composition, and fixed in the refinement. Refinement with anisotropic temperature factors converged to $R_{F2}=0.0184$ with residual electron densities smaller than $\pm 2.2 \text{ e}^-/1000 \text{ nm}^3$. Details of the final refinement are summarized in Appendix Tab. 5. A three-dimensional representation of the structures is shown in Fig. 5.9.

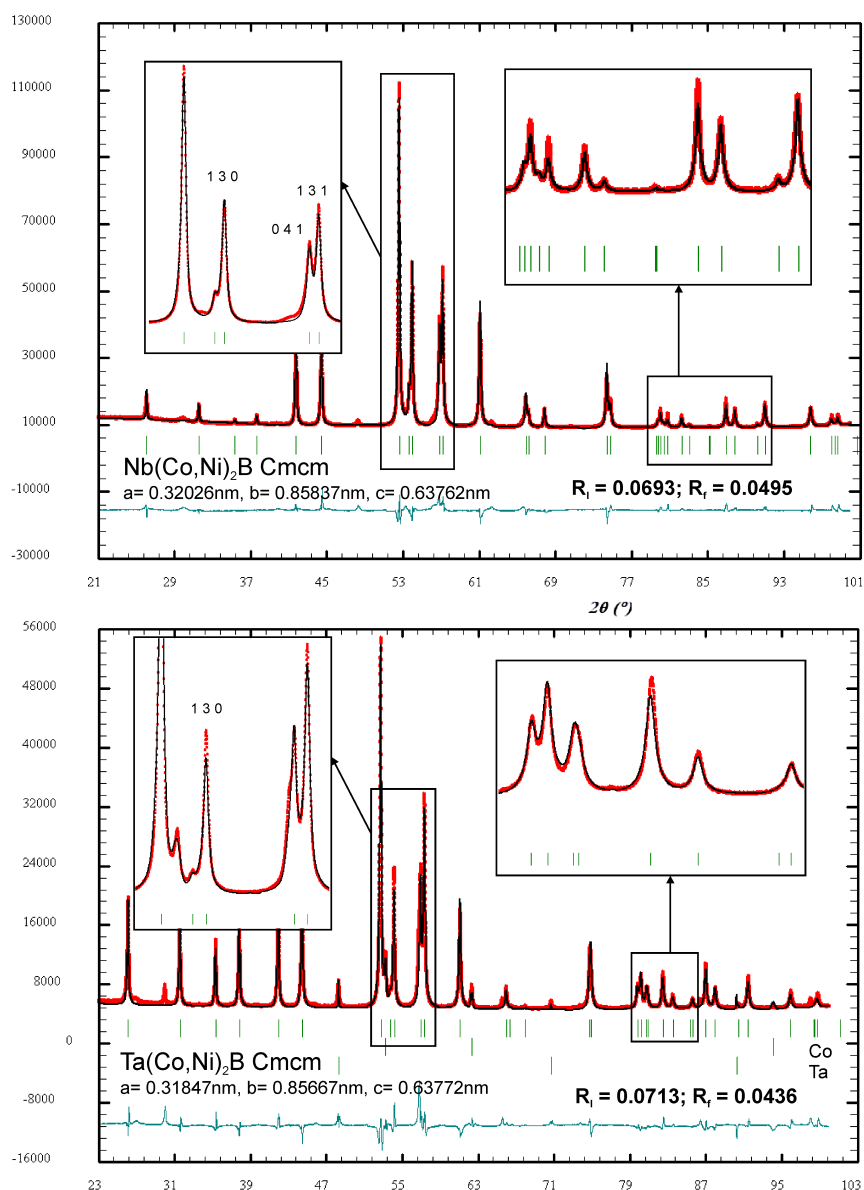


Fig. 5.13: Rietveld refinement for the specimens a) Nb(Co,Ni)₂B and b) Ta(Co,Ni)₂B, both crystallizing with orthorhombic Re₃B-type.

The structural solution was confirmed by Rietveld analyses of the X-ray powder pattern (see Fig. 5.13), which do not exhibit any splitting of the reflections characteristic for the monoclinic distortion in NbCo₂B-type. Space group, lattice parameter as well as atomic position and Wyckoff sequence confirm the structure type of Re₃B. However, due to the difference in atomic radii between Ta and Co, the coordination sphere of the B-atoms changes slightly. The B atoms in the Re₃B structure are surrounded by trigonal prisms of two Re2 (in 4c, $d_{B-Re} = 0.2287$ nm) and four Re1 atoms (in 8f, $d_{B-Re} = 0.2338$ nm); completing the tetrakaidekahedra with two atoms of Re1 (in 8f, $d_{B-Re} = 0.2532$ nm) and one Re2 (in 4c, $d_{B-Re} = 0.2960$ nm). In the {Nb,Ta}(Co_{1-x}Ni_x)₂B structure, the two T atoms (in 4c) move further away resulting in six 8f-(Co,Ni) atoms in the innermost coordination sphere ($4d_{B-Co}=0.2145$ nm, $2d_{B-Co}=0.2225$ nm, $2d_{B-Nb}=0.2426$ nm, $1d_{B-Nb}=0.2469$ nm). A comparison of the respective B coordination for $\tau 4$ -{Nb,Ta}Co₂B (P2₁/c), {Nb,Ta}(Co_{1-x}Ni_x)₂B and Re₃B is given in .

in form of distance histograms.

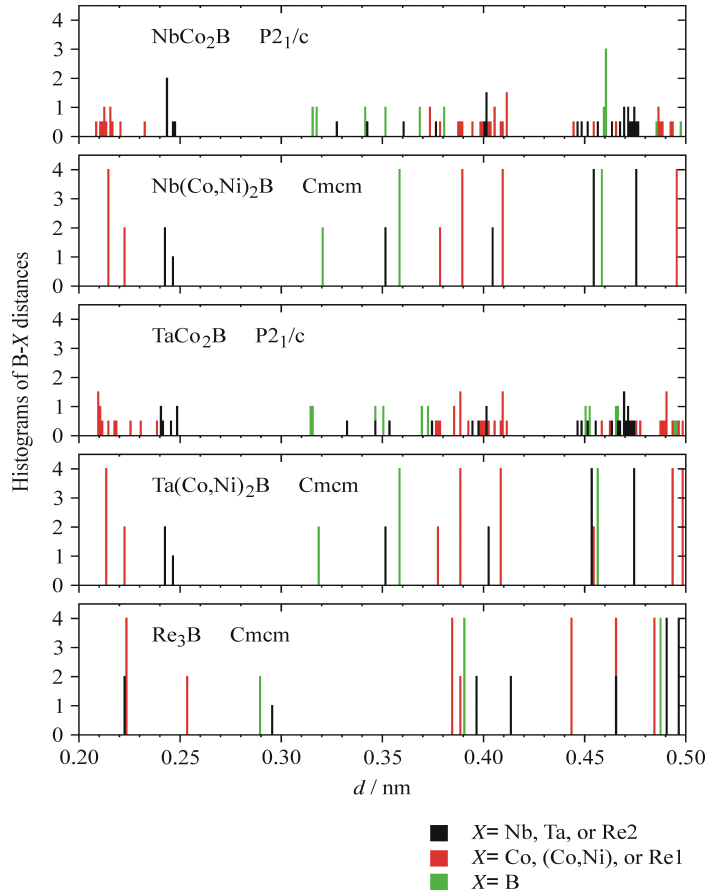


Fig. 5.14: Histograms of the distances between a B atom and the other atoms in {Nb,Ta}Co₂B (P2₁/c, NbCo₂B-type), {Nb,Ta}(Co,Ni)₂B (Cmcm, Re₃B-type), and, for comparison, Re₃B [2011Vil]. In the case of the P2₁/c structures, the histograms are averaged over the crystallographic positions B1 and B2.

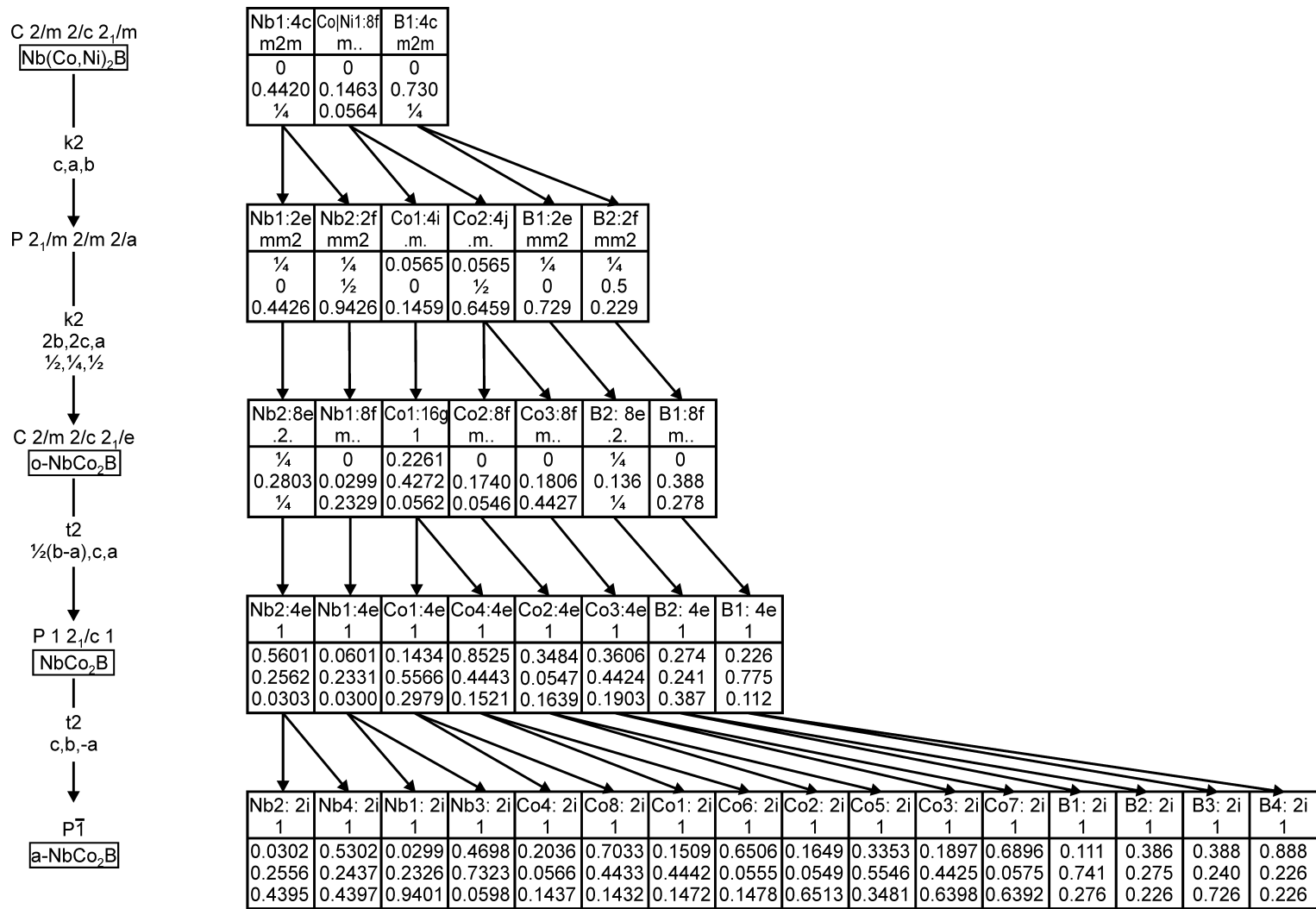


Fig. 5.15: Bärnighausen group-subgroup scheme, relating the orthorhombic Re_3B -type with triclinic NbCo_2B .

The group-subgroup scheme comprising the orthorhombic $\{\text{Nb,Ta}\}(\text{Co}_{1-x}\text{Ni}_x)_2\text{B}$ structure as well as the many solutions for $\{\text{Nb,Ta}\}\text{Co}_2\text{B}$ is shown in form of a Bärnighausen tree in Fig. 5.15.

Lattice parameters as a function of the Co/Ni exchange in the solid solution $\{\text{Nb,Ta}\}(\text{Co}_{1-x}\text{Ni}_x)_2\text{B}$ annealed at 1400°C for 100 hrs are shown in Fig. 5.16 revealing an almost linear dependence. Ni contents in the range of $x = 0$ to $x = 0.15$ still show the monoclinic NbCo_2B structure type, however, beyond that point the powder pattern could be fully indexed on the Re_3B - type until the end of the solubility at $x = 0.62$ (see Fig. 5.17).

Tab. 5.5a: Lattice parameters for $\text{Nb}(\text{Co}_{1-x}\text{Ni}_x)_2\text{B}$

at%Ni	a		b		c	
	[1979Ste2]	This work	[1979Ste2]	This work	[1979Ste2]	This work
0.00	0.3160		0.8625		0.6420	
0.02		0.3159		0.8629		0.6417
0.04		0.3161		0.8626		0.6413
0.07		0.3166		0.8623		0.6409
0.10	0.3175	0.3169	0.8613	0.8615	0.6410	0.6400
0.15		0.3182		0.8611		0.6396
0.20	0.3188		0.8590		0.6376	
0.25		0.3193		0.8590		0.6380
0.28		0.3201		0.8578		0.6373
0.30	0.3193		0.8587		0.6390	
0.38		0.3208		0.8562		0.6364
0.40	0.3208		0.8580		0.6375	
0.50	0.3219	0.3217	0.8553	0.8552	0.6367	0.6364
0.60	0.3225		0.8540		0.6355	
0.625		0.3236		0.8520		0.6352
0.70	0.3226		0.8533		0.6351	
0.75		0.3233		0.8525		0.6343

Tab. 5.5b: Lattice parameters for $\text{Ta}(\text{Co}_{1-x}\text{Ni}_x)_2\text{B}$

at%Ni	a		b		c	
	[1979Ste2]	This work	[1979Ste2]	This work	[1979Ste2]	This work
0.00	0.3150	0.3144	0.8608	0.8611	0.6410	0.6413
0.02		0.3148		0.8607		0.6410
0.04		0.3149		0.8600		0.6406
0.07		0.3153		0.8600		0.6400
0.10	0.3160	0.3158	0.8588	0.8595	0.6380	0.6397
0.15		0.3166		0.8588		0.6391
0.20	0.3162		0.8575		0.6376	
0.25		0.3175		0.8574		0.6381
0.28		0.3183		0.8562		0.6374
0.30	0.3178		0.8560		0.6373	
0.38		0.3189		0.8542		0.6365
0.40	0.3185		0.8544		0.6350	
0.50	0.3193	0.3202	0.8528	0.8529	0.6350	0.6360
0.60	0.3200		0.8521		0.6350	
0.625		0.3222		0.8498		0.6345
0.70	0.3205		0.8505		0.6351	
0.75		0.3227		0.8495		0.6347

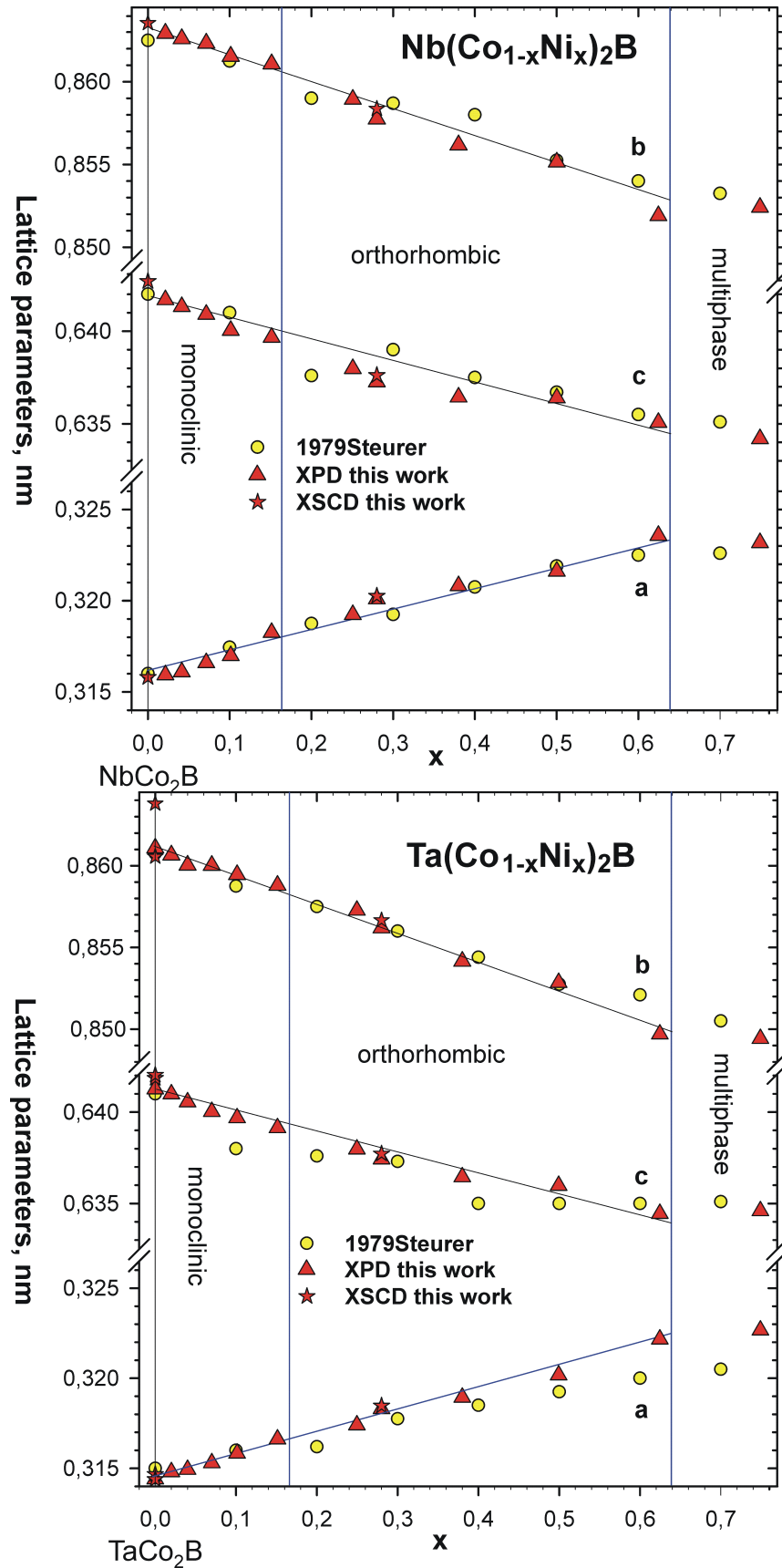


Fig. 5.16: Lattice-parameters versus nickel content x in the alloy systems a) $\text{Nb}(\text{Co}_{1-x}\text{Ni}_x)_2\text{B}$ and b) $\text{Ta}(\text{Co}_{1-x}\text{Ni}_x)_2\text{B}$.

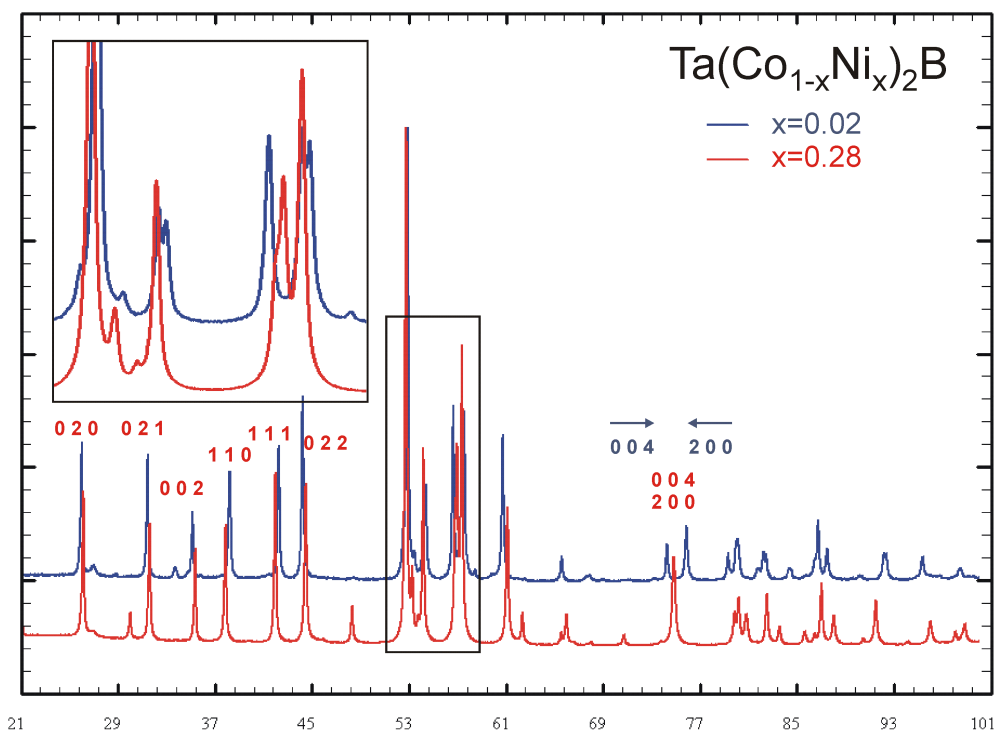


Fig. 5.17: Comparison of X-ray powder patterns $\text{Ta}(\text{Co}_{1-x}\text{Ni}_x)_2\text{B}$ for $x=0.02$ (NbCo₂B-type) and $x=0.28$ (Re₃B-type).

The continuous change of the lattice parameters with Ni-content may indicate a second order transition from the monoclinic to the orthorhombic structure type. Although Steurer [1979Ste2] claimed the stabilization of the orthorhombic structure at much lower Ni contents ($x=0.05$) for alloys annealed at 1400°C, lattice parameters from his X-ray films are in good agreement with the present data.

A check on the solid solutions $\{\text{Nb,Ta}\}(\text{Co}_{1-x}\text{Fe}_x)_2\text{B}$ in samples with $x=0.25$ for Ta resulted in the formation of $\text{Ta}(\text{Co}_{1-x}\text{Fe}_x)_2\text{B}$ ($x = 0.18$, $P2_1/c$, NbCo₂B-type) and $\text{TaFe}_x\text{Co}_{1-x}\text{B}$ ($x = 0.32$, ZrAlNi-type). Contrary to the substitution by Ni, no stabilization of the orthorhombic structure was observed. Samples containing Nb, besides some amounts of (Co,Fe), only showed $\text{NbFe}_x\text{Co}_{1-x}\text{B}$ ($x = 0.225$, ZrAlNi-type). Lattice parameter and compositions for $\{\text{Nb,Ta}\}\text{Fe}_x\text{Co}_{1-x}\text{B}$ nicely fit to the lattice parameter dependence evaluated above.

5.2.4 First-principles Calculations on Crystal Structure and Stability of Nb(Ta)Co₂B

By Gunther Schoellhammer

The structures of TaCo₂B and NbCo₂B were optimized by means of first-principles structure relaxations. To this end, four independent calculations for the relevant space groups were performed for each of the two systems, starting from the experimental structures:

- (1) *Cmcm* with a 16-atom unit cell $Nb_4Co_8B_4$ or $Ta_4Co_8B_4$ (number of formula units per unit cell $Z = 4$). The Co atoms occupy Wyckoff position 8f, i.e. the position with mixed occupation by Co and Ni in $\{Nb, Ta\}(Co_{1-x}Ni_x)_2B$.
- (2) *Cmce* with a 64-atom unit cell $Nb_{16}Co_{32}B_{16}$ or $Ta_{16}Co_{32}B_{16}$ ($Z = 16$).
- (3) $P2_1/c$ with a 32-atom unit cell $Nb_{16}Co_{32}B_{16}$ or $Ta_8Co_{16}B_8$ ($Z = 8$).
- (4) $P\bar{1}$ with a 32-atom unit cell $Nb_{16}Co_{32}B_{16}$ or $Ta_8Co_{16}B_8$ ($Z = 8$).

Each of the first three space groups within this sequence is a supergroup of its successor (see Bärnighausen tree in Fig. 5.15). The respective adopted space-group symmetry was conserved during the relaxation procedure. The crystallographic parameters of the optimized structures with space groups *Cmcm*, *Cmce*, and $P2_1/c$ are compared to the experimental data in Tab. 5.6. For each of the starting structures and the optimized structures, the total energy was calculated. The relative total energies are given in the scheme shown in Fig. 5.18.

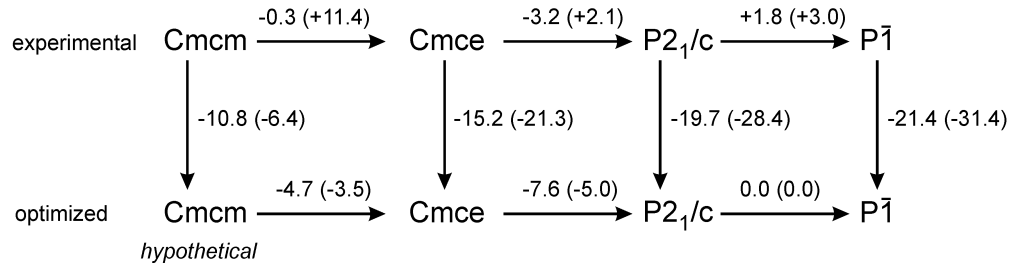


Fig. 5.18: Relative energies given in meV/formula unit for the crystal structures of $NbCo_2B$ ($TaCo_2B$) in various crystal symmetries.

The opening of additional relaxational degrees of freedom upon symmetry reduction from *Cmcm* to *Cmce* and from *Cmce* to $P2_1/c$ induces a lowering, albeit a rather weak lowering, of the total energy. The optimized triclinic structures, on the other hand, turned out to be close approximants of the optimized monoclinic structures; the differences of the lattice parameters and the shortest interatomic distances are of the order of magnitude of 0.1 pm, and the total energies differ only insignificantly. From the total energy calculations for the experimental structures, i.e. the starting structures of the optimization procedure, a reversed energetic sequence was obtained in the case of $TaCo_2B$, the orthorhombic structures and the monoclinic structure are slightly stabilized with respect to the triclinic structure; among the experimental structures of $NbCo_2B$, only the monoclinic structure appeared to be slightly stabilized compared to the triclinic structure. Thereby, one has to keep in mind that the X-ray diffraction measurements were carried out at room temperature, whereas in the course of the performed DFT calculations temperature effects were neglected; furthermore in the DFT calculations the Ni-substitution in the *Cmcm* structures were not taken into account. However, rather than drawing conclusions from the energetic sequence, it is inferred from the small energetic differences that none

of the involved structure types can be classified as a distinctly preferred structure type neither for NbCo₂B nor for TaCo₂B.

The electronic densities of states (DOS) calculated for the experimental structures of NbCo₂B and TaCo₂B with P2₁/c symmetry are shown in Fig. 5.19. Very similar DOS have been obtained for the structures with supergroup symmetry as well as for the corresponding optimized structures. This again reflects the similarities between the involved structures.

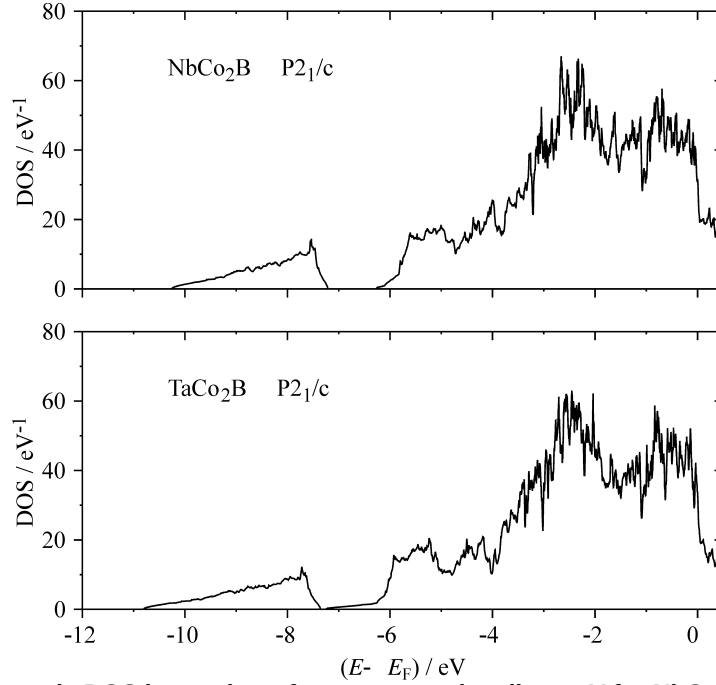


Fig. 5.19: Electronic DOS in number of states per unit cell per eV for NbCo₂B and TaCo₂B with P2₁/c symmetry.

Tab. 5.6: Comparison of DFT calculated and optimized structures of NbCo₂B and TaCo₂B

		NbCo₂B						TaCo₂B					
		<i>Experimental structure</i>			<i>Optimized structure</i>			<i>Experimental structure</i>			<i>Optimized structure</i>		
		P2 ₁ /c	Cmce	Cmcm	P2 ₁ /c	Cmce	Cmcm	P2 ₁ /c	Cmce	Cmcm	P2 ₁ /c	Cmce	Cmcm
<i>a/nm</i>		0.9190	0.9200	0.9162	0.9172	0.9175	0.9161	0.9167	0.9171	0.9140	0.9162	0.9166	0.9156
<i>b/nm</i>		0.6426	0.6427	0.6376	0.6378	0.6328	0.6301	0.6418	0.6419	0.6377	0.6363	0.6330	0.6314
<i>c/nm</i>		0.6314	0.6316	0.6405	0.6276	0.6349	0.6396	0.6293	0.6293	0.6369	0.6294	0.6344	0.6373
<i>β/°</i>		109.95	110.08	110.46	109.62	110.24	110.43	110.01	110.07	110.39	109.80	110.25	110.36
<i>V/nm³</i>		0.3505	0.3508	0.3506	0.3458	0.3459	0.3460	0.3479	0.3480	0.3480	0.3452	0.3453	0.3454
<i>M1</i> 4e	x	0.0601	0.0598	0.0580	0.0637	0.0606	0.0592	0.0588	0.0588	0.0574	0.0610	0.0591	0.0580
	y	0.2331	0.2329	0.2500	0.2343	0.2373	0.2500	0.2336	0.2333	0.2500	0.2364	0.2386	0.2500
	z	0.0300	0.0299	0.0290	0.0321	0.0303	0.0296	0.0297	0.0294	0.0287	0.0307	0.0296	0.0290
<i>M2</i> 4e	x	0.5601	0.5605	0.5580	0.5637	0.5604	0.5592	0.5590	0.5589	0.5574	0.5610	0.5590	0.5580
	y	0.2562	0.2500	0.2500	0.2657	0.2500	0.2500	0.2532	0.2500	0.2500	0.2636	0.2500	0.2500
	z	0.0303	0.0303	0.0290	0.0321	0.0302	0.0296	0.0292	0.0295	0.0287	0.0307	0.0295	0.0290
<i>Co1</i> 4e	x	0.1434	0.1458	0.1463	0.1383	0.1462	0.1459	0.1447	0.1454	0.1459	0.1395	0.1460	0.1458
	y	0.5565	0.5562	0.5563	0.5584	0.5548	0.5551	0.5560	0.5556	0.5565	0.5571	0.5552	0.5555
	z	0.2979	0.2990	0.3232	0.2948	0.3031	0.3230	0.2994	0.2995	0.3229	0.2993	0.3055	0.3229
<i>Co2</i> 4e	x	0.3484	0.3480	0.3537	0.3490	0.3495	0.3541	0.3490	0.3486	0.3541	0.3495	0.3501	0.3542
	y	0.0547	0.0546	0.0563	0.0541	0.0553	0.0551	0.0546	0.0550	0.0565	0.0546	0.0555	0.0555
	z	0.1639	0.1740	0.1768	0.1500	0.1747	0.1770	0.1689	0.1743	0.1771	0.1539	0.1751	0.1771
<i>Co3</i> 4e	x	0.3606	0.3613	0.3537	0.3617	0.3611	0.3541	0.3608	0.3605	0.3541	0.3605	0.3598	0.3542
	y	0.4424	0.4427	0.4437	0.4416	0.4434	0.4449	0.4428	0.4423	0.4435	0.4429	0.4436	0.4445
	z	0.1903	0.1806	0.1768	0.2053	0.1805	0.1770	0.1857	0.1803	0.1771	0.2007	0.1799	0.1771
<i>Co4</i> 4e	x	0.8525	0.8542	0.8537	0.8490	0.8538	0.8541	0.8536	0.8546	0.8541	0.8495	0.8540	0.8542
	y	0.4443	0.4438	0.4437	0.4459	0.4452	0.4449	0.4446	0.4444	0.4435	0.4454	0.4448	0.4445
	z	0.1521	0.1532	0.1768	0.1500	0.1568	0.1770	0.1537	0.1541	0.1771	0.1539	0.1595	0.1771
<i>B1</i> 4e	x	0.2258	0.2232	0.2296	0.2192	0.2236	0.2273	0.2298	0.2305	0.2298	0.2236	0.2262	0.2286
	y	0.7745	0.7782	0.7500	0.7778	0.7717	0.7500	0.7695	0.7697	0.7500	0.7715	0.7677	0.7500
	z	0.1125	0.1116	0.1148	0.1074	0.1118	0.1136	0.1135	0.1152	0.1149	0.1104	0.1131	0.1143
<i>B2</i> 4e	x	0.2743	0.2720	0.2704	0.2808	0.2740	0.2727	0.2792	0.2777	0.2702	0.2764	0.2722	0.2714
	y	0.2407	0.2500	0.2500	0.2222	0.2500	0.2500	0.2469	0.2500	0.2500	0.2285	0.2500	0.2500
	z	0.3875	0.3860	0.3852	0.3926	0.3870	0.3864	0.3869	0.3889	0.3851	0.3895	0.3861	0.3857

5.2.5 The Crystal Structure of $\text{Ta}_3\text{Co}_4\text{B}_7$

The X-ray powder spectrum of a sample with initial composition TaCo_2B_3 (heat treatment 1100-1400-1100°C) represented a new pattern that could be fully indexed on a C-centred orthorhombic unit cell. Rietveld analysis confirmed isotypism with the structure of $\text{Nb}_3\text{Co}_4\text{B}_7$ as supposed by Kuzma and Chaban [1990Kuz], thus the compounds “ TaCo_2B_3 ” and “ $\text{Ta}_2\text{Co}_3\text{B}_5$ ” as listed earlier [1990Kuz] are both represented by the proper formula $\text{Ta}_3\text{Co}_4\text{B}_7$. Results of the refinement are shown in Tab. 5.7 and Fig. 5.21. A three-dimensional representation of the structure is presented in Fig. 5.20. A detailed description of the $\text{Nb}_3\text{Co}_4\text{B}_7$ type structure was already given by Kuzma and Akselrud [1986Kuz]: $\text{Ta}_3\text{Co}_4\text{B}_7$ combines isolated B-B pairs ($d_{\text{B3-B3}} = 0.175\text{nm}$) besides the typical 5-membered boron rings ($d_{\text{B2-B2}} = 0.195\text{nm}$, $d_{\text{B2-B4}} = 0.163\text{nm}$, $d_{\text{B1-B4}} = 0.173\text{nm}$) linked via a B-B single bond ($d_{\text{B4-B4}} = 0.179\text{nm}$) to form bands parallel to the c-axis.

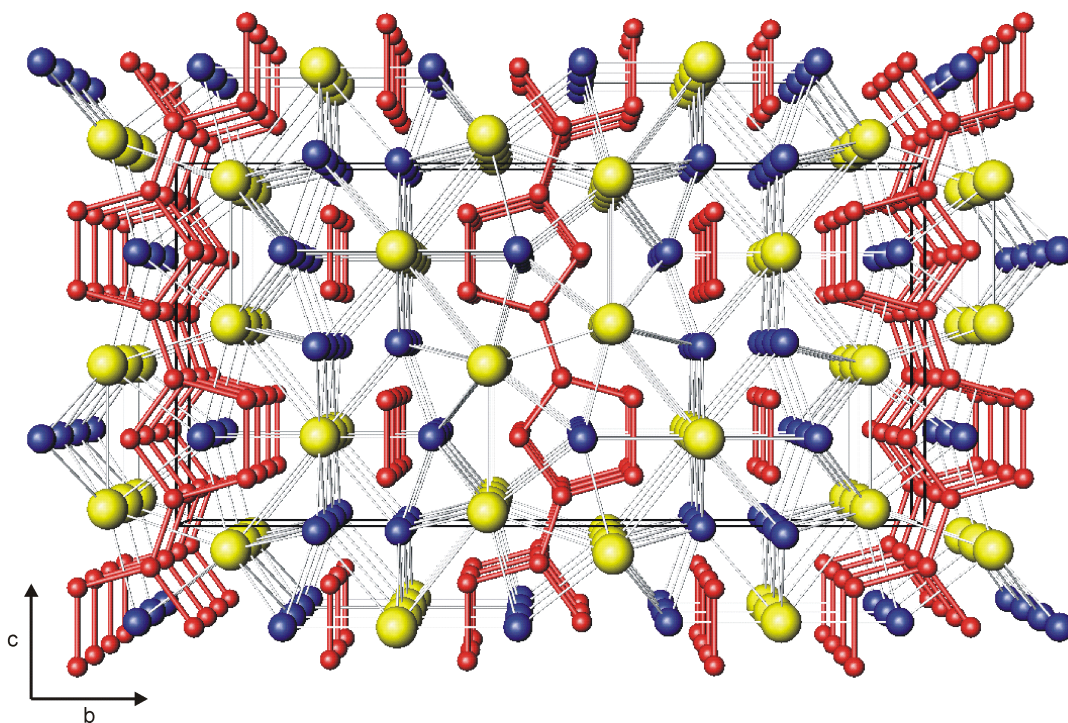


Fig. 5.20: The crystal structure of $\text{Ta}_3\text{Co}_4\text{B}_7$ projected along $[1\ 0\ 0]$.

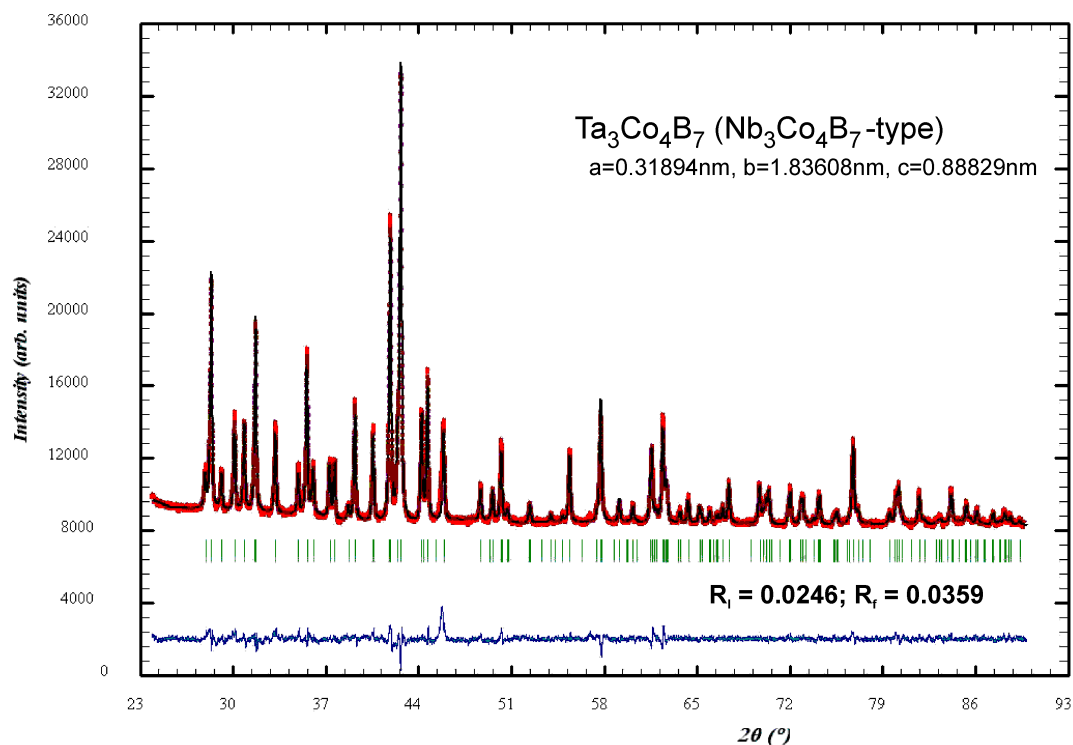


Fig. 5.21: Rietveld refinement for $\text{Ta}_3\text{Co}_4\text{B}_7$ ($\text{Nb}_3\text{Co}_4\text{B}_7$ -type).

Tab. 5.7: Results of the Rietveld refinement of $\text{Ta}_3\text{Co}_4\text{B}_7$; (B_{iso} values for B (0.7) and Co (0.5) fixed in refinement.

Compound	$\text{Ta}_3\text{Co}_4\text{B}_7$
Heat treatment	1100°C
Structure type	$\text{Nb}_3\text{Co}_4\text{B}_7$
Space group	Cmcm
Radiation	XRD, $\text{CuK}\alpha$
2θ range (degrees)	$8 \leq 2\theta \leq 100$
a (nm), Guinier	0.31895(2)
b (nm), Guinier	1.83333(3)
c (nm), Guinier	0.88809(5)
V (nm ³)	0.5193(1)
Reflections in refinement	187
Number of variables	53
$R_F = \sum F_o - F_c / \sum F_o$	0.0246
$R_I = \sum I_o - I_c / \sum I_o$	0.0359
$R_{\text{WP}} = [\sum w_i y_{oi} - y_{ci} ^2 / \sum w_i y_{oi} ^2]^{1/2}$	0.0987
$R_p = \sum y_{oi} - y_{ci} / \sum y_{oi} $	0.121
$R_e = [(N - P + C) / (\sum w_i y_{oi}^2)]^{1/2}$	0.0667
$\chi^2 = (R_{\text{WP}} / R_e)^2$	2.19
Ta1 in 4c (0, x, 1/4)	0.6974(5)
B _{iso}	0.11(4)
Ta2 in 8f (0, y, z)	0.4190(4), 0.0558(7)
B _{iso}	0.11(4)
Co1 in 4c (0, x, 1/4)	0.541(2)
Co2 in 4c (0, x, 1/4)	0.841(2)
Co3 in 8f (0, y, z)	0.198(2), 0.005(2)
B1 in 4c (0, x, 1/4)	0.965(2)
B2 in 8f (0, y, z)	0.106(2), 0.14(2)
B3 in 8f (0, y, z)	0.272(9), 0.15(2)
B4 in 8f (0, y, z)	0.021(1), 0.091(2)

5.2.6 TEM Investigations

For further conformation of the crystal structures described above as well as for a check on superstructures, TEM investigations were carried out. For each sample a series of selected area diffraction (SAD) patterns was taken at various sample tilts. Fig. 5.22 summarizes the most representative diffraction patterns and their simulations using software JEMS [2007Sta]. All diffraction patterns were fully indexed using the lattice parameters found by X-ray diffraction techniques. No superstructure spots were detected confirming the unit cell dimensions derived from X-ray diffraction data. The observed intensities of diffraction spots correlate well with the simulations based on the atomic positions given in above.

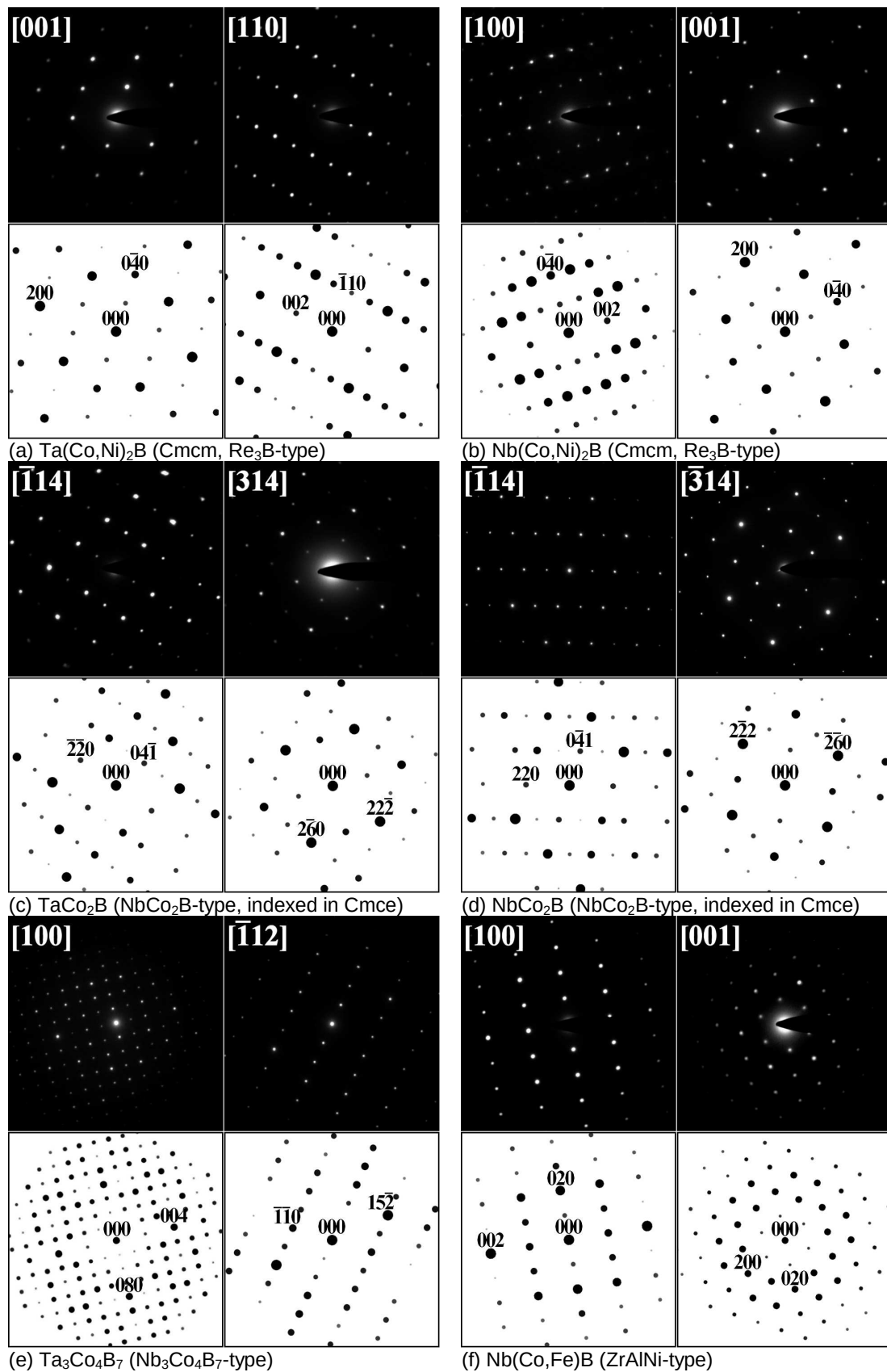


Fig. 5.22: TEM selected area diffraction patterns together with their simulations.

5.3 Physical Properties

5.3.1 Hardness

Fig. 5.23 plots the results of the hardness measurements for selected compounds as a function of the indentation loads. The obtained hardness-values are very high for low indentation loads, and asymptotically reach the real hardness values, summarized in Tab. 5.8. Ta-compounds show higher hardness than the corresponding Nb-compounds. Ni substitution in τ_4 for Ta as well as for Nb lowers the hardness significantly.

The data measured for NiB (HV=1611) is in good agreement with the value published by Sobolev et al. [1967Sob] (HV=1546).

Tab. 5.8: Vickers micro-hardness

Compound	HV	HV/MPa
τ_4 -TaCo ₂ B	1815	17.6
Ta(Co _{0.77} Ni _{0.23}) ₂ B	1448	14.5
τ_5 -Ta _{2.5} Co _{20.5} B ₆	1438	14.5
τ_4 -NbCo ₂ B	1601	14.7
Nb(Co _{0.77} Ni _{0.23}) ₂ B	1356	13.3
τ_5 -Ta _{2.1} Co _{20.9} B ₆	1407	13.8
NiB	1611	15.8
NiB [1967Sob]	1546	15.3
"TaCo ₅ B ₂ " [1961Lav]	1213	11.9

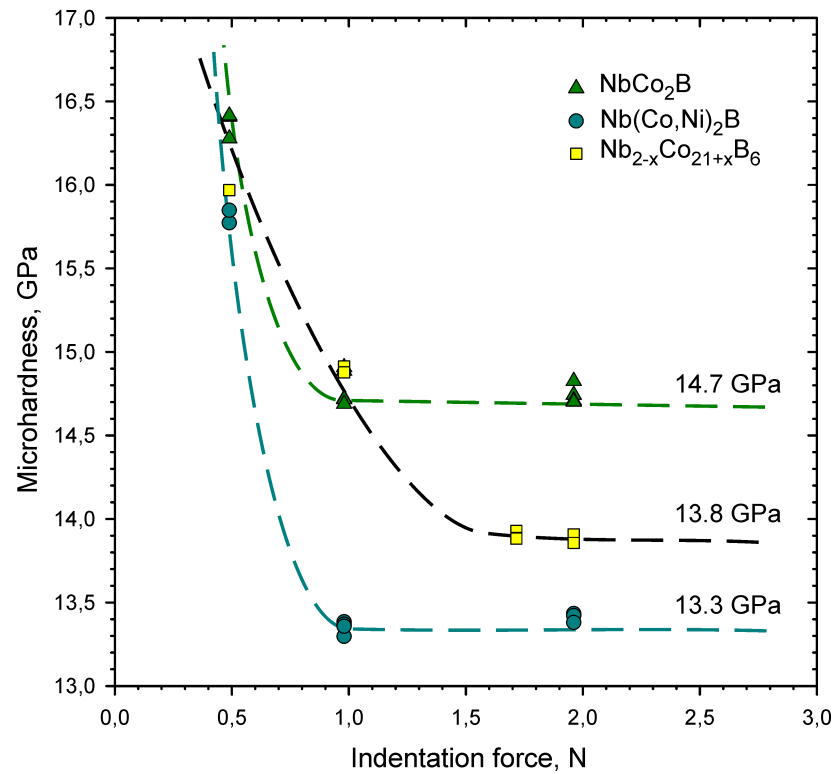
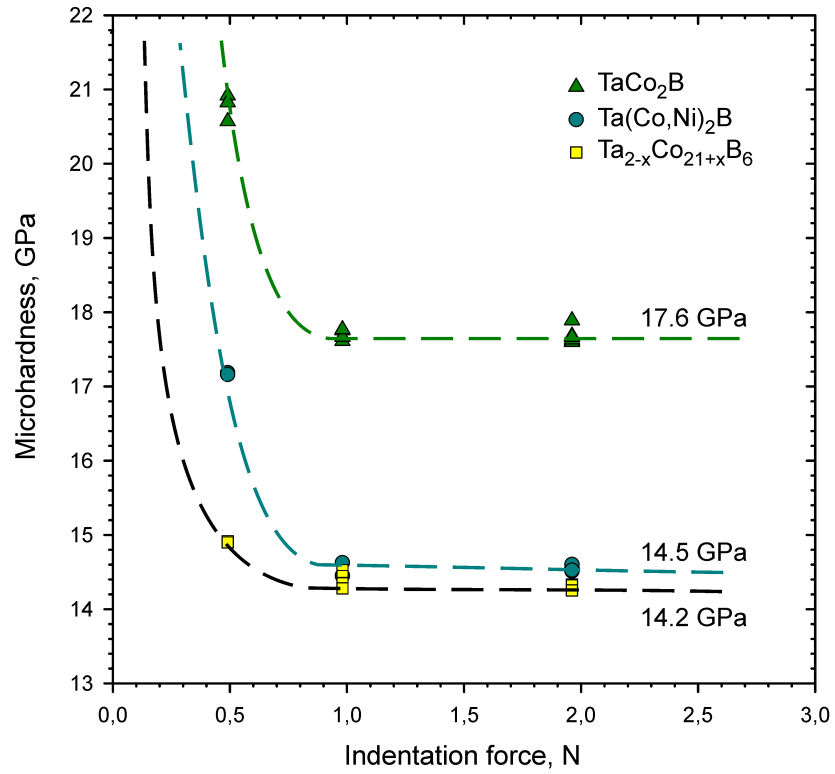


Fig. 5.23: Hardness measurements (at room temperature) for $\{\text{Nb},\text{Ta}\}(\text{Co},\text{Ni})_2\text{B}$, $\{\text{Nb},\text{Ta}\}\text{Co}_2\text{B}$ and $\{\text{Nb},\text{Ta}\}_{2-x}\text{Co}_{21+x}\text{B}_6$ at various loads.

5.4 The Liquidus Surface and Invariant Reactions in the Melting-Crystallization Region

5.4.1 The System Ta-Co-B

Fig. 5.24 presents a projection of the liquidus surface for the Co rich part of the Ta-Co-B system, based on SEM analysis of microstructures (Fig. 5.25), EPMA, X-ray and DTA data. As a result, a scheme of reactions was derived in form of a Schultz-Scheil-Diagram, shown in Fig. 5.26, invariant reactions are summarized in Tab. 5.9.

The microstructure of the as cast sample $\text{Ta}_{20}\text{Co}_{68}\text{B}_{12}$ (Fig. 5.25a) shows the joint crystallization of τ_4 and λ_3 and a ternary eutectic E_4 , whereas the microstructure of the as cast sample $\text{Ta}_{7.5}\text{Co}_{78.5}\text{B}_{14}$ identifies almost exclusively a eutectic structure E_4 . The well-defined peak at 1222°C of a DTA measurement corresponds to the eutectic temperature E_4 (see Fig. 5.25b) and a little effect assigned to the transition reaction U_5 at 1337°C: $L + \lambda_2 \Leftrightarrow \lambda_3 + \tau_4$.

The primary crystallization of (Co) extends up to a limit of 82 at.% Co in the section between (Co) and τ_4 and terminates in a two-phase eutectic invariant reaction e_4 : $L \Leftrightarrow \tau_4 + (\text{Co})$ that corresponds to the maximum on the monovariant line connecting the two ternary eutectics E_3 and E_4 . This reaction agrees with data of Stadelmaier and Hofer [1964Sta] and the temperature of this invariant reaction determined by DTA is 1230°C, confirming the temperature reported by Sprenger et al. [1977Spr].

Alloy $\text{Ta}_{8.75}\text{Co}_{82.5}\text{B}_{8.75}$ (Fig. 5.25c) still shows the primary crystallization of (Co), however, in alloy $\text{Ta}_{12.5}\text{Co}_{75}\text{B}_{12.5}$ (Fig. 5.25d) we see already primary crystallization of τ_4 , in both cases surrounded by the two-phase eutectic (Co)+ τ_4 .

Stadelmaier and Hofer [Sta1964] suggested the ternary phase τ_4 to be congruently melting. Indeed τ_4 crystallizes from the liquid (see Fig. 5.25e) but forms incongruently. This is well visible from the microstructures of a series of samples along the tie line between (Co) and τ_4 . Already samples at Co contents of 61 at.% showed primary crystallization of the high temperature modification of τ_3 . Fig. 5.25f presents the microstructure of that sample: the primary crystallizing phase is $h\text{-}\tau_3$, surrounded by τ_4 and the finally crystallized liquid corresponding to the two-phase eutectic of τ_4 and (Co). This observation is compatible with the invariant peritectic formation of τ_4 : $L + h\text{-}\tau_3 \Leftrightarrow \tau_4$. The temperature corresponding to this reaction was determined by the Pirani-Altherthum technique ($1470 \pm 15^\circ\text{C}$) on a single-phase τ_4 sample.

The as cast alloy $\text{Ta}_{7.5}\text{Co}_{78.5}\text{B}_{14}$ shows separated crystallization of two two-phase eutectics $(\text{Co})+\tau_4$ and $(\text{Co})+\tau_5$ (Fig. 5.25g). The same microstructure is observed in the sample after DTA in Fig. 5.25h. Such a microstructure and the composition of the eutectics measured by microprobe (with a Co:Ta ratio of 90:10 and 92:8, respectively) agree well with the report of Stadelmaier and Hofer [1964Sta] on the existence of an invariant ternary eutectic E_3 . The position of this eutectic evaluated from microprobe and DTA is at a Co:Ta ratio of 91:9 at 1209°C.

Fig. 5.25i shows the microstructure of the as cast sample $\text{Ta}_{2.4}\text{Co}_{74}\text{B}_{23.6}$: primary crystallization of cubic τ_5 , some binary eutectic $\text{I} \Leftrightarrow (\text{Co})+\text{Co}_3\text{B}$ as well as Co_3B and darker Co_2B . The dark grey grains of Co_3B already give some hints for the solid state decomposition of Co_3B associated with the eutectoid decomposition $\text{Co}_3\text{B} \Leftrightarrow \text{Co}_2\text{B}+\text{CoB}$ in the Co-B binary system (845°C) also being present in the ternary. However, we were not able to quench this phase after annealing at 1100°C. XPD of the annealed sample reveals only three phases: (Co) , Co_2B and τ_5 . However, considering the constitution of the accepted binary Co-B system and the microstructure of the as cast alloys, Co_3B has to participate in the equilibria at a temperature above 845°C. DTA measurement of the annealed sample responds to two effects – a strong peak at 1155°C can unambiguously be assigned to the transition reaction $U_1: \text{L}+\text{Co}_2\text{B} \Leftrightarrow \text{Co}_3\text{B}+\tau_5$, only 6°C below the binary peritectic temperature for the formation of Co_3B . The second and weak peak at 1135°C, which could be assigned either to some amount of ternary eutectic E_3 still left in the sample, or to an overheated formation of Co_3B .

Fig. 5.25j depicts the microstructure of a sample (as cast, small image: annealed) with composition in the three-phase field $(\text{Co})+\text{Co}_3\text{B}+\tau_5$: the primary phase is τ_5 , followed by the crystallized liquid corresponding to the ternary invariant eutectic E_1 . From EPMA measurements (Co:Ta=99.5:0.5) as well as from evaluation of the relative amounts of the three constituents we can conclude that E_1 is situated close to the Co-B binary. The measured reaction temperature of 1135°C is consistent with the eutectic in the Co-B binary system at 1136°C and the transition reaction U_1 described above.

Considering the two invariant eutectics E_1 and E_3 in neighbouring three-phase fields, one requests the existence of a non-variant two-phase eutectic $e_3: \tau_5+(\text{Co})$. This two-phase eutectic can be observed in Fig. 5.25k, which presents the micrograph of a sample from the two-phase region $(\text{Co})+\tau_5$ on the solidus surface. It seems that the temperature corresponding to e_3 is very close to the temperature of E_3 and therefore temperatures measured by DTA for two-phase alloys $(\text{Co})+\tau_5$ are between the temperatures of E_3 and E_1 . It is interesting to note that τ_5 also forms quasi-binary eutectics with Co_2B and τ_4 . The

monovariant lines defining the primary crystallization field of τ_5 at lower Co contents $\text{Co}_2\text{B}+\tau_5$ and $\tau_4+\tau_5$ both lead via a maximum on the liquidus and solidus surfaces, $e_{1\max}=1201^\circ\text{C}$ and $e_{2\max}=1252^\circ\text{C}$, into the ternary eutectic E_2 : $L \Leftrightarrow \text{Co}_2\text{B}+\tau_4+\tau_5$, located close to the $\text{Co}_2\text{B}+\tau_4$ tie line. Fig. 5.25l shows the joint crystallization of Co_2B and τ_5 and the ternary eutectic E_2 .

The micrograph (Fig. 5.25m, Fig. 5.25n) of sample $\text{Ta}_{12}\text{Co}_{57}\text{B}_{31}$, located in the three-phase field $h-\tau_3+\tau_4+\text{Co}_2\text{B}$, shows the peritectic formation of τ_4 from primarily crystallized $h-\tau_3$, subsequent crystallization of τ_5 and ternary eutectic E_2 . The presence of the four phases $h-\tau_3+\tau_4+\tau_5+\text{Co}_2\text{B}$ (especially the presence of the non-equilibrium phase τ_5) excludes a min-max point, separating the two corresponding three phase fields ($h-\tau_3+\tau_4+\text{Co}_2\text{B}$ and $\tau_4+\tau_5+\text{Co}_2\text{B}$) and thus indicates a ternary transition reaction U_2 : $L + h-\tau_3 \Leftrightarrow \tau_4+\text{Co}_2\text{B}$ at 1199°C as measured by DTA.

EPMA and XPD analysis of as cast samples located in the three-phase field $\tau_2+\tau_3+\text{Co}_2\text{B}$ also show some amounts of τ_4 . The peak in the DTA curve (1218°C) could thus be assigned to a ternary transition reaction U_3 : $L+\tau_2 \Leftrightarrow \tau_3+\text{Co}_2\text{B}$. Nevertheless it has to be noted that τ_3 was not observed in sample $\text{Ta}_7\text{Co}_{57}\text{B}_{36}$. In sample $\text{Ta}_{11.5}\text{Co}_{53}\text{B}_{35.5}$, although EPMA confirmed a Ta:Co ratio consistent with τ_3 , this phase could not be indexed in the XPD pattern because some peaks remain unindexed. Samples situated at higher B contents in the three-phase field $\tau_2+\text{CoB}+\text{Co}_2\text{B}$ show primary crystallization of a Ta-rich phase surrounded by dendritic crystallization of an unidentified phase τ_6 (see Fig. 5.25o). XPD analysis revealed CoB and Co_2B and some residual peaks. However, no further known binary or ternary phase could be indexed in the present patterns and thus suggests the presence of novel phases.

Further samples located at the section of 50 at.% Co indicate the end of the primary crystallization field of $h-\tau_3$ already before 50 at.% Co: samples located at 37-40 at.% B show primary crystallization of τ_1 , at 20-30 at.% B the primarily crystallizing phase is TaB , indicating a peritectic formation of $h-\tau_3$ around grains of TaB (see Fig. 5.25p).

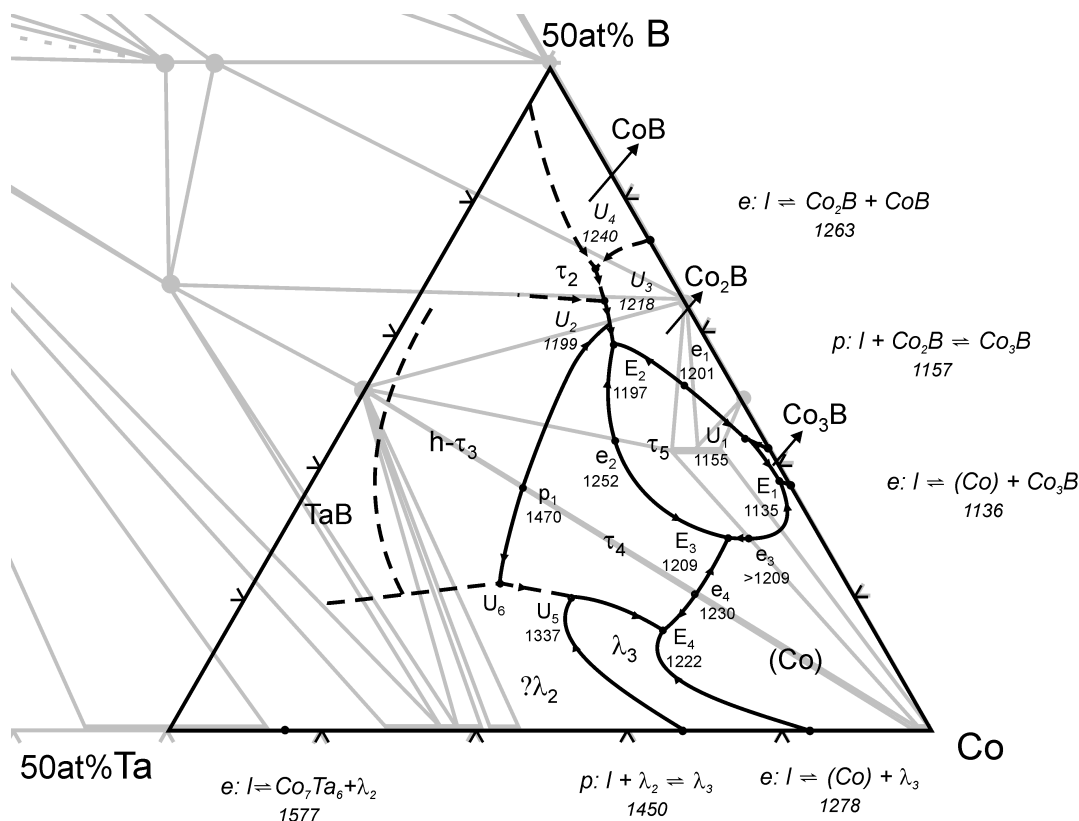
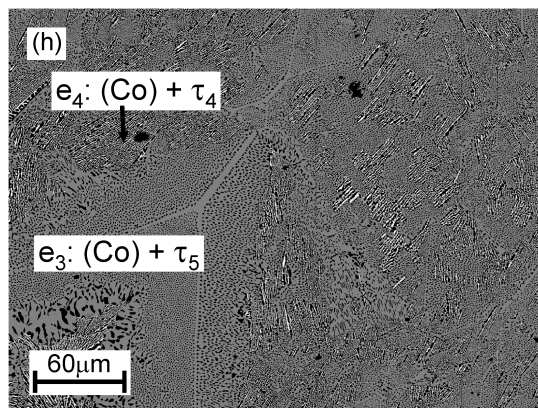
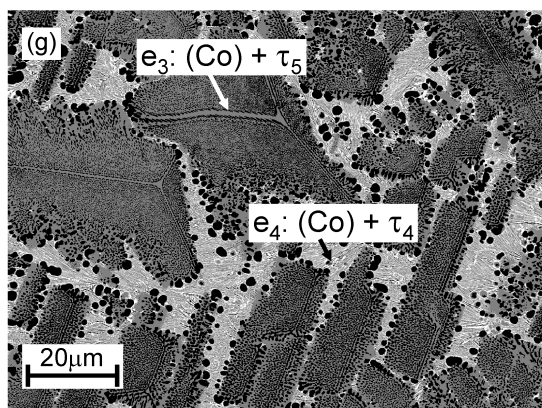
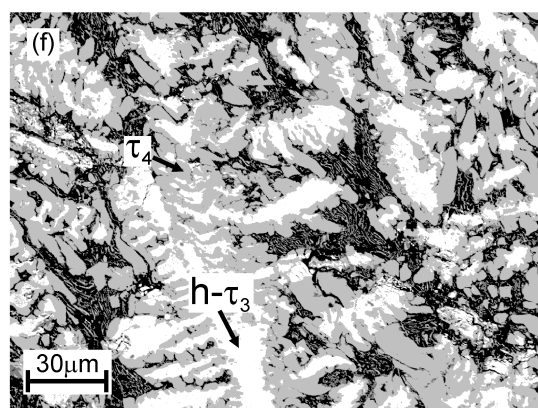
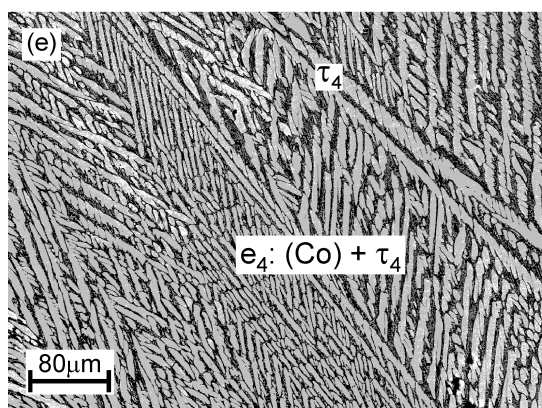
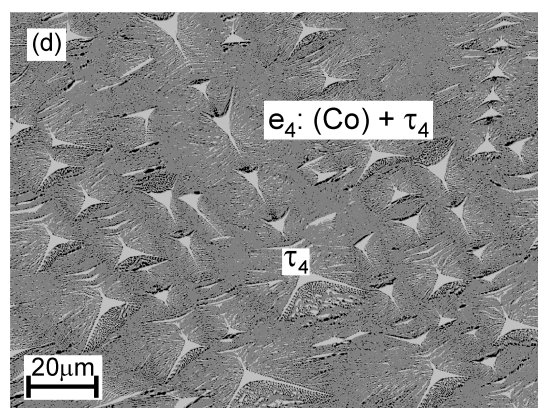
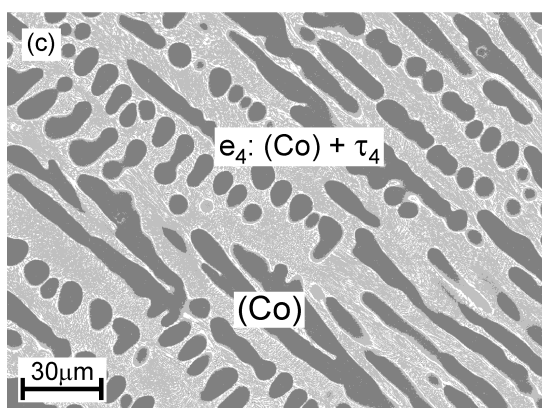
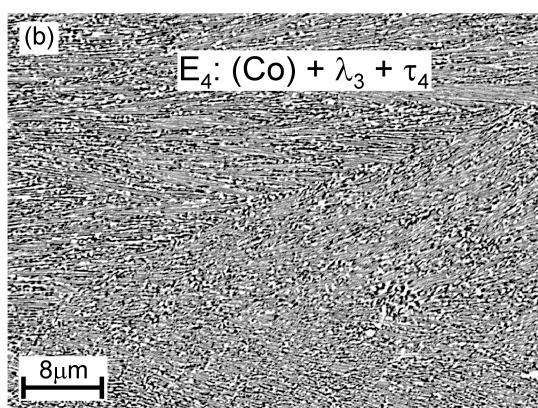
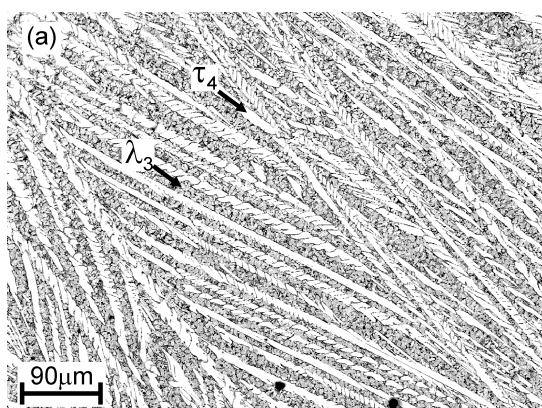


Fig. 5.24: The Liquidus Surface Projection for the Co-rich (>50at.% Co) part of the Ta-Co-B system; grey: corresponding solidus surface (isothermal section at 1100°C).

Tab. 5.9: Invariant reactions in the Ta-Co-B system

Invariant reaction		T/°C
E ₁	L ↔ Co ₃ B + τ ₅ + (Co)	1135
E ₂	L ↔ Co ₂ B + τ ₄ + τ ₅	1197
E ₃	L ↔ (Co) + τ ₄ + τ ₅	1209
Et	L ↔ (Co) + λ ₃ + τ ₄	1222
U ₁	L + Co ₂ B ↔ Co ₃ B + τ ₅	1155
U ₂	L + τ ₃ ↔ Co ₂ B + τ ₄	1199
U ₃	L + τ ₂ ↔ Co ₂ B + τ ₃	1218
U ₄	L + CoB ↔ Co ₂ B + τ ₂	1240
U ₅	L + λ ₂ ↔ λ ₃ + τ ₄	1337
U ₆	L + λ ₃ ↔ λ ₂ + τ ₄	1337 ≤ T ≤ 1470
U ₇	τ ₂ + τ ₃ ↔ Co ₂ B + τ ₁	800 ≤ T ≤ 1100
U ₈	Co ₂ B + τ ₄ ↔ τ ₃ + τ ₅	800 ≤ T ≤ 1100
U ₉	(Co) + λ ₃ ↔ Ta ₂ Co ₇ + τ ₄	800 ≤ T ≤ 1100
U ₁₀	TaB ₂ + τ ₁ ↔ Ta ₃ B ₄ + τ ₂	800 ≤ T ≤ 1100
D	Co ₃ B, (Co), Co ₂ B, τ ₅	800 ≤ T ≤ 1100
e ₁	L ↔ Co ₂ B + τ ₅	1201
et	L ↔ τ ₄ + τ ₅	1252
e ₃	L ↔ (Co) + τ ₅	≥ 1209
e ₄	L ↔ (Co) + τ ₄	1230
p ₁	L + τ ₃ ↔ τ ₄	1470



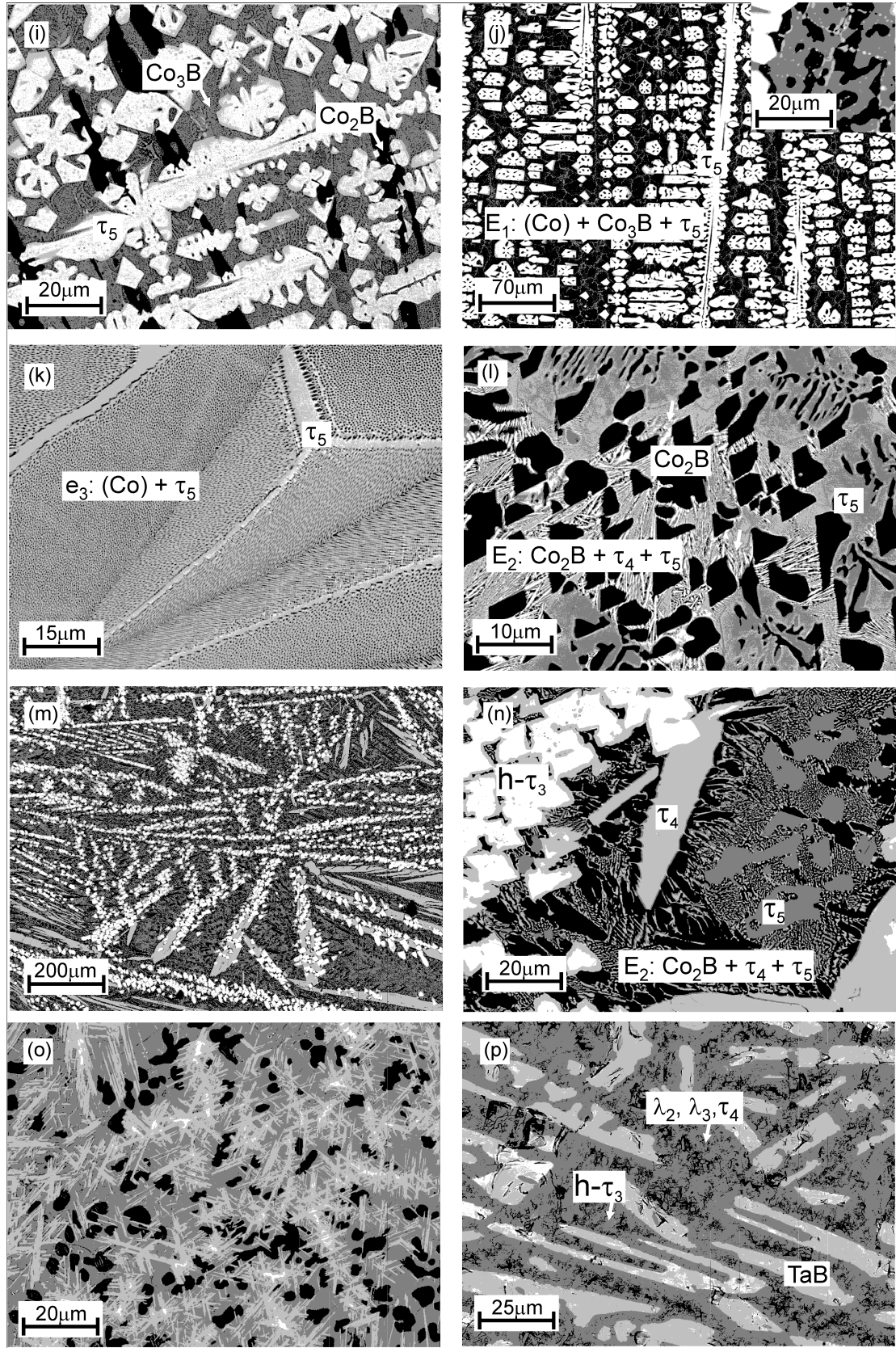


Fig. 5.25: Selected microstructures of Ta-Co-B-alloys: a) $\text{Ta}_{20}\text{Co}_{68}\text{B}_{12}$, b) $\text{Ta}_{14}\text{Co}_{78.5}\text{B}_{7.5}$, c) $\text{Ta}_{8.75}\text{Co}_{82.5}\text{B}_{8.75}$, d) $\text{Ta}_{12.5}\text{Co}_{75}\text{B}_{12.5}$, e) $\text{Ta}_{17.5}\text{Co}_{65}\text{B}_{17.5}$, f) $\text{Ta}_{19.5}\text{Co}_{61}\text{B}_{19.5}$, g) $\text{Ta}_{7.5}\text{Co}_{78.5}\text{B}_{14}$, h) $\text{Ta}_{7.5}\text{Co}_{78.5}\text{B}_{14}$, i) $\text{Ta}_{2.4}\text{Co}_{74}\text{B}_{23.6}$, j) $\text{Ta}_{2.5}\text{Co}_{78.5}\text{B}_{19}$, k) $\text{Ta}_{5}\text{Co}_{79.5}\text{B}_{15.5}$, l) $\text{Ta}_{6}\text{Co}_{65.5}\text{B}_{28.5}$, m) and n) $\text{Ta}_{12}\text{Co}_{57}\text{B}_{31}$, o) $\text{Ta}_{8}\text{Co}_{47}\text{B}_{45}$, p) $\text{Ta}_{30}\text{Co}_{50}\text{B}_{20}$.

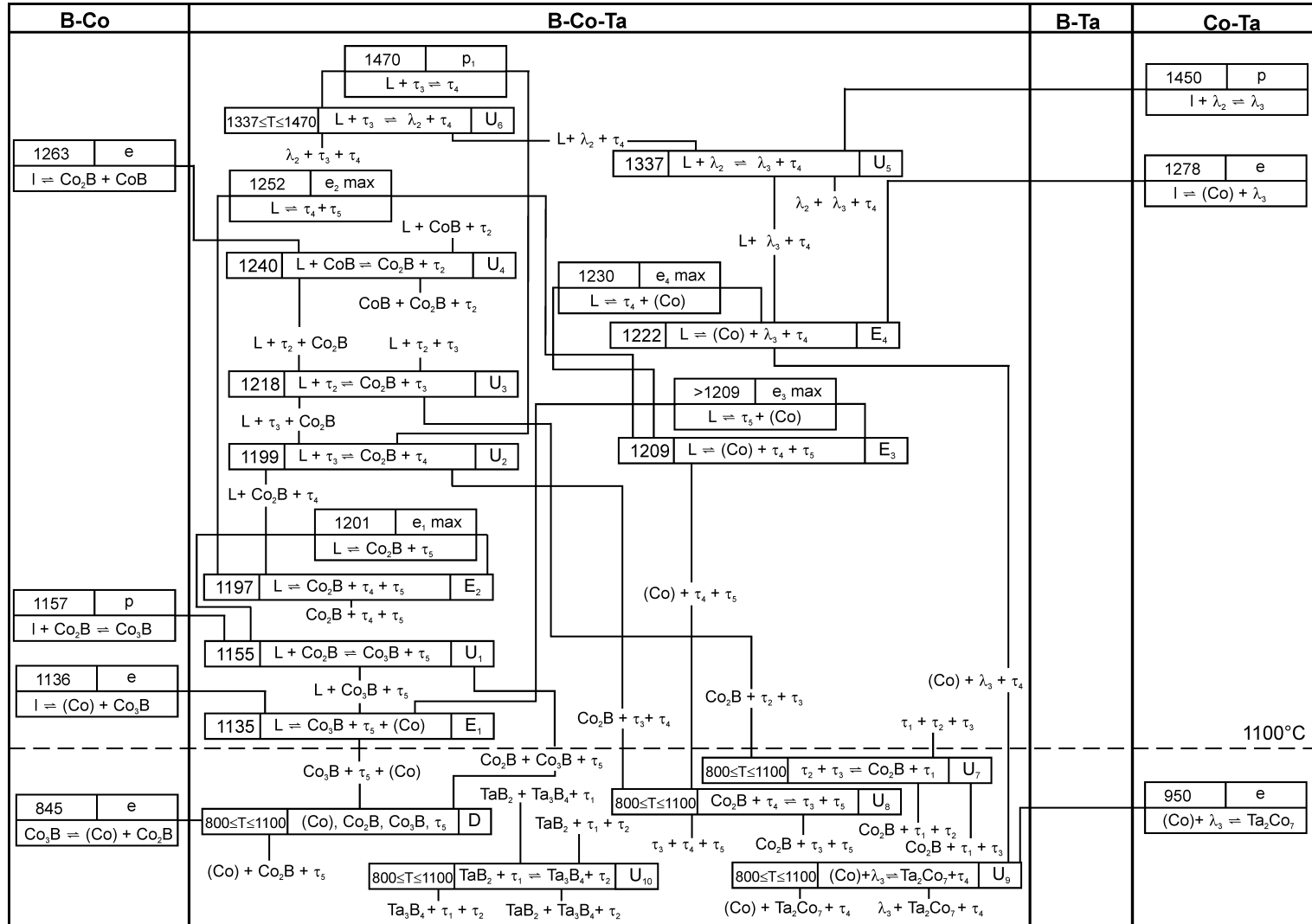


Fig. 5.26: Schultz-Scheil diagram for the Co-rich part (>50at.% Co) of the Ta-Co-B system.

5.4.2 The System Nb-Co-B

Fig. 5.27 presents the liquidus surface projection of the Co-rich part of the Nb-Co-B system, based on SEM analysis of microstructures (Fig. 5.28), EPMA, X-ray and DTA data. As a result, a scheme of reactions was derived in form of a Schultze-Scheil-Diagram, presented in Fig. 5.29; invariant reactions are summarized in Tab. 5.10.

Especially the part up to 30 at.% Co shows almost similar behaviour to the corresponding Ta-system and is in good agreement with data of Stadelmaier and Schöbl [1966Sta]. The ternary invariant eutectic E_3 : $L \Leftrightarrow (Co) + \lambda_3 + \tau_4$ is situated at a Co:Nb ratio 85:15 and a temperature of 1150°C (see Fig. 5.28a). This eutectic is connected via a min-max point at 1188°C (see Fig. 5.28b) on the monovariant crystallization line of τ_4 and (Co) with the ternary invariant eutectic E_4 : $L \Leftrightarrow \tau_4 + \tau_5 + (Co)$ at a reaction temperature of 1166°C and a Co:Nb ratio of 90:10. The microstructure of a sample at the composition $Nb_8Co_{77.5}B_6$ (Fig. 5.28c) shows the separated crystallization of the two two-phase eutectics $(Co) + \tau_4$ and $(Co) + \tau_5$, as already described above for the corresponding Ta-sample.

Fig. 5.28d shows the very fine ternary eutectic E_1 : $(Co) + Co_2B + \tau_5$, for which a DTA measurement revealed a well-defined peak at 1133°C. In this sample the stable binary compound Co_3B could not be quenched, but however was present in the sample at composition $Nb_{2.5}Co_{73.5}B_{24}$. DTA of this sample showed a peak at 1155°C, as well as a little peak at the reaction temperature of E_1 . Analysis of XPD and microstructure are in good agreement with a transition reaction U_1 : $L + Co_2B \Leftrightarrow Co_3B + \tau_5$. The two ternary invariant eutectics E_1 and E_4 are connected with the quasi-binary eutectic e_3 : $L \Leftrightarrow \tau_5 + (Co)$ at a maximum temperature of 1180°C.

The primary crystallization of (Co) extends up to a limit of 81 at.% Co. The end of the primary crystallization field of τ_4 was confirmed with a series of samples along the tie line between (Co) and τ_4 . Fig. 5.28e shows the micrograph of sample $Nb_{18.75}Co_{62.5}B_{18.75}$: primary crystallization of $l - \tau_3$ surrounded by τ_4 and the finally crystallizing liquid corresponding to the two-phase eutectic of τ_4 and (Co). This invariant peritectic formation of τ_4 : $L + l - \tau_3 \Leftrightarrow \tau_4$ stays in contrast to the primary crystallization field of NbB suggested by Stadelmaier and Schöbl [1966Sta].

Fig. 5.28f shows primary crystallization of τ_5 , whereas the finally crystallized liquid is the ternary invariant eutectic E_2 : $L \Leftrightarrow Co_2B + \tau_2 + \tau_5$. DTA measurement shows one peak at 1176°C attributed to this eutectic. This ternary eutectic is connected with U_5 via the quasi-binary eutectic e_2 : $L \Leftrightarrow \tau_5 + Co_2B$ (see Fig. 5.28g) at a maximum temperature of 1197°C.

Accepting the isothermal section at 1100°C as the corresponding solidus and considering all available data, the reactions U_1 , U_2 and U_4 were included in the liquidus surface projection and the corresponding reaction scheme for higher B contents was constructed (see Fig. 5.27 and Fig. 5.29, respectively). However, we have to mention that powder patterns of samples in the region closer to 50at.% Co could not be completely indexed considering all the currently known binary and ternary phases pertinent to the system, and thus indicate the formation of novel phase(s).

Fig. 5.28h shows the microstructure of the sample located in the three-phase field $\tau_2 + \text{CoB} + \text{Co}_2\text{B}$: primary crystallization of a Nb-rich phase surrounded by dendritic crystallization of an unidentified phase τ_6 . Similar to the corresponding sample in the Ta system, XPD analysis revealed CoB and Co_2B and some residual peaks that could not be indexed.

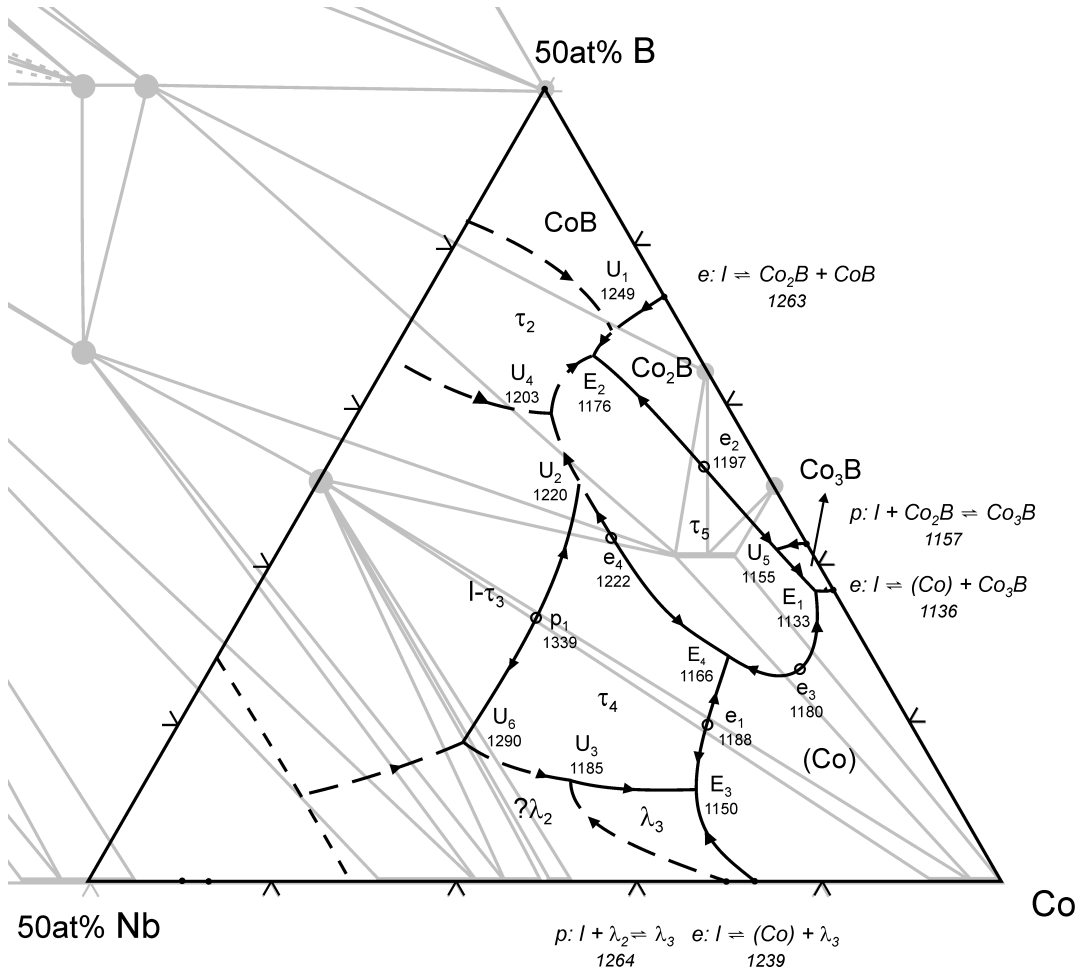


Fig. 5.27: The Liquidus Surface Projection for the Co-rich part (>50at.% Co) of the Nb-Co-B system; grey: corresponding solidus surface (isothermal section at 1100°C).

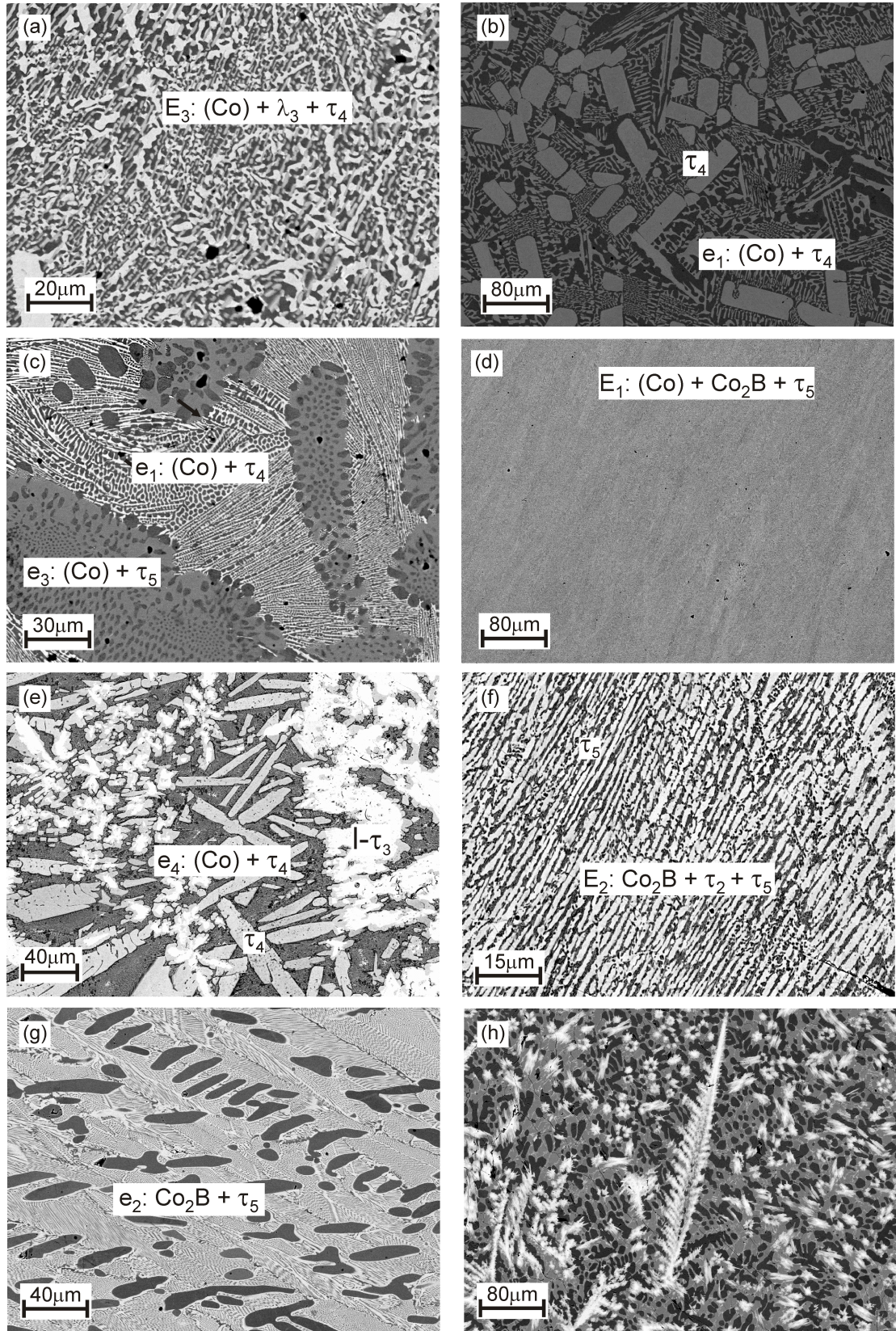


Fig. 5.28: Selected microstructures of Nb-Co-B-alloys: a) $\text{Nb}_{12.5}\text{Co}_{81.5}\text{B}_6$ b) $\text{Nb}_{13.25}\text{Co}_{73.5}\text{B}_{13.25}$ c) $\text{Nb}_8\text{Co}_{77.5}\text{B}_{14.5}$ d) $\text{Nb}_1\text{Co}_{81}\text{B}_{18}$ e) $\text{Nb}_{18.75}\text{Co}_{62.5}\text{B}_{18.75}$ f) $\text{Nb}_{2.4}\text{Co}_{74}\text{B}_{23.6}$ g) $\text{Nb}_7\text{Co}_{63}\text{B}_{30}$ h) $\text{Nb}_5\text{Co}_{52}\text{B}_{43}$.

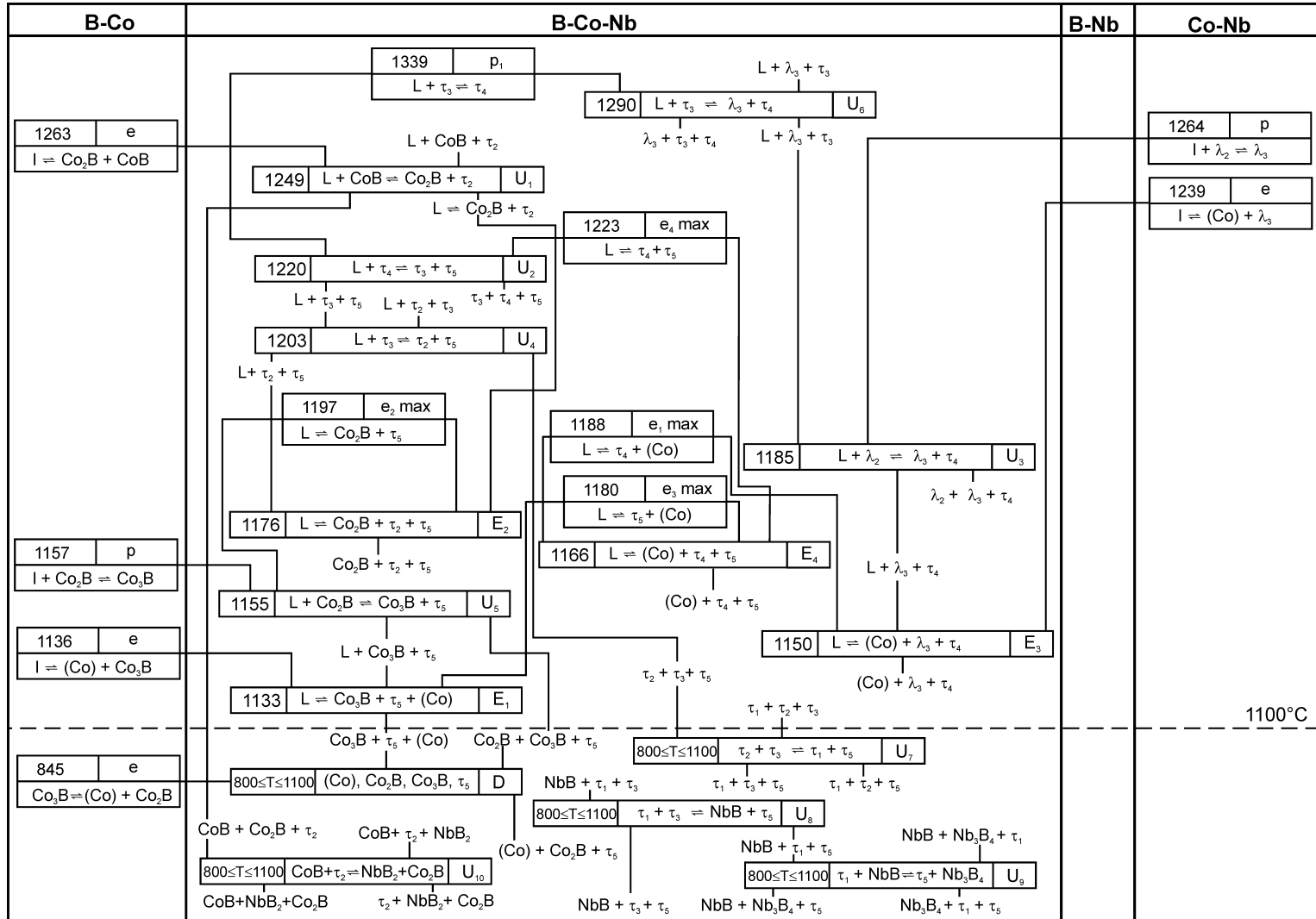


Fig. 5.29: Schultz-Scheil diagram for the Co-rich part (>50at.% Co) of the Nb-Co-B system.

Tab. 5.10: Invariant reactions in the Nb-Co-B system

<i>Invariant reaction</i>		<i>T/°C</i>
E ₁	$L \leftrightarrow Co_3B + \tau_5 + (Co)$	1135
E ₂	$L \leftrightarrow Co_2B + \tau_2 + \tau_5$	1176
E ₃	$L \leftrightarrow (Co) + \lambda_3 + \tau_4$	1150
E ₄	$L \leftrightarrow (Co) + \tau_4 + \tau_5$	1166
U ₁	$L + CoB \leftrightarrow Co_2B + \tau_2$	1249
U ₂	$L + \tau_4 \leftrightarrow \tau_3 + \tau_5$	1220
U ₃	$L + \lambda_2 \leftrightarrow \lambda_3 + \tau_4$	1185
U ₄	$L + \tau_3 \leftrightarrow \tau_2 + \tau_5$	1203
U ₅	$L + Co_2B \leftrightarrow Co_3B + \tau_5$	1155
U ₆	$L + \tau_3 \leftrightarrow \lambda_3 + \tau_4$	1290
U ₇	$\tau_2 + \tau_3 \leftrightarrow \tau_1 + \tau_5$	800≤T≤1100
U ₈	$\tau_1 + \tau_3 \leftrightarrow NbB + \tau_5$	800≤T≤1100
U ₉	$\tau_1 + NbB \leftrightarrow \tau_5 + Nb_3B_4$	800≤T≤1100
U ₁₀	$CoB + \tau_2 \leftrightarrow NbB_2 + Co_2B$	800≤T≤1100
D	$Co_3B, (Co), Co_2B, \tau_5$	800≤T≤1100
e ₁	$L \leftrightarrow (Co) + \tau_4$	1188
e ₂	$L \leftrightarrow Co_2B + \tau_5$	1197
e ₃	$L \leftrightarrow (Co) + \tau_5$	1180
e ₄	$L \leftrightarrow \tau_4 + \tau_5$	1223
p ₁	$L + \tau_3 \leftrightarrow \tau_4$	1339

6 References

	Year	Authors	Title	Journal	Pages
1923Pir	1923	M. Pirani, H. Alterthum	Method for the Determination of the Melting Point of Metals which Fuse at High Temperatures	Z. Elektrochemie 29	5-8
1961Lav	1961	H.W. Lavendel	Alloys of Tantalum Diboride with Iron, Cobalt, and Nickel	Planseeberichte für Pulvermetallurgie 9	80-95
1964Sta	1964	H.H. Stadelmaier, G. Hofer	Die kobaltreichen Kobalt-Tantal-Bor- Legierungen um die Phase $\text{Co}_{21}\text{Ta}_2\text{B}_6$	Metall 18(5)	460-462
1966Sch	1966	J.D. Schöbel, H.H. Stadelmaier	Das Zweistoffsystem Kobalt-Bor	Z. Metallkunde 57(4)	323-325
1966Sta	1966	H.H. Stadelmaier, J.D. Schöbl	Die Kobaltecke im Dreistoffsystem Kobalt-Niob-Bor	Metall 20(1)	31-32
1967Kuz	1967	Yu.B. Kuzma	Crystal Structures of NbFeB and TaFeB compounds	Dopov. Akad. Nauk. Ukr. RSR, Ser.A	939-940
1967Pon	1967	J. Ponsioen, J. Van Vucht	The Structure of $\beta\text{-TaCo}_3$ and the Effect of the Substitution of Ta and Co by related Elements	Philipps Research Report, 22	161-169
1967Sob	1967	A.S. Sobolev, Yu.B. Kuzma	System Niobium-Nickel-Boron	Izv. Akad. Nauk SSSR, Neorg. Mater. 3	638-643
1968Hun	1968	C.R. Hunt, A. Raman	Alloy chemistry of sigma (βU) related phases	Z. Metallkunde 59	701
1968Kuz 1	1968	Yu.B. Kuzma, T.I. Tsolkovskii, O.P. Baburova	The Systems Nb-Fe-B and Nb-Co-B	Inorgan. Materials, translated from Izv. Akad. Nauk SSSR, Neorg. Mater. 4(7)	950-953
1971Kry	1971	P.I. Krypyakevich, Yu.B. Kuzma, Yu.V. Voroshilov, C.B. Shoemaker, D.P. Shoemaker	The Crystal Structure of NbCoB	Acta Crystallogr. B27	257-261
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1971Por	1971	K. Portnoi, V. Romashov, S. Salibekov	Constitution Diagram of the System Tantalum-Boron	Powder Metallurgy and Metal Ceramics, 10	925-927
1973Kuz	1973	Yu.B. Kuzma, O.M. Rudakevich	Crystal Structure of the Compounds TaCoB and NbCoB ₂	Dopov. Akad. Nauk. Ukr. RSR, Ser.A(2)	164-167
1974And	1974	Y. Andersson, V. Kaewchansilp, M. Del Rosario Casteleiro Soto, S. Rundqvist	The Crystal Structure of Pd ₆ P	Acta Chemica Scandinavica A28	797-802
1976Kuz	1975	Yu.B. Kuzma	Crystal Structure of the Compound NbCoB ₂	Sov. Phys. Crystallogr. 20(5)	636-638

1976Omo	1976	S. Omori, Y. Hashimoto	Eutectoid Decomposition of Co_3B and Phase Diagram of the System $\text{Co-Co}_2\text{B}$	Trans. Japan Inst. Metals 17(9)	571-574
1977Spr	1977	H. Sprenger, H. Richter, J.J. Nickl	Boride und Silizide als Verstärkungsphasen in eutektischen Hochtemperaturwerkstoffen	Z. Metallkunde 68(4)	241-252
1978Rog	1978	P. Rogl, E. Rudy	New Complex Borides with ReB_2 - and Mo_2IrB_2 -Type Structure	Journal of Solid State Chemistry 24	175-181
1978Ste	1978	W. Steurer, P. Rogl, H. Nowotny	New Borides with NbCoB_2 Type Structure	Monatshefte Chemie 109	919-924
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1979Ste1	1979	W. Steurer, P. Rogl, H. Nowotny	The Tau-Borides in the Systems Ta-Co-B and (Nb,Ta)-Ru-B	Monatshefte Chemie 110	791-798
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1980Rog	1980	P. Rogl, J.C. Schuster, H. Nowotny	Phase Equilibrium and Compound Formation in Fe-M (Metal)-B-X (Nonmetal) Systems	Boron Steel, Proc. Int. Symp., 1979	33-43
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1990Kuz	1990	Yu.B. Kuzma, N.F. Chaban	Binary and Ternary Systems which Contain Boron	Metallurgia, Moscow	118-119 128-129
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1990Oka	1990	S. Okada, K. Hamano, I. Higashi, T. Lundström, L.E. Tegenius	Preparation of Single Crystals of the New Compound Ta_5B_6 by the Aluminium Flux Method	Bull. Chem. Soc. Japan, 63	687-691
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1998Non	1998		Nonius Kappa CCD Program Package COLLECT, DENZO, SCALEPACK, SORTAV	Nonius Delft, The Netherlands	
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2001Roi	2001	T. Roisnel, J. Rodriguez-Carvajal		Materials Science Forum 118	378-381
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2006Pöt	2006	R. Pöttgen, M. Lakachuk, R. Hoffmann	Re ₃ B type intermetallics - crystal chemistry, bonding and properties	Z. Kristallographie 221	435-444
2007Cha	2007	V.M. Chad, É.C.T. Ramos, G.C. Coelho, C.A. Nunes, P.A. Suzuki, F. Ferreira, P.Rogl	Evaluation of the Invariant Reactions in the Ta-rich Region of the Ta-B System	J. Phase Equilibria and Diffusion, 27(5)	452-455

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2007Sta	2007	P. Stadelmann	JEMS: Java Electron Microscopy Software	Available from: http://cimewww.epfl.ch/people/stadelmann/jemswebsite/jems.html	
2008Cha	2008	V.M. Chad, F. Ferreira, P.B. Fernandes, G.C. Coelho, C.A. Nunes	Modelagem Termodinâmica do Sistema Ta-B	63º Congresso Anual da ABM, Santos, Sao Paulo, Brasil, 2008	1412-1423
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1993Kre	1993	G. Kresse, J. Hafner	Ab initio molecular dynamics for liquid metals	Phys. Rev. B 47	558-561
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Theoretical background

2007Mas	2007	W. Massa	Kristallstrukturbestimmung	Teubner (5.Auflage)	-
2009Bla	2009	A.J. Blake et.al	Crystal Structure Analysis	Oxford Science Publications (2nd edition)	-
2009Ric	2009	K. Richter	Charakterisierung Anorganischer Materialien	Lecture Notes, Univie, WS09	-
2010Rog	2010	P. Rogl	High-precision sampling for Brillouin-zone integration in metals	Lecture Notes, Univie, WS10	-

7 Apendices

7.1 Crystallographic data of solid phases

Appendix Tab. 1: Crystallographic data of solid phases.

Phase T-Range/°C	Pearson Symbol, Space Group, Structure Type	Lattice Parameters/nm	References, Comments
β B <2092	hR333 $R\bar{3}m$ (166) β B	a=1.09265 c=2.38096	[2000Oka] dissolves <0.7 at% Ta at 2055°C <0.7 at% Nb at 2035°C 5 at% Co in as cast alloys
α Co 1495-422	cF4 $Fm\bar{3}m$ (225) Cu	a=0.35447	[1990Mas] [2000Oka] dissolves 4.5 at% Ta at 1280°C 5.5 at% Nb at 1239°C 0.5 at% B at 1100°C
ϵ Co <422	hP2 $P6_3/mmc$ (194) Mg	a=0.2507 c=0.4069	[1990Mas] [2000Oka]
Nb <2475	cl2 $Im\bar{3}m$ (229) W	a=0.3324	[1990Mas] [2000Oka] dissolves 1.6 at% B at 1600°C 5.3 at% Co at 1364°C
Ta <3020	cl2 $Im\bar{3}m$ (229) W	a=0.3303	[1990Mas] [2000Oka] dissolves 2 at% B at 2385°C ~20 at% Co at 1800°C

Co-B

CoB <1460	oP8 Pnma (62) FeB	a=0.5260 b=0.3042 c=0.3954	[1980Rog]
Co ₂ B <1285	tl12 I4/mcm (140) C16, CuAl ₂	a=0.5014 c=0.4215	[1983Bus]
Co ₃ B 845-1157	oP16 Pnma (62) Fe ₃ C	a=0.5229 b=0.6631 c=0.4432	[1983Bus]

Nb-B

NbB ₂ <3036	hP3 P6/mmm (191) C32, AlB ₂	a=0.31037-0.31115, c=0.33237-0.32657 a=0.30861-0.31126, c=0.33069-0.32627	~30-35 at% Nb (1100°C) [2003Bor] [1991Oka] [1992Rog]
Nb ₂ B ₃	oC20 Cmcm (63) V ₂ B ₃	a=0.33058 b=1.948 c=0.31293	40 at% Nb (1100°C) [1991Oka]
Nb ₃ B ₄ <2935	ol14 Immm (71) Ta ₃ B ₄	a=0.3143 b=0.3303 c=1.408 a=0.31530 b=0.33019 c=1.41062	43 at% Nb (1100°C) [1991Oka] [1992Rog]
Nb ₅ B ₆ ~<2870	oC22 Cmmm(65) V ₅ B ₆	a=0.31567 b=2.2767 c=0.33034 a=0.31530 b=2.2744 c=0.33049	45.5 at% Nb (1100°C) [1991Oka] [1992Rog]

NbB <2917	oC8 Cmcm (63) CrB	a=0.32961 b=0.87224 c=0.31653 a=0.32974 b=0.87238 c=0.31669	[1991Oka] [1992Rog]
Nb ₃ B ₂ <2080	tP10 P4/mbm (127) U ₃ Si ₂	a=0.61979 c=0.32926	60 at% Nb (1100°C) [1992Rog]

Co-Nb

Nb ₂ Co ₇ <1086	mS18 C2/m Hf ₂ Ni ₇	a=0.45874 b=0.81509, β=107.18° c=0.62223	22.1-22.3 at% Nb [2008Stein]
λ ₁ , NbCo ₂ 1250-1424	hP12 P ₆ ₃ /mmc (194) C14, MgZn ₂	a=0.4833 c=0.7847	35.8-37.4 at% Nb [2008Stein] at 36.3at%Nb
λ ₂ , NbCo ₂ <1484	cF24 Fd $\bar{3}$ m (227) C15, MgCu ₂	a=0.6713-0.6802	[2008Stein] 26.0-35.3 at% Nb (27-34 at% Nb at 1100°C)
λ ₃ , NbCo ₂ 1040-1264	hP24 P ₆ ₃ /mmc (194) C36, MgNi ₂	a=0.47414-0.4747, c=1.5458-1.5484	[2008Stein] 24.5-25.5 at% Nb (24.5-25 at% Nb at 1100°C)
Nb ₇ Co ₆ <1424	hR39 R $\bar{3}$ m (166) D ₈ ₅ , W ₆ Fe ₇	a=0.498 c=2.650 a=0.4898 c=2.619	[2008Stein] 46.5-56.1 at% Nb (47-53 at% Nb at 1100°C) Nb ₇ Co ₆ [1968Hun] Co-rich [2008Ste]

Ta-B

TaB ₂ <3037	hP3 P6/mmm (191) AlB ₂	a=0.30586-0.30973, c=0.32892-0.32257	30-35 at% Ta at 1100°C [1993Oka]
Ta ₃ B ₄ <3030	oI14 Immm (71) Ta ₃ B ₄	a=0.31327 b=0.32914 c=1.3994	43 at% Ta at 1100°C [1993Oka]
Ta ₅ B ₆ <3040	oC22 Cmmm (65) V ₅ B ₆	a=0.31385 b=2.2609 c=0.32865	45.5 at% Ta [1993Oka]
TaB <3090	oC8 Cmcm (63) CrB	a=0.328 b=0.867 c=0.3155	50 at% Ta [1993Oka]
Ta ₃ B ₂ <2180	tP10 P4/mbm (127) U ₃ Si ₂	a=0.61847 c=0.3284	60 at% Ta [1971Por]
Ta ₂ B _{1-x} 2380-~1900	tI12 I4/mcm (140) CuAl ₂	a=0.57793 c=0.48638	~30 at% Ta [2007Cha]

Co-Ta

Ta ₂ Co ₇ <950	unknown		[2000Oka] 22.2 at% Ta
λ ₁ , TaCo ₂ 1538-1130	hP12 P ₆ ₃ /mmc (194) C14, MgZn ₂	a=0.4735-4838, c=0.7806-0.7835	37at% Ta [2000Oka]
λ ₂ , TaCo ₂ <1620	cF24, Fd $\bar{3}$ m (227) C15, MgCu ₂	a=0.6710-0.6788	29.9-36at% Ta [2000Oka]
λ ₃ , TaCo ₂ <1450	hP24 P ₆ ₃ /mmc (194)	a=0.4700-0.4747, c=1.5420-1.5470	[2000Oka] [2011Vil]

	C36, MgNi ₂		
Ta ₇ Co ₆ <1700	hR39 R $\bar{3}$ m (166) W ₆ Fe ₇	a=0.4900 c=2.6420 a=0.4947 c=2.6570	46-54at% Ta for Ta ₆ Co ₇ [1968Hun] for Ta ₇ Co ₆ [1968Hun]
Ta ₂ Co <1800	tI12 I4/mcm (140) CuAl ₂	a=0.6116-0.6128 c=0.4936-0.4969	66.7at%Ta [2000Oka]
TaCo ₃	cP4 Pm $\bar{3}$ m (221) AuCu ₃	a=0.367	[1971Pet]
TaCo ₃	hR36 R $\bar{3}$ m (166) BaPb ₃	a=0.51864 c=1.887	[1967Pon]
Nb-Co-B			
τ_1 , NbCoB ₂	oP16 Pnma (62) NbCoB ₂	a=0.6057 b=0.3127 c=0.8215 a=0.6012 b=0.3122 c=0.8207	[1976Kuz] This work
τ_2 , Nb ₃ Co ₄ B ₇	oS56 Cmcm (63) Nb ₃ Co ₄ B ₇	a=0.3202 b=1.8432 c=0.8917 a=0.3196 b=1.8412 c=0.8909	[1986Kuz] This work
h- τ_3 , NbCoB	hP9 P $\bar{6}$ 2m (189) ZrNiAl	a=0.59527(5) c=0.32478(4)	This work
l- τ_3 , NbCoB	oP30 Pmmn (59) NbCoB	a=0.3266 b=1.7177 c=0.5947 a=0.3264 b=1.7134 c=0.5937	[1971Kry] This work
τ_4 , NbCo ₂ B	mP16 P2 ₁ /c (14) NbCo ₂ B	a=0.9190 (0.9184) b=0.64263 (0.6426) c=0.63144 (0.6315) β =109.954° (109.873°)	X-ray SC (powder), This work
τ_5 , Nb _{2-x} Co _{21+x} B ₆	cF116 Fm $\bar{3}$ m (225) W ₂ Cr ₂₁ C ₆	a=1.052 a=1.0540-1.0574 a=1.05387 a=1.05818	x=0 [1968Kuz] [1966Sta] for Nb _{1.38} Co _{21.62} B ₆ this work for Nb _{2.53} Co _{20.47} B ₆ , this work
Nb ₃ Co ₅ B ₂	tP20 P4/mbm (127) Ti ₃ Co ₅ B ₂	a=0.846 c=0.3073	[1979Kuz] not observed in this work (unstable?)
Ta-Co-B			
τ_1 , TaCoB ₂	oP16 Pnma (62) NbCoB ₂	a=0.6007 b=0.3115 c=0.8191 a=0.6002 b=0.3109 c=0.8187	[1978Ste] This work
τ_2 , Ta ₃ Co ₄ B ₇	oS56 Cmcm (63) Nb ₃ Co ₄ B ₇	a=0.31895 b=1.8333 c=0.88809	This work earlier "TaCo ₂ B ₃ " [1979Kuz]
h- τ_3 , TaCoB	hP9	a=0.59264(1)	This work

	P $\bar{6}$ 2m (189) ZrNiAl	c=0.32467(5)	
τ_3 , TaCoB	oP30 Pmmn (59) NbCoB	a=0.3259 b=1.7070 c=0.5920 a=0.3255 b=1.7049 c=0.5907	[1973Kuz] This work
τ_4 , TaCo ₂ B	mP16 P2 ₁ /c (14) NbCo ₂ B	a=0.91677 (0.9159) b=0.64186 (0.6418) c=0.62934 (0.6294) $\beta=110.019^\circ$ (109.900)	X-ray SC (powder), This work
τ_5 , Ta _{2-x} Co _{21+x} B ₆	cF116 Fm $\bar{3}$ m (225) W ₂ Cr ₂₁ C ₆	a=1.0548-1.0549 a=1.0515-1.0562 a=1.0552 a=1.0505 a=1.0576	for x=0 and in $\tau_5+\tau_4+\text{Co}_2\text{B}$ [1964Sta] 0 $\leq$ x $\leq$ 1 [1979Ste1] for Ta _{2.18} Co _{20.82} B ₆ [1989Sta] X-ray SC for Ta _{0.97} Co _{22.03} B ₆ this work for Ta _{2.48} Co _{20.52} B ₆ , this work
Ta ₃ Co ₅ B ₂	tP20 P4/mbm (127) Ti ₃ Co ₅ B ₂	a=0.846, c=0.3083	[1979Kuz] not observed in this work (unstable?)

7.2 Solutions from SC-Analysis

Appendix Tab. 2a: X-ray single crystal data for Nb(Co,Fe)B (ZrNiAl-type, space group $P\bar{6}2m$; No 189) standardized with program *Structure Tidy*; room temperature data, redundancy >8). ADP's (U_{ij}) are given in [10^2 nm^2].

Parameter	NbCo _{0.82} Fe _{0.18} B
Co:Fe ratio from EPMA	4.5:1 (NbCo _{0.82} Fe _{0.18} B)
Composition from refinement	NbCo _{0.82} Fe _{0.18} B
a [nm], c [nm]	0.59679(2), 0.32419(1)
μ_{abs} [mm ⁻¹]	19.98
Data collection, 2 θ range (°)	3 ≤ 2 θ ≤ 70; 150 sec/frame
Total number of frames	534; scan width=2°
Reflections in refinement	191 ≥ 4 σ (F _o) of 191
Mosaicity	<0.5
Number of variables	14
R _F ² = $\Sigma F_o^2 - F_c^2 /\Sigma F_o^2$	0.0190
R _{int}	0.0283
wR2	0.0451
GOF	1.138
Extinction (Zachariasen)	0.138(9)
Nb1 in 3f (x,0,0); occ.=1	0.5871(1)
U ₁₁ ; U ₂₂ ; U ₃₃	0.0050(3); 0.0044(3); 0.0044(3)
U ₁₂	0.0022(2)
Co1 in 3g (x,0,1/2); occ.=0.819	0.2420(2)
U ₁₁ ; U ₂₂ ; U ₃₃	0.0049(4); 0.0050(5); 0.0138(5)
U ₁₂	0.0025(3)
Fe1 in 3g (x,0,1/2); occ.=0.181	0.2420(2)
U ₁₁ ; U ₂₂ ; U ₃₃	0.0049(4); 0.0050(5); 0.0138(5)
U ₁₂	0.0025(3)
B1 in 1a (0,0,0); occ.=1	-
U _{iso}	0.009(3)
B2 in 2d (1/3,2/3,1/2); occ.=1	-
U _{iso}	0.005(2)
Residual density; max; min [e/1000nm ³]	0.67 (0.166 nm from Nb1); -0.66 (0.058 nm from Nb1)
Principal mean square atomic displacements U; U _{eq}	Nb1: 0.0053 0.0044 0.0044; 0.0047(2) (Co1,Fe1): 0.0138 0.0050 0.0049; 0.0079(3)

Appendix Tab. 2b: Interatomic distances for Nb(Co,Fe)B; standard deviations less than 0.0003 nm (Co1 denotes the mixed position Co1|Fe1).

Nb1	4B2	0.2422	Co1	2B1	0.2171	B1	6Co1	0.2171	B2	3Co1	0.2311
	1B1	0.2464		2B2	0.2311		3Nb1	0.2464		6Nb1	0.2422
	2Co1	0.2621		2Co1	0.2501						
	4Co1	0.2688		2Nb1	0.2621						
	4Nb1	0.3117		4Nb1	0.2688						
	2Nb1	0.3242		2Co1	0.3242						

Appendix Tab. 3a: X-ray single crystal data for {Nb,Ta}Co₂B (standardized with program *Structure Tidy*; room temperature data, redundancy >8); space group *Cmce*; No. 64. ADP's (U_{ij}) are given in [10^2nm^2].

<i>Parameter</i>	<i>NbCo₂B</i>	<i>TaCo₂B</i>
Co/M-ratio from EPMA	2.1	2.0
Composition from refinement	NbCo ₂ B	TaCo ₂ B
a [nm], b [nm], c [nm]	0.63162(3), 1.72710(7), 0.64270(3)	0.62934(2), 1.7276(6), 0.64186(5)
μ_{abs} [mm ⁻¹]	24.53	80.99
Data collection, 2 θ range (°)	3 ≤ 2 θ ≤ 70; 80 sec/frame	3 ≤ 2 θ ≤ 70; 150 sec/frame
Total number of frames	512; scan width=2°	475; scan width=2°
Reflections in refinement	578 ≥ 4 σ (F_o) of 829	609 ≥ 4 σ (F_o) of 814
Mosaicity	<0.5	<0.5
Number of variables	34	34
$R_F^2 = \sum F_o^2 - F_c^2 / \sum F_o^2$	0.0418	0.0409
R_{int}	0.1308	0.1044
wR2	0.0957	0.1375
GOF	1.517	1.262
Extinction (Zachariasen)	0.0020(2)	0.0056(4)
M1 in 8f (0,y,z); occ.=1 U ₁₁ ; U ₂₂ ; U ₃₃ U ₂₃	0.0299(1); 0.2329(2) 0.0059(4); 0.0048(3); 0.0008(4) -0.0004(2)	0.0294(1); 0.2333(1) 0.0048(4); 0.0041(4); 0.0005(4) -0.0003(2)
M2 in 8e (1/4,y,1/4); occ.=1 U ₁₁ ; U ₂₂ ; U ₃₃ U ₁₃	0.2803(1) 0.0046(4); 0.0045(3); 0.0120(4) -0.0003(3)	0.2795(1) 0.0038(4); 0.0051(4); 0.0120(4) 0.0001(2)
Co1 in 16g (x,y,z); occ.=1 U ₁₁ isotropic	0.2261(2); 0.4272(1); 0.0562(2) 0.0034(2)	0.2268(3); 0.4273(1); 0.0560(2) 0.0031(3)
Co2 in 8f (0,y,z); occ.=1 U ₁₁ ; U ₂₂ ; U ₃₃ U ₂₃	0.1740(1); 0.0546(3) 0.0230 (7); 0.0070(5); 0.0055(6) -0.0001(4)	0.1743(1); 0.0550(4) 0.0231 (9); 0.0051(6); 0.0046(8) 0.0004(6)
Co3 in 8f (0,y,z); occ.=1 U ₁₁ ; U ₂₂ ; U ₃₃ U ₂₃	0.1806(1); 0.4427(3) 0.0239(8); 0.0059(5); 0.0053(5) -0.0004(4)	0.1803(1); 0.4424(3) 0.0196(9); 0.0050(6); 0.0056(8) -0.0003(7)
B1 in 8f (0,y,z); occ.=1 U _{iso}	0.3884(6); 0.278(2) 0.084(2)	0.3848(8); 0.270(3) 0.003(3)
B2 in 8e (1/4,y,1/4); occ.=1 U _{iso}	0.1360(5) 0.009(2)	0.139(1) 0.009(3)
Residual density; max; min [$\text{\AA}^{-3}$]	4.10 (0.008 nm from Co1); -4.80 (0.041 nm from Co1)	9.86 (0.050 nm from Ta1); -4.31 (0.06 nm from Ta1)
Principal mean square atomic displacements U; U _{eq}	Nb1: 0.0059 0.0049 0.0008; 0.0038(2) Nb2: 0.0120 0.0046 0.0045; 0.0071(2) Co2: 0.0230 0.0070 0.0055; 0.0118(3) Co3: 0.0239 0.0059 0.0053; 0.0117(3)	Ta1: 0.0048 0.0041 0.0005; 0.0031(3) Ta2: 0.0119 0.0051 0.0038; 0.0070(3) Co2: 0.0231 0.0053 0.0044; 0.0109(4) Co3: 0.0196 0.0057 0.0048; 0.0100(4)

Appendix Tab. 3b: Interatomic distances for NbCo₂B; standard deviations less than 0.0003 nm.

Nb1	2B2	0.2422	Co1	2Co2	0.2728	Co2	1B1	0.2078	B1 6[9]*	1Co2	0.2078
	1B1	0.2446		2Co1	0.2832		2B2	0.2122		2Co1	0.2127
	2Co1	0.2628		2Nb2	0.3158		1Co3	0.2497		2Co1	0.2139
	2Co1	0.2645					2Co1	0.2651		1Nb1	0.2446
	2Co1	0.2651		1B1	0.2127		1Co3	0.2613		2Nb2	0.2454
	2Co1	0.2726		1B1	0.2139		2Nb2	0.2636		1Co3	0.2464
	1Co2	0.2741		1B2	0.2256		2Nb2	0.2728			
	1Co3	0.2934		1Co3	0.2459		1Nb1	0.2741		B2 6[9]	2Co2
	2Nb1	0.3166		1Co1	0.2509	Co3	2B2	0.2150		2Co3	0.2150
	1Nb1	0.3166		1Co2	0.2561		2Co1	0.2459		2Co1	0.2558
Nb2	2B1	0.2454	1Co1	0.2618	1B1		0.2464	2Nb1	0.2442		
	1B2	0.2493	1Nb1	0.2628	1Co2		0.2497	1Nb2	0.2493		
	2Co3	0.2616	1Nb1	0.2645	1Co2	0.2613					
	2Co2	0.2636	1Nb1	0.2651	2Nb2	0.2618					
	2Co3	0.2644	1Nb1	0.2726	2Nb2	0.2644					
			1Nb2	0.2832	1Nb1	0.2934					
			1Co1	0.2856							

Appendix Tab. 3c: Central positions in empty octahedra and distances to neighbouring atoms for NbCo₂B.

A1 in 4b: $\frac{1}{2} \frac{1}{2} \frac{1}{2}$	A1	2Nb1	0.1793	A2	2Nb1	0.1583	A3	2Nb2	0.1690
A2 in 4a: $0 \frac{1}{2} \frac{1}{2}$	6[8]	4Co1	0.1937	6[8]	4Co1	0.2170	6[8]	2Co3	0.2016
A3 in 8c: $\frac{1}{4} \frac{1}{4} \frac{1}{2}$		2B1	0.2630		2B1	0.2398		2Co2	0.2084
								2B2	0.2542

*Coordination numbers. Values in the squared brackets denote coordination number for second coordination figure around the atoms.

Appendix Tab. 4a: X-ray single crystal data for {Nb,Ta}Co₂B (standardized with program *Structure Tidy*; room temperature data, redundancy >8); space group *P2₁/c*; No. 14. ADP (*U_{ij}*) are given in [10²nm²].

<i>Parameter</i>	<i>NbCo₂B</i>	<i>TaCo₂B</i>
Co/M-ratio from EPMA	2.1	2.0
Composition from refinement	NbCo ₂ B	TaCo ₂ B
<i>a</i> [nm], <i>b</i> [nm], <i>c</i> [nm], β [°]	0.9190(6), 0.64263(2), 0.63144(2), 109.954(6)	0.91677(3), 0.64186(5), 0.62934(2), 110.019(2)
μ_{abs} [mm ⁻¹]	24.55	81.01
Data collection, 2 θ range (°)	3 ≤ 2 θ ≤ 70; 80 sec/frame	3 ≤ 2 θ ≤ 70; 150 sec/frame
Total number of frames	512; scan width=2°	475; scan width=2°
Reflections in refinement	1032 ≥ 4 σ (<i>F_o</i>) of 1518	1135 ≥ 4 σ (<i>F_o</i>) of 1514
Mosaicity	<0.5	<0.5
Number of variables	64	64
$R_F^2 = \Sigma F_o^2 - F_c^2 / \Sigma F_o^2$	0.0313	0.0420
<i>R_{int}</i>	0.0388	0.0620
<i>wR2</i>	0.0879	0.1424
GOF	1.100	1.219
Extinction (Zachariasen)	0.0104(5)	0.0246(2)
M1 in 4e (x,y,z); occ.=1 <i>U₁₁</i> ; <i>U₂₂</i> ; <i>U₃₃</i> <i>U₂₃</i> ; <i>U₁₃</i> ; <i>U₁₂</i>	0.0601(1); 0.2331(1); 0.0300(1) 0.0055(3); 0.0020(2); 0.0060(3) -0.0003(2); 0.0020(2); -0.0001(2)	0.0588(1); 0.2336(1); 0.0297(1) 0.0041(3); 0.0012(3); 0.0046(3) 0.0001(1); 0.0016(2); -0.0002(1)
M2 in 4e (x,y,z); occ.=1 <i>U₁₁</i> ; <i>U₂₂</i> ; <i>U₃₃</i> <i>U₂₃</i> ; <i>U₁₃</i> ; <i>U₁₂</i>	0.5601(1); 0.2562(1); 0.0303(2) 0.0056(3); 0.0116(3); 0.0046(3) -0.0001(2); 0.0018(3) 0.0002(2)	0.5590(1); 0.2532(1); 0.0292(1) 0.0053(3); 0.0114(3); 0.0050(3) -0.0000(1); 0.0030(2) 0.0000(1)
Co1 in 4e (x,y,z); occ.=1 <i>U₁₁</i> ; <i>U₂₂</i> ; <i>U₃₃</i> <i>U₂₃</i> ; <i>U₁₃</i> ; <i>U₁₂</i>	0.1434(1); 0.5566(2); 0.2979(2) 0.0063(3); 0.0049(3); 0.0048(3) 0.0000(3); 0.0023(3); -0.0003(3)	0.1447(2); 0.5560(2); 0.2994(2) 0.0030(3) -
Co2 in 4e (x,y,z); occ.=1 <i>U₁₁</i> ; <i>U₂₂</i> ; <i>U₃₃</i> <i>U₂₃</i> ; <i>U₁₃</i> ; <i>U₁₂</i>	0.3484(2); 0.0547(2); 0.1639(2) 0.0055 (4); 0.0054(4); 0.0189(4) 0.0001(3); 0.0024(3); -0.0002(3)	0.3490(2); 0.0546(3); 0.1689(3) 0.0058 (5); 0.0051(6); 0.0193(6) -0.0005(6); 0.0032(5); 0.0004(5)
Co3 in 4e (x,y,z); occ.=1 <i>U₁₁</i> ; <i>U₂₂</i> ; <i>U₃₃</i> <i>U₂₃</i> ; <i>U₁₃</i> ; <i>U₁₂</i>	0.3606(2); 0.4424(2); 0.1903(2) 0.0055(4); 0.0056(4); 0.0181(4) -0.0002(3); 0.0023(3); 0.0004(3)	0.3608(2); 0.4428(3); 0.1857(3) 0.0052(5); 0.0052(6); 0.0175(6) 0.0003(6); 0.0028(5); -0.0003(5)
Co4 in 4e (x,y,z); occ.=1 <i>U₁₁</i> ; <i>U₂₂</i> ; <i>U₃₃</i> <i>U₂₃</i> ; <i>U₁₃</i> ; <i>U₁₂</i>	0.8525(1); 0.4443(2); 0.1521(2) 0.0064(3); 0.0048(3); 0.0021(3) -0.0001(3); 0.0024(3); -0.0002(3)	0.8536(2); 0.4446(2); 0.1538(2) 0.0029(3) -
B1 in 4e (x,y,z); occ.=1 <i>U_{iso}</i>	0.2258(9); 0.775(2); 0.112(2) 0.007(2)	0.230(2); 0.769(2); 0.113(2) 0.005(2)
B2 in 4e (x,y,z); occ.=1 <i>U_{iso}</i>	0.274(2); 0.241(1); 0.387(2) 0.012(2)	0.279(2); 0.247(2); 0.387(3) 0.011(3)
Residual density; max; min [e/1000nm ³]	2.57 (0.058 nm from Co3); -2.79 (0.061 nm from Co1)	7.76 (0.054 nm from Ta1); -5.03 (0.06 nm from Ta2)
Principal mean square atomic displacements <i>U</i> ; <i>U_{eq}</i> .	Nb1: 0.0060, 0.0054, 0.0020; 0.0045(2) Nb2: 0.0116, 0.0058, 0.0055; 0.0076(2) Co1: 0.0064, 0.0049, 0.0019; 0.0044(2) Co2: 0.0204, 0.0057, 0.0052; 0.0104(2) Co3: 0.0195, 0.0060, 0.0051; 0.0102(2) Co4: 0.0064, 0.0046, 0.0014; 0.0042(2)	Ta1: 0.0046, 0.0040, 0.0012; 0.0033(2) Ta2: 0.0114, 0.0061, 0.0033; 0.0070(2) Co2: 0.0203, 0.0059, 0.0048; 0.0103(3) Co3: 0.0185, 0.0054, 0.0048; 0.0069(3)

Appendix Tab. 4b: Interatomic distances for NbCo₂B; standard deviations less than 0.0003 nm.

Nb1	B2	0.2434	Co1	B1	0.2124	Co3	B2	0.2129	B1 6[9]*	Co2	0.2090		
	B2	0.2437		B1	0.2161		B2	0.2153		Co4	0.2113		
	B1	0.2470		B2	0.2329		Co1	0.2431		Co1	0.2124		
	Co1	0.2624		Co3	0.2431		B1	0.2432		Co4	0.2156		
	Co4	0.2626		Co4	0.2510		Co4	0.2480		Co1	0.2161		
	Co1	0.2639		Co2	0.2535		Co2	0.2497		Co3	0.2432		
	Co1	0.2640		Co4	0.2615		Nb2	0.2614		Nb2	0.2436		
	Co4	0.2649		Nb1	0.2624		Co2	0.2616		Nb2	0.2438		
	Co4	0.2661		Nb1	0.2639		Nb2	0.2629		Nb1	0.2470		
	Co1	0.2712		Nb1	0.2640		Nb2	0.2630		B2 6[9]	Co2	0.2104	
	Co2	0.2742		Nb1	0.2712		Nb2	0.2661			Co3	0.2129	
	Co4	0.2744		Co4	0.2855		Nb1	0.2924			Co2	0.2131	
	Co3	0.2924		Nb2	0.2869		Co4	B1			0.2113	Co3	0.2153
	2Nb1	0.3165		Co2	B1			0.2156			Co4	0.2202	
	Nb1	0.3171			B2			0.2202			Co1	0.2329	
Nb2	B1	0.2436	B2		0.2131	Co3		0.2480	Nb1		0.2434		
	B1	0.2438	Co3		0.2497	Co1		0.2510	Nb1		0.2437		
	B2	0.2469	Co1		0.2535	Co2	0.2593	Nb2	0.2469				
	Co3	0.2614	Co4	0.2593	Co1	0.2615							
	Co2	0.2628	Co3	0.2616	Nb1	0.2626							
	Co3	0.2629	Nb2	0.2628	Nb1	0.2649							
	Co3	0.2630	Nb2	0.2647	Nb1	0.2661							
	Co2	0.2647	Nb2	0.2701	Nb1	0.2744							
	Co3	0.2661	Nb1	0.2742	Nb2	0.2804							
	Co2	0.2701	Nb2	0.2746	Co1	0.2855							
	Co2	0.2746											
	Co4	0.2804											
	Co1	0.2869											
	2Nb2	0.3158											

Appendix Tab. 4c: Central positions in empty octahedral and distances to neighboring atoms for NbCo₂B.

A1 in 2a: 0; 0; 0	A1	2Nb1	0.1586	A2	2Nb	0.1727	A3	2Nb1	0.1792	A4	2Nb2	0.1650
A2 in 2b: ½; 0; 0	6[8]	2Co1	0.2155	6[8]	2Co3	0.1973	6[8]	2Co1	0.1928	6[8]	2Co3	0.2067
A3 in 2c: 0; ½; 0		2Co4	0.2182		2Co2	0.2030		2Co4	0.1944		2Co2	0.2133
A4 in 2d: ½; ½; 0		2B1	0.2430		2B2	0.2565		2B1	0.2630		2B2	0.2488

* Coordination numbers. Values in the squared brackets denote coordination number for second coordination figure around the atoms.

Appendix Tab. 5a: X-ray single crystal data for {Nb,Ta}(Co,Ni)₂B (Re₃B-type, space group *Cmcm*, No. 63; standardized with program *Structure Tidy*; room temperature data, redundancy >8); ADP's (U_{ij}) are given in [10²nm²].

<i>Parameter</i>	<i>Nb(Co,Ni)₂B</i>	<i>Ta(Co,Ni)₂B</i>
Composition from EPMA	Nb ₄ Co _{6.16} Ni _{1.84} B ₄	Ta ₄ Co _{6.16} Ni _{1.84} B ₄
Composition from refinement	Nb ₄ Co _{6.16} Ni _{1.84} B ₄	Ta ₄ Co _{6.16} Ni _{1.84} B ₄
<i>a</i> [nm], <i>b</i> [nm], <i>c</i> [nm]	0.32026(2), 0.85837(4), 0.63762(3)	0.31847(1), 0.85667(4), 0.63772(3)
μ _{abs} [mm ⁻¹]	25.82	82.28
Data collection, 2θ range (°)	3 ≤ 2θ ≤ 70; 150 sec/frame	3 ≤ 2θ ≤ 70; 150 sec/frame
Total number of frames	471; scan width=2°	458; scan width=2°
Reflections in refinement	237 ≥ 4σ(F _o) of 237	234 ≥ 4σ(F _o) of 236
Mosaicity	<0.5	<0.5
Number of variables	16	16
R _F ² = Σ F _o ² - F _c ² /ΣF _o ²	0.0184	0.0239
R _{int}	0.0413	0.0560
wR2	0.0472	0.0621
GOF	1.086	1.187
Extinction (Zachariasen)	0.094(5)	0.0056(4)
Nb1 in 4c (0,y,1/4); occ.=1	0.44197(4)	0.44257(3)
U ₁₁ ; U ₂₂ ; U ₃₃	0.0050(2); 0.0051(2); 0.0048(2)	0.0014(3); 0.0038(3); 0.0056(3)
Co1 in 8f (0,y,z); occ.=0.774	0.14633(4); 0.05635(6)	0.14589(1); 0.0565(2)
U ₁₁ ; U ₂₂ ; U ₃₃	0.0091(3); 0.0060(3); 0.0034(3)	0.0059(5); 0.0044(4); 0.0041(4)
U ₂₃	0.0000(1)	0.0002(3)
Ni1 in 8f (0,y,z); occ.=0.226	0.14633(4); 0.05635(6)	0.14589(1); 0.0565(2)
U ₁₁ ; U ₂₂ ; U ₃₃	0.0091(3); 0.0060(3); 0.0034(3)	0.0059(5); 0.0044(4); 0.0041(4)
U ₂₃	0.0000(1)	0.0002(3)
B1 in 4c (0,y,1/4); occ.=1	0.7296(6)	0.729(2)
U _{iso}	0.0082(7)	0.003(3)
Residual density; max; min [e/1000nm ³]	0.89 (0.12 nm from B1); -2.19 (0.06 nm from Nb1)	4.60 (0.07 nm from Ta1); -3.98 (0.06 nm from Ta1)
Principal mean square atomic displacements U; U _{eq} .	Nb1: 0.0051, 0.0050, 0.0048; 0.0050(2) Co1: 0.0092, 0.0060, 0.0034; 0.0062(2) Ni1: 0.0092, 0.0060, 0.0034; 0.0062(2)	Ta1: 0.0056 0.0038 0.0014; 0.0036(3) Co1: 0.0059 0.0044 0.0040; 0.0048(3) Ni1: 0.0059 0.0044 0.0040; 0.0048(3)

Appendix Tab. 5b: Interatomic distances for Nb(Co,Ni)₂B; standard deviations less than 0.0003 nm.

Nb1	2B1	0.2426	B1	4Co1	0.2145
	B1	0.2469		2Co1	0.2225
	4Co1	0.2637		2Nb1	0.2426
	4Co1	0.2677		Nb1	0.2469
	2Co1	0.2822			
	2Nb1	0.3203			
	2Nb1	0.3340			
Co1 Ni1	2B1	0.2145			
	B1	0.2225			
	3Co1	0.2470			
	Co1	0.2613			
	2Nb1	0.2637			
	2Nb1	0.2677			
	Nb1	0.2822			

Appendix Tab. 5c: Central positions in empty octahedra and distances to neighboring atoms for Nb(Co,Ni)₂B.

A in 4b: 0 ½ 0	A	2Nb1	0.16701
		4Co1	0.20666
		2B1	0.25349

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Curriculum Vitae

Personal Data:

Date of Birth: 21st April 1988
Place of Birth: Eisenstadt, Austria
Citizenship: Austria

Education:

1994 - 1998 Primary School in St. Georgen, Eisenstadt
1998 - 2002 Secondary School; Hauptschule Theresianum, Eisenstadt
2002 - 2006 High school; BRG Kurzweide, Eisenstadt, Graduation with honors
(June 2006)

Studies at the University of Vienna

2006-2009 Bachelor Study of Chemistry (Graduation June 2009, Bakk.rer.nat.)
Since March 2007 Diploma Study of Mathematics
Since October 2009 Master Study of Chemie

Sept 2008-Feb 2009 Erasmus-study-visit in Lisbon, Portugal

Publication:

Ewa Bogel-Lukasik, Julia Wind, Rafał Bogel-Lukasik, Manuel Nunes da Ponte; "The influence of hydrogen pressure on the heterogeneous hydrogenation of β -myrcene in a CO₂-expanded liquid"; The Journal of Supercritical Fluids, 54(1), 46-52, 2010