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HREM on $T_c = 14.5$ K superconducting $\text{ThPd}_2\text{B}_{2-x}\text{C}$

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Abstract

The compound $\text{ThPd}_2\text{B}_2\text{C}$ has been studied with high-resolution electron microscopy and electron diffraction. $\text{ThPd}_2\text{B}_{2-x}\text{C}$ adopts the $\text{LuNi}_2\text{B}_2\text{C}$ structure with a layer sequence $(\text{B}_y\text{-Ni}_2\text{-B}_z\text{-LuC})_n$ in which the B composition and the exact position of the C are still uncertain. No intergrowths or planar defects are observed. The c -axis in the thinner parts of the crystals (< 50 nm) was observed to decrease up to about 0.5 nm when irradiated by the electron beam.

1. Introduction

Cava et al. [11] have reported superconductivity at 16.6 K for the compound $\text{LuNi}_2\text{B}_2\text{C}$. $\text{LuNi}_2\text{B}_2\text{C}$ has a fairly simple structure, which is based on the stacking of LuC layers with Ni_2B_2 blocks [2,3] e.g. $(\text{B-Ni}_2\text{-B-LuC})_n$, as is shown in Fig. 1. In the system Lu-Ni-B-C at least two other quaternary phases with similar structures are present: LuNiBC [2,3] having an extra LuC layer $(\text{B-Ni}_2\text{-B-LuC-LuC})_n$, and Lu_2NiBC_2 [4], having a stacking sequence $(\text{Lu-LuC-B-Ni}_2\text{-B-LuC-Lu-C}_2)_n$ or $(\text{LuC-LuC-B-Ni}_2\text{-B-LuC-LuC-B})_n$ [5]; in the latter case the composition is $\text{Lu}_2\text{NiB}_{1.5}\text{C}_2$. In the related system Y-Pd-B-C, a T_c of 23 K [6] was observed, which is the highest T_c reported for a bulk intermetallic alloy. In contrast with the system Lu-Ni-B-C, in which the supercon-

ducting phase could be easily identified, it was found to be very difficult to determine the composition of the superconducting phase in the system Y-Pd-B-C. The best superconducting properties were found for specimens of nominal composition $\text{YPd}_5\text{B}_3\text{C}_{0.35}$. Although it was simple to identify in those specimens a phase with an I-centred tetragonal structure with $a = 0.375$ nm and $c = 1.07$ nm and an Y/Pd ratio suggesting this phase to be $\text{YPd}_2\text{B}_2\text{C}$, being an analogue of $\text{LuNi}_2\text{B}_2\text{C}$, it was not possible to synthesise this compound as a single phase. Fujii et al. [7] have reported that the superconducting phase in the Y-Pd-B-C system is $\text{YPd}_2\text{B}_2\text{C}$. Zandbergen et al. [8] have suggested that the composition of the Y-Pd compound having a $\text{LuNi}_2\text{B}_2\text{C}$ -like structure is quite deficient in B, which would require a formula $\text{YPd}_2\text{B}_{2-x}\text{C}$ with x close to 1. Recently Sarrac et al. [9] have succeeded in preparing $\text{ThPd}_2\text{B}_2\text{C}$, having a T_c of 14.5 K. A T_c of 21.5 K was observed in Th-Pd-B-C specimens with nominal composition Th-

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Fig. 1. Schematic representation of the structures of (a) $\text{LuNi}_2\text{B}_2\text{C}$ and (b) ThCr_2Si_2 . The c -axis of the first structure is longer because of the B–C–B unit in this direction compared to a Si–Si unit in ThCr_2Si_2 .

$\text{Pd}_3\text{B}_3\text{C}$, which do not contain $\text{ThPd}_2\text{B}_2\text{C}$ according to X-ray powder diffraction.

In this paper we report an electron-microscopy study on the (micro)structure of $\text{ThPd}_2\text{B}_{2-x}\text{C}$. Because of the possibility of a B deficiency the notation $\text{ThPd}_2\text{B}_{2-x}\text{C}$ will be used in the rest of the text.

2. Experimental

A specimen with nominal composition $\text{ThPd}_2\text{B}_2\text{C}$ was prepared by mixing elemental Th, Pd, C and B (all 99.9%) in the appropriate proportions and arc melting on a water-cooled copper hearth. Four melts were performed, with the samples turned over between each melt. Samples were then wrapped in Ta foil, placed in an evacuated quartz tube and annealed at 1050°C for several days. Details on the synthesis and property characterization can be found in Ref. [9].

Thin specimens for electron microscopy were obtained by crushing under ethanol and mounting the

crystal fragments on a Cu grid covered with a carbon-coated holey film. Electron microscopy was performed with a Philips CM30ST electron microscope with a field emission gun, operating at 300 kV, and equipped with a side-entry double tilt specimen holder and a Link EDX element analysis system.

The HREM images were recorded at a series of defocus values. Image calculations were carried out for several models using a MacTempas software program, in which the following parameters were used: $\text{Cs} = 1.3 \text{ mm}$, defocus spread 5 nm, objective aperture 10 nm^{-1} , beam convergence 0.1 mrad , and mechanical vibration 0.03 nm . The thickness and defocus were varied.

Through-focus image reconstruction [10,11] was applied to obtain more detailed information on the structure of $\text{ThPd}_2\text{B}_{2-x}\text{C}$. This technique is also called through-focus electron holography [10,11]. The through-focus high-resolution images and the electron-diffraction patterns were recorded using a Tietz software package and a 1024×1024 pixel Photometrix CCD camera having a dynamic range of 12 bits. The images were binned resulting in 512×512 pixel images. For those images where one is only interested in the average structure, image averaging was applied as described earlier [3].

3. Experimental results

Electron diffraction was carried out with a number of crystals of $\text{ThPd}_2\text{B}_{2-x}\text{C}$, indicating an I-centred tetragonal unit cell with $a = 0.38$, $c = 1.07 \text{ nm}$. Electron-diffraction patterns of the [100], [110], and [001] orientations are given in Fig. 2. No streaking or extra spots could be observed, indicating that there is no significant deviation of the stacking sequence of the layers or intergrowth of other phases.

[100] and [110] HREM images (after averaging over 8 unit cells), compared with calculated images, are given in Fig. 3. In the [100] images the columns of Th atoms are imaged as a large bright dots, and the columns of Pd atoms as small bright dots. In the [110] images the two Pd atoms coincide, resulting in the rather simple images shown in Fig. 3(b), where the Lu and Ni columns are imaged as bright dots.

The image calculations for $\text{ThPd}_2\text{B}_{2-x}\text{C}$ were done with a model based on the atomic position deter-

Fig. 2. Electron-diffraction patterns of $\text{ThPd}_2\text{B}_{2-x}\text{C}$ along (a) $[001]$, (b) $[100]$, (c) $[110]$.

Fig. 3. HREM images of $\text{ThPd}_2\text{B}_{2-x}\text{C}$ obtained by averaging over 8 unit cells in the horizontal direction. (a) shows a $[100]$ image; the Th and Pd atoms are imaged as bright dots. (c) shows a $[110]$ image, in which the Th and Pd atoms are imaged as bright dots. Calculated images for a thickness of 2 nm and a defocus of -100 nm and -80 nm for (a) and (c) are given in (b) and (d), respectively.

mined for $\text{LuNi}_2\text{B}_2\text{C}$ using X-ray single-crystal diffraction [2]. The B position was 50% occupied and the C position was fully occupied. With this model a good agreement was obtained between experimental images and images using a thickness of 2 nm, as can be seen in Fig. 3. The contribution of the occupancy of C and B to these images is so small that it is not possible to determine from them the occupancies of the B and C sites.

In order to obtain some information on the occupancies of the B and C positions, through-focus image reconstruction was applied, a technique briefly explained in Section 4 and more fully in Refs. [10] and [11]. The reconstruction using 20 images (all at different focus values) resulted in the image shown in Fig. 4. Since the reconstructed image is a complex image, Fig. 4 shows the phase as well as the modulus

of the image. Fig. 5 shows an average (translational average over 8 unit cells and mirror averaged over the two mirror planes through the Th atom) of the phase of the reconstructed image. All atoms and images are dark dots. The positions of the Th, Pd and C atoms can be clearly distinguished; the B atoms are visible as a tail on one side of the Pd atoms. This image was compared with calculated images using models with

- (1) full occupancies of the C and B sites,
- (2) an empty C site, and
- (3) half occupied B sites. From comparison of the images the C site seems to be fully occupied whereas no definite conclusion about the occupancy of the B site could be drawn.

No planar stacking defects were observed. Thus all investigated crystals showed a strict layer sequence

Fig. 4. Experimental and reconstructed images of $\text{ThPd}_2\text{B}_{2-x}\text{C}$ viewed along the a -axis. (a) shows one experimental $[100]$ image of the 20 images used for the reconstruction; (b) and (c) show the reconstructed image with the phase part and modulus part of the complex image, respectively.

Fig. 5. Reconstructed experimental phase image but averaged by translational average over 8 unit cells and mirror average over the two mirror planes through the central Th atom. The unit cell is indicated by the lines. Also some atoms are indicated.

$\{\text{B}_x\text{-Pd}_2\text{-B}_x\text{-ThC}\}_n$. At the edges of all crystals an electron beam induced structural change occurred, leading to a cubic-like structure with $a=0.41$ nm, an example of which is given in Fig. 6. In addition to this structure change, the unit cell of $\text{ThPd}_2\text{B}_{2-x}\text{C}$ was found to be changed by the electron beam. In the thinner regions (thinner than about 50 nm) the c -axis was observed to be up to 0.06 nm shorter than the bulk value.

Fig. 6. $[010]$ HREM image showing the presence of cubic $a=0.42$ nm structure near the edge of the specimen. Compared to the $\text{ThPd}_2\text{B}_{2-x}\text{C}$ structure, this cubic structure requires a lattice contraction along the c -axis and a lattice expansion along the a -axis resulting in strong bending of the lattice, which is partly indicated by white lines.

4. Discussion

The conventional HREM images show that the Th and Pd atoms occupy the same positions as Lu and Ni in $\text{LuNi}_2\text{B}_2\text{C}$, but do not provide information on the occupancies of the B or C sites. In trying to obtain the latter information, through-focus image reconstruction was applied. The technique of through-focus image reconstruction uses the information of a

series of high-resolution electron microscope images taken at different defocus values with well defined defocus increments. Using algorithms developed by Van Dyck [10] and Coene [11] all useful information can be extracted from these images into one image in which the distortion introduced by the electron microscope is restored.

In conventional high-resolution electron microscopy one often chooses a defocus setting, 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 cannot be interpreted directly and is often omitted by choosing an objective aperture. The point resolution is mainly set by the aberrations of the objective lens. The information limit of the microscope is mainly determined by the wavelength spread of the electron source.

The through-focus image reconstruction uses the focus dependence of the image distortion by the electron microscope. The image distortion due to the imperfectness of the microscope can be described by a transfer function. By combination of images recorded at various focus values one can correct for the effect of the transfer function and thus obtain the information beyond the point resolution in a direct interpretable image: the reconstructed image. This reconstructed image represents the exit wave function, which describes the electron wave at the exit plane of the specimen. Using the image-reconstruction method the information obtainable is set by the information resolution of the electron microscope, which is 0.14 nm for the microscope which was used. This information limit is in principle sufficient to image the Pd, Th and C atoms as individual dots; the B atoms should be visible as well. However, since the scattering of the C and B atoms is much less than that of the Pd and Th atoms, the effect of the absence or presence of the B or C atoms will be small, and imaging of the B and C will require sophisticated data analysis.

The through-focus reconstructed image indicates that the C position is fully occupied, whereas no definite conclusion can be drawn on the precise occupancy of the B site. For this reason the composition will be written as $\text{ThPd}_2\text{B}_{2-x}\text{C}$.

A complicating factor in this respect is the ob-

served decrease in the *c*-axis upon irradiation by the electron beam. Such a decrease in the *c*-axis is also observed for $\text{LuNi}_2\text{B}_2\text{C}$ and $\text{YPd}_2\text{B}_{2-x}\text{C}$ [5]. This decrease is not related to the structure transformation in the very thin parts of the crystal, as shown in Fig. 6, since decrease is also observed in much thicker areas. The decrease in the *c*-axis could be related to a loss of B or C from the structure. With sufficient loss of B to a composition ThPd_2BC the structure is likely to adopt the ThCr_2Si_2 structure for which a *c*-axis being about 0.06 nm shorter than that of the $\text{LuNi}_2\text{B}_2\text{C}$ structure is expected. On the other hand it is also possible that the structure is already deficient in B and that the decrease in the *c*-axis is merely catalysed by the electron beam. This will be subject to further research.

In the system Lu-Ni-B-C , besides $\text{LuNi}_2\text{B}_2\text{C}$ two other phases can be formed with structures similar to that of $\text{LuNi}_2\text{B}_2\text{C}$: LuNiBC [2,3] and Lu_2NiBC_2 [4]. These structures are based on introducing an extra LuC layer and a $\text{Lu-C}_2\text{-Lu-LuC}$ block, respectively. Furthermore, planar defects are observed in these phases [3]. In the system Th-Pd-B-C , no other phases with structures similar to that of $\text{ThPd}_2\text{B}_{2-x}\text{C}$ have been observed nor related planar defects. This is in agreement with the absence of such phases in the system Y-Pd-B-C and is probably related to the mismatch in the *a-b* plane between the Pd_2 layer and the ThC layer. Addition of an extra ThC layer resulting in ThPdBC could result in a too large misfit energy. This assumption is in agreement with the increasing difficulty of synthesising pure $\text{APd}_2\text{B}_{2-x}\text{C}$ with decreasing size of A.

Exposure to the electron beam leads to the formation of another more simple structure in the very thin parts of the crystal, e.g. the edges. This simple structure has lattice fringes of 0.21 nm, indicating a cubic F-centred structure with $a=0.42$ nm, which is adopted by many metals and alloys. No indication for the superstructure due to ordering of the Th and Pd atoms is observed. This structure can accommodate up to about 25% B or C atom per metal atom. This electron beam induced surface change is also observed for $\text{YPd}_2\text{B}_{2-x}\text{C}$ but not for $\text{LuNi}_2\text{B}_2\text{C}$. This could be related to a lower stability of the Pd compounds. $\text{YPd}_2\text{B}_{2-x}\text{C}$ indeed decomposes upon annealing at 800°C but $\text{ThPd}_2\text{B}_{2-x}\text{C}$ is stable up to at least 1050°C.

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