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The structure of the 21 K superconductor $\text{ThPd}_x\text{B}_{6-2x}$, $x = 0.65$, determined by quantitative electron diffraction and through-focus electron holography

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ABSTRACT

Through-focus electron holography and quantitative electron diffraction have been applied to determine the structure of the 21 K superconductor $\text{ThPd}_x\text{B}_{6-2x}$ with $x \approx 0.65$. This compound adopts a cubic structure ($a = 0.42$ nm; space group, $Pm\bar{3}m$), which is an intermediate between the structures of the CaB_6 and Cu_3Au . Short-range ordering results in a superstructure as is evident from diffuse streaks in the electron diffraction pattern.

§ 1 INTRODUCTION

Recently Cava *et al.* (1994a, b), Nagajaran *et al.* (1994) and Sarrao *et al.* (1994) have reported superconductivity in a number of intermetallic compounds containing B and C. Many of the reported intermetallic compounds having the highest values of T_c adopt a structure like that of $\text{LuNi}_2\text{B}_2\text{C}$ (Siegrist *et al.* 1994, Zandbergen, Cava, Krajewski and Peck 1994a). For most systems, the determination of the superconducting phase was fairly straightforward. However, in two systems the identification of the superconducting phase turned out to be difficult: Y–Pd–B–C and Th–Pd–B–C. In the first system, this is caused by the difficulty in preparing a specimen with the superconducting compound as the major phase. In the second system, two superconducting phases are actually present having T_c values of 14.5 and 21 K. Whereas evidence has been obtained that the superconducting phase in the system Y–Pd–B–C is $\text{YPd}_2\text{B}_{2-x}\text{C}$ (Fujii *et al.* 1994, Zandbergen, Cava, Krajewski and Peck 1994b), no definite proof has yet been presented. In the system Th–Pd–B–C it was established that the 14.5 K superconductor in $\text{ThPd}_2\text{B}_2\text{C}$ (Sarrao *et al.* 1994, Zandbergen *et al.* 1994d). Electron-probe microanalysis and electron diffraction (Zandbergen *et al.* 1994c) indicated that the 21 K superconductor has the approximate composition $\text{ThPd}_{0.7}\text{B}_5\text{C}_x$ (x small or zero) and a cubic unit cell with $a = 0.415$ nm. However, the atomic structure of the phase is still lacking.

For the 21 K superconducting phase in the system Th–Pd–B–C, the positions of the atoms and their occupancies are of fundamental importance for the interpretation of the

physical properties. Since no single crystals are available, and since the specimens with the highest superconducting fraction contain only 40% of the superconducting phase, conventional structure determination methods such as X-ray single-crystal diffraction and neutron powder diffraction cannot be applied. Therefore we used quantitative electron diffraction and through-focus exit-wave reconstruction to determine the structure of this phase. The latter method is also called through-focus electron holography (van Dyck and op de Beeck 1990, Coene, Janssen, op de Beeck and van Dyck 1992), because both amplitude and phase information are obtained.

§ 2. EXPERIMENTAL DETAILS

Electron-transparent areas of a specimen with nominal composition $\text{ThPd}_3\text{B}_3\text{C}$, prepared by arc melting (Sarroa *et al.* 1994), were obtained by crushing. Electron microscopy was performed with a Philips CM30ST electron microscope with a field emission gun operated at 300 kV. The high-resolution images and the electron diffraction patterns were recorded using a Tietz software package and a 1024×1024 pixel Photometrix charge-coupled device (CCD) camera having a dynamic range of 12 bits. The images were binned, resulting in 512×512 pixel images.

§ 3. STRUCTURE REFINEMENT FROM ELECTRON DIFFRACTION DATA

A most important requirement in the recording of electron diffraction data is that the diffracting region is very thin (less than 3 nm). This is essential because the interaction of the electrons with a specimen is very strong, resulting in dynamical scattering, which will change the intensities of all reflections with respect to each other as a function of the specimen thickness. If such a change has occurred, the intensities of the reflections cannot be used for structure determination unless the dynamical scattering is taken into account. In structure determinations using X-ray diffraction and neutron diffraction, the contribution of the dynamical scattering is in general negligible, which allows straightforward structure determination (assuming only kinematical diffraction). The use of the intensities obtained by electron diffraction in kinematical structure refinement requires the specimen thickness to be in the range 1–5 nm, depending on the scattering potential of the specimen. To test the effect of the specimen thickness, for example the contribution of the dynamical scattering, diffraction patterns of $\text{ThPd}_2\text{B}_2\text{C}$ with full occupancies of the C and B sites were calculated using a multislice simulation program EMS (Stadelmann 1987) for thicknesses from 0.4 to 6 nm. After correction for the curvature of the Ewald sphere in a kinematical approach, structure refinements were performed with an XTAL3.2 program (Hall and Stewart 1993) with scattering potentials for electron scattering and purely kinematical scattering. It was observed that the occupancies of the B and C sites were very dependent on the specimen thickness. Reliable occupancies of the B and C sites could only be obtained for thicknesses up to about 1.2 nm.

To obtain diffraction information from regions about 1.5 nm thick, a very thin edge of a crystal was selected in high-resolution mode, after tilting the crystal to the required orientation. This edge was searched in diffraction mode with an electron beam 10 nm wide for diffraction patterns in which the Friedel pairs were almost equal, because quite often the very thin areas are bent from the bulk orientation. Alternatively, the electron beam can be tilted to correct for a small misalignment of the diffracting area. To reduce the electron-microscope-induced contamination, the specimen was cooled to about 100 K. Typical CCD exposure times were 10–50 ms.

A number of diffraction patterns were recorded in [100], [110], [111] and [120]

Atomic positional parameters, isotropic temperature factors and occupancies for $\text{ThPd}_{0.65}\text{B}_{4.7}$ with the cubic space group $Pm\bar{3}m$. Th and Pd positions are determined from the electron diffraction data. The B positions are deduced from the through-focus exit wave reconstruction.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ($\text{\AA}^2$)	<i>n</i>
Th	0	0	0	0.043(6)	1
Pd	$\frac{1}{2}$	$\frac{1}{2}$	0	0.027(11)	0.22 ^b
B	$\frac{1}{2}$	$\frac{1}{2}$	0.21 ^a		0.78 ^c

^a The position occurring in CaB_6 is taken and not refined.

^b This value of *n* is taken from electron EPMA (Zandbergen *et al.* 1994c). Refinement results in $n(\text{Pd}) = 0.24(1)$.

^c This value is taken using $n(\text{Pd}) = 0.22$ and the general composition formula $\text{ThPd}_x\text{B}_{6-2x}$.

orientations. The intensities of the reflections were corrected for the misorientation of the crystal fragment and for the curvature of the Ewald sphere assuming a specimen thickness of 2 nm. Refinement using XTAL3.2 was done with the whole set of data for the four orientations, each with its own refinable scale factor. Symmetry-related reflections were not averaged but were used independently. Refinement (90 significant reflections (greater than 2σ)) was started with Th at 0, 0, 0 and Pd at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ with an occupancy of 0.66. This, however, resulted in about zero occupancy of the Pd site. Fourier analysis showed a strong peak $\frac{1}{2}, \frac{1}{2}, 0$, indicating that Pd partially occupies this position. Refinement of a model with Th on 0, 0, 0 and Pd on $\frac{1}{2}, \frac{1}{2}, 0$ with an occupancy of 0.22 resulted in *R* values ($R = 22\%$; $R_w = 15.5\%$) indicating that this structure is basically correct. Addition of the B atoms at the positions occurring in CaB_6 or any other position suggested by Fourier analysis did not result in a lower *R* value or significant occupancies. Thus the position of the B atoms could not be determined by this method. The final results are listed in the table.

The inability to detect B by the kinematic structure refinement of the electron diffraction data can be explained in two ways: firstly the dynamical scattering is already too strong, which is quite plausible since the crystal has to be less than about 1.5 nm thick, and secondly the presence of the B vacancies might lead to shifts of the other B atoms, which will result in a smearing out of the positionally averaged B atom, since many variants of the Pd occupations of the six cube faces can occur locally.

§ 4. STRUCTURE DETERMINATION FROM THROUGH-FOCUS ELECTRON HOLOGRAPHY

Through-focus holography is a new electron microscopy technique (Van Dyck and op de Beeck 1990, Coene *et al.* 1992) which combines the information from a series of high-resolution electron microscopy images to give detailed information which is not distorted by the optics of the electron microscope. In conventional high-resolution electron microscopy, one often chooses a defocus setting and objective aperture which provides information up to the point resolution of the electron microscope. This point resolution defines the minimum distance at which, for a very thin specimen, two individual atoms can still be distinguished. Information beyond this point resolution is present in the image but is scrambled by the imperfect optics of the microscope. The point resolution is mainly set by the aberrations of the objective lens. The information limit of the microscope, on the other hand, is mainly determined by the energy spread of the electrons and the microscope's vibration. For most electron microscopes the

information limit reaches quite far beyond the point resolution, being 0.14 and 0.20 nm respectively for the electron microscope used in this study.

The through-focus exit wave reconstruction uses the focus dependence of the image distortion by the electron microscope to restore the distortion by the microscope optics. Using algorithms developed by van Dyck and op de Beeck (1990) and Coene *et al.* (1992), all the useful information is extracted from a series of high-resolution electron microscopy images taken at different defocus values with well defined defocus increments. The result is the exit wavefunction which contains amplitude as well as phase information up to the information limit of the microscope. The exit wave is the electron wave at the exit of the specimen. Since the electron wave passing through the crystal is continuously changed, the exit wavefunction is still thickness dependent, but not dependent on the distortion introduced by the electron microscope. As

Fig. 1

(a) Phase and (b) amplitude of the reconstructed exit wave of $\text{ThPd}_{0.65}\text{B}_{4.7}$ viewed along the a axis. (c) Enlargement of part of the phase image showing the non-random distribution of Pd. The dark dots resulting from a relatively high number of Pd atoms are indicated by arrowheads. The Th atoms in the upper left corner are indicated. The crystal is about five unit cells (2 nm) thick along the viewing direction. Note that the dark dots at the positions of the Th atoms also show a rather strong variation, indicating that the thickness of the crystal varies locally. (d) A $[111]$ diffraction pattern with diffuse scattering.

such it provides major advantages over conventional high-resolution electron microscopy.

The parameters required as input for the exit wave reconstruction from the experimental images are as follows:

- (1) The spherical aberration of the objective lens, which was determined to be 1.35 mm from a through-focus series of an amorphous film by the method described by Coene and Denteneer (1991);
- (2) the defocus step, which was determined to be 5.2 nm from the focus increment necessary to obtain a repeat in the structure image of MgO;
- (3) the starting focus, which can be estimated from the contrast bands in the Fourier transform resulting from the amorphous part in the images (accuracy about 4 nm).

After the exit wave is calculated, the starting defocus can be fine tuned by minimization of the contrast in the amplitude of the amorphous areas (1–2 nm accuracy).

Since the structure contains Th, Pd and B, the imaging of B will be rather difficult because of the huge difference in scattering cross-sections. consequently, the imaging of the B atoms requires sophisticated data analysis.

Using the atomic coordinates of Th and Pd as determined by electron diffraction and the B atoms at the B site in CaB_6 , exit wavefunctions were calculated for crystal thicknesses from 1 to 5 nm. Exit wavefunctions were also calculated for a model without

Fig. 2

Comparison of experimental and calculated phase images of 3×3 unit cells. The very dark dots are the Th atoms as indicated in the schematic projection of the structure in (d). (a) Part of the phase of the experimental exit wave shown in fig. 1 (a) but averaged over 12 unit cells and averaged according to the symmetries of space group $Pm\bar{3}m$. (b), (c) The phase of the calculated exit waves of the models (b) with and (c) without B for a thickness of 1.6 nm convoluted with a microscope vibration function. (e), (f) The difference images obtained by subtracting the calculated images from the experimental image (a).

B. A significant distinction between the absence or presence of B could only be obtained for the phase part of the exit wave because B is a weak scatterer, resulting in hardly any amplitude contrast.

Figure 1 shows the experimental exit wavefunction (phase and amplitude). Figure 2(a) shows a part of the phase image, image processed such that it is averaged over 12 (3×4) unit cells and averaged according to the symmetries of the space group (mirror planes parallel to (100) and (110) and the fourfold axis). Visual comparison of the averaged experimental exit wavefunction with the set of calculated images reveals that the black dots corresponding to the atom columns of Th and Pd are larger than those of the calculated images. This is caused by the mechanical vibration of the electron microscope. Convolution of the calculated phase images for a sample thickness of 1.6 nm with a Gaussian function (chosen so that a good fit with the shape of the experimental Th peak is obtained) resulted in the images in figs. 2(b) and (c). Good agreement is obtained only for the model with B present, which is in particular evident from the difference images obtained by subtraction of the calculated images from the experimental one (see figs. 2(d) and 2(e)). A considerable contribution to the difference image for the model with B present is obtained from the inaccuracy in the correction for the microscope vibration and from the subpixel mismatch between experimental and calculated image.

§ 5. DISCUSSION

From firstly no significant scattering at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ as shown by electron diffraction, secondly the difference images of the phase images of the experimental and calculated exit waves and thirdly the composition as determined by electron probe microanalysis (EPMA) (Zandbergen *et al.* 1994c), we conclude that B occupies positions similar to the B positions in CaB_6 , as given in the table.

The structure of $\text{ThPd}_{0.65}\text{B}_{4.7}$ is related to the CaB_6 structure. Whereas in the CaB_6 structure the cube faces are empty, in the $\text{ThPd}_{0.7}\text{B}_{4.6}$ structure the faces are partially filled by Pd. The presence of a Pd atom at a given cube face must result in the removal of the two neighbouring B atoms because the resulting interatomic distance would be too short (0.1 nm), as shown in fig. 3. This removal results in the general composition $\text{ThPd}_x\text{B}_{6-2x}$. No indications have been obtained of a solid solution with variable x , although at one limit a structure with completely filled cube faces is adopted by many metals and alloys (but not ThPd_3) and at the other limit ThB_6 exists. The Pd–Th distance

Fig. 3

Schematic representation of the structures of ThB_6 , $\text{ThPd}_{0.65}\text{B}_{4.7}$ and ThPd_3 . In the structure of $\text{ThPd}_{0.65}\text{B}_{4.7}$, only one Pd is situated in the middle of one of the faces, whereas on average the occupancy is 0.22. A Pd atom occupying a face results in a B vacancy as indicated in the figure.

is 0.293 nm. This distance agrees well with the distance of 0.293 nm occurring in ThPd_3 (Dwight, Downey and Conner 1961). The Th atoms could shift slightly, thus resulting in locally larger Th–Pd distances but this is rather unlikely because the thermal parameter of Th is quite normal. On the assumption that the B atoms are positioned according to the CaB_6 structure (Blum and Bertaut 1954), the Th–B and Pd–B bond lengths are 0.306 and 0.240 nm respectively, which are chemically reasonable. The local distribution of the Pd atoms over the possible sites on an atomic scale can be observed in the exit-wave phase images, given in figure 1 (c). In this figure, one can observe a strong variation in occupancy of the possible Pd sites, as is to be expected since only about a fifth of the available positions are occupied.

All crystals show the presence of a superstructure (see fig. 1 (d)), which is reflected in rather complicated diffuse scattering. The origin of the superstructure of $\text{ThPd}_{0.65}\text{B}_{4.7}$ must be very short ordered, since only diffuse scattering is observed. It is probably caused by a cluster-like ordering of the Pd atoms.

The CaB_6 structure has been reported for several superconductors (Matthias *et al.* 1968), for example ThB_6 is reported to have a T_c of 0.78 K and a T_c of 6.5–7.1 K is reported by YB_6 . This indicates that the CaB_6 structure is, in principle, a structure allowing a relatively high superconducting temperature. It is intriguing that in the Y–Pd–B–C system a phase with a structure similar to that of $\text{ThPd}_{0.65}\text{B}_{4.7}$ is also present: $\text{YPd}_{1.2}\text{B}_{3.3}$ (Zandbergen *et al.* 1994b), which also has a cubic unit cell with $a = 0.42$ nm, but with sharp superstructure reflections, indicating long-range order. In the case when $\text{YPd}_{1.2}\text{B}_{3.3}$ has an analogous structure to $\text{ThPd}_{0.65}\text{B}_{4.7}$ the composition should be $\text{YPd}_{1.2}\text{B}_{3.6}$, which is quite possible considering the inaccuracy in the determination of the B content by EPMA.

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