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LETTER TO THE EDITOR

HREM on Lu_2NiBC_2, a Phase Related to Superconducting $LuNi_2B_2C$

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The compound Lu_2NiBC_2 has been studied with high resolution electron microscopy. Lu_2NiBC_2 adopts a layer structure with a sequence $(Ni_2–B–LuC–Lu–C_2–Lu–LuC–B)_n$. The monoclinic unit cell consists of two of these layer sequences and has cell dimensions $a = 0.5$, $b = 0.5$, $c = 2.64$ nm, $\beta = 93°$. The stacking part LuC–B–Ni_2–B–LuC is like that of the superconducting compound $LuNi_2B_2C$ ($T_c = 16.6$ K). The possibility of rendering this compound superconducting is discussed.

INTRODUCTION

Recently, superconductivity at 16.6 K has been reported for the compound $LuNi_2B_2C$ (1), and in the system Y–Pd–B–C a T_c of 23 K (2) was observed, which is the highest T_c reported for a bulk intermetallic alloy. Lu Ni_2B_2C has a fairly simple structure, based on the stacking of LuC layers with Ni_2B_2 blocks (3), as is shown in Fig. 1. Electron microscopy on $LuNi_2B_2C$ showed the presence of an intergrowth with LuNiBC (see Fig. 1b), which could be obtained as a single phase compound (3).

The existence of LuNiBC, as well as other stacking defects observed in $LuNi_2B_2C$ (4), suggested the possible existence of other phases of composition; e.g., $(LuC)_m$ $B(Ni_2B)_n$ with m or n not equal to 1. In view of these results, we tried to prepare the phase with $m = 3$, $n = 1$, which would lead to a further separation of the Ni_2B_2 blocks. However, this synthesis resulted in the formation of a different phase. The results of an electron microscopy study on this new phase, Lu_2NiBC_2, are presented in this paper. A full description of the structure and microstructure of this compound will be published elsewhere.

EXPERIMENTAL METHODS

Lu_2NiBC_2 was prepared as a mixture of nominal composition $Lu_3Ni_2B_2C_3$ by mixing elemental Lu (99.99%), Ni (99.99%), C (99.99%), and B (99.6%) in the appropriate proportions and arc melting these in a water cooled copper hearth. Four melts were performed, with the samples turned over between each two melts. The samples were then wrapped in Ta foil, placed in an evacuated quartz tube, and annealed at 1200°C for 3 days. We could not prepare single phase material by arc melting and annealing in the temperature range 1200–1250°C, perhaps because the compound is very refractory. As-melted samples of composition Lu_2NiBC_2 were of considerably better phase purity, however, than samples of alternative compositions.

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-FEG electron microscope equipped with a Link EDX element analysis system. Parallel Electron Energy Loss Spectroscopy (PEELS) was done with a Philips CM200T electron microscope.

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: Cs = 1.3 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.

EXPERIMENTAL RESULTS

Energy dispersive X-ray (EDX) analysis of this compound indicated that the Lu/Ni ratio was close to 2, using the EDX results for $LuNi_2B_2C$ as a standard. PEELS was performed to determine the Ni/B/C ratios; it suggested a B/Ni ratio near 1 and a C/Ni ratio of 1.8. The PEELS results were, however, strongly dependent on the thickness of the specimen. The thinnest parts were taken, but in these areas oxygen was encountered, due to surface oxidation. The combination of the two analysis techniques

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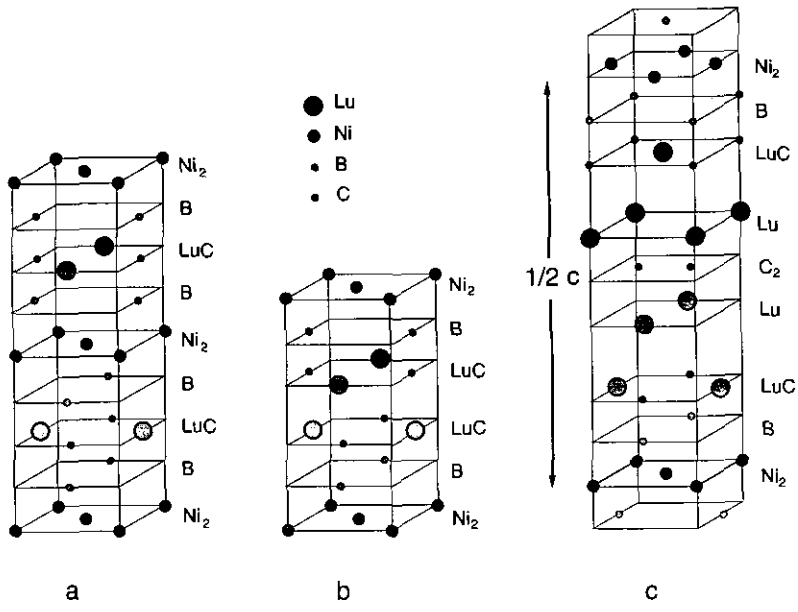

FIG. 1. Schematic representation of the basic structures of (a) $LuNi_2B_2C$, (b) LuNiBC. These compounds can be considered as members of the series $(LuC)_mB(Ni_2B)_n$ with $m = n = 1$ and $m = 2$, $n = 1$ respectively. (c) shows half the unit cell of Lu_2NiBC_2.

suggests the composition to be close to that of Lu_2NiBC_2. In this paper this notation will be used for the composition but the B and C content can be slightly different.

Electron diffraction was carried out with a number of crystals, which were rotated to scan the reciprocal space. This indicated that Lu_2NiBC_2 has a monoclinic unit cell of $a = 0.50$, $b = 0.50$, $c = 2.64$ nm, $\beta = 93°$. However, to retain the same basal plane as in $LuNi_2B_2C$, a triclinic unit cell of $a = b = 0.35$, $c = 2.64$, $\alpha = \beta = 92°$, and $\gamma = 90°$ (the triclinic basal plane is $a/\sqrt{2}$, $a/\sqrt{2}$ of the monoclinic one) will be adopted. Along the c^* axis extra spots and some streaking could be observed. These extra spots and streaking do not occur along the line of the 001 relections, indicating that there is no significant deviation of the stacking sequence of the layers, but that layers may only be shifted in the (001) plane with respect to each other. Also, twinning due to an interchange of [1 1 0] and [1 $\bar{1}$ 0] was observed.

High resolution electron microscopy showed that the stacking of layers along the c axis of Lu_2NiBC_2 is $(LuC_x\text{–}LuC\text{–}B\text{–}Ni_2\text{–}B\text{–}LuC_x\text{–}(B, C)_y)_n$, in which x and y are unknown. A typical example of a [100] micrograph is shown in Fig. 2a. The structure images differ in the manner in which the bright dots (representing the Lu atoms) are stacked along the c axis: an ABAB type of stacking versus an ABBA type (B represents the positions halfway between the A positions). Viewing along [010] shows that these types are complementary: the stacking ABBA in [100] coincides with ABAB in [010]. The composition of the $(B,C)_y$ layer cannot be determined from the HREM images because of the low scattering amplitude of B and C; however, this layer does not contain Ni or Lu, since no bright dots can be observed at the position of this layer. Figure 3 shows the stacking viewed along the [110] direction, from which an ABBAABAABBA stacking can be inferred.

From the combination of the stacking in the [100] and [110] images and the similarities of these images with the corresponding HREM images of $LuNi_2B_2C$ and LuNiBC, the structural model shown in Fig. 1c was derived.

Image calculations were done with the model in Fig. 2c. The atomic positions[1] were based on the atomic positions of the Ni_2–B–LuC–LuC block of LuNiBC (3), such that the same atomic distances were obtained in the related blocks in the Ni_2–B–LuC–Lu–C_2–Lu–LuC–B layer sequence of Lu_2NiBC_2. The actual positions of the B and C atoms and their occupancies or interexchanges of B and C, as well as the actual composition of the C_2 layer, cannot be deduced from the HREM images, because the scattering potentials of these atoms compared to those of Lu and Ni are too small to result in bright or black dots at the positions of the B or C atoms. Therefore, they have been deduced from the similar structures $LuNi_2B_2C$ and LuNiBC. The model resulted in calculated images which agreed well with the observed images, as can be seen from the insets in Figs. 2 and 3.

[1] The following atomic positions were used in the image calculations: Ni 0,0,0; Lu 0.5,0,0.098; Lu 0,0.5,0.188; C 0,0.5,0.090; C 0,0.25,0.25; C 0,0.25,0.75; B 0,0.5,0.004. The used symmetry is A-centering with an n-glide mirror plane on $z = 0$ and cell axes $a = b = 0.346$, $c = 2.64$ nm.

DISCUSSION

Lu_2NiBC_2 adopts a monoclinic unit cell with unit cell dimensions $a = 5.0$, $b = 5.0$, $c = 26.4$, $\beta = 93°$. The structure of Lu_2NiBC_2 consists of a layer structure with a sequence $(Ni_2–B–LuC–Lu–C_2–Lu–LuC–B)_n$. The monoclinic unit cell consists of two of these layer sequences. The ordering in the Lu–LuC–B–Ni_2–B–LuC–Lu is always the same, and is identical to that of the superconducting compound $LuNi_2B_2C$. The ordering between the two Lu layers neighboring to the C_2 layer, however, can occur in two ways, thus resulting in many stacking defects.

The structural model consists of Lu–LuC–B–Ni_2–B–LuC–Lu blocks sandwiched with C_2 layers. The atomic distances in the above-mentioned block will be approximately the same as in LuNiBC and from the structural data (4) of the latter the width of the block is calculated to be 1.04 nm. This width and the distances between the C atoms in the C_2 layer and Lu in the adjacent layers determine the length of the c axis. Using the Lu–C (0.25 nm) distance observed in LuNiBC the c axis is calculated to be 2.68 nm, in good agreement with the experimental value. The composition Lu_2NiBC_2 also permits a stacking of four LuC layers, but this would lead to a different c axis and to HREM images which were not compatible with the experimental ones.

Band structure calculations (5) on $LuNi_2B_2C$ and LuNiBC have shown that for the superconductor Lu Ni_2B_2C the Fermi level falls in a Ni3*d* dominated electronic band with a relatively high density of states. For LuNiBC the same band is present, but the electron count is such that the Fermi level no longer falls in that band. Thus, it may be possible to induce superconductivity in either LuNiBC or Lu_2NiBC_2 through suitable adjustment of the electron count by chemical substitutions.

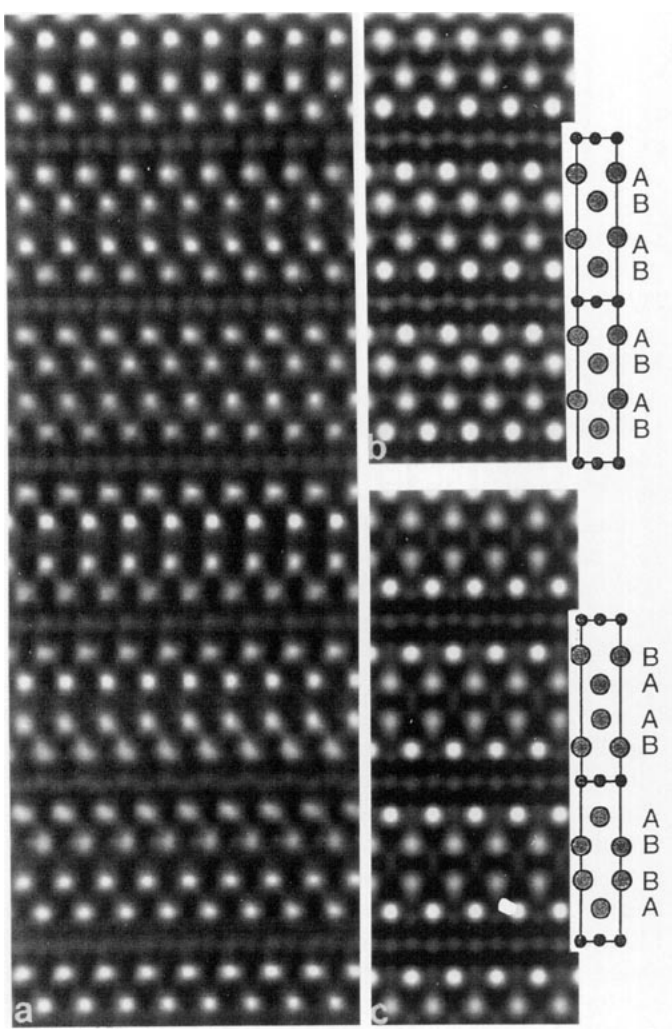

FIG. 2. A [100] micrograph at high magnification. (a) shows the experimental image averaged over 8 unit cells in the horizontal direction and (b) and (c) the calculated image along the a and b axis, respectively. Note that two types of stacking occur, ABAB and ABBA, due to [001] 90° rotation twins resulting in an exchange of the a and the b axis.

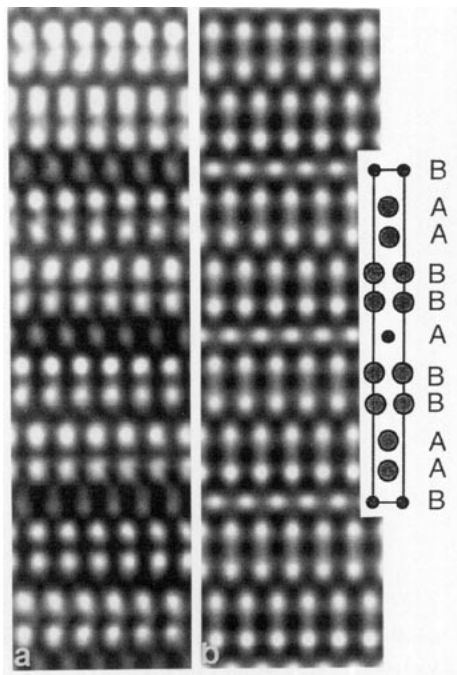

FIG. 3. A [110] micrograph at high magnification. A stacking sequence ABBAABAABBA can be deduced. (a) shows the experimental image averaged over 8 unit cells in the horizontal direction and (b) the calculated image based on the model given in Fig. 1c.

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