

## Brief Reports

*Brief Reports are accounts of completed research which, while meeting the usual Physical Review standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

### Elementary physical properties and crystal structures of $\text{LaRh}_2\text{B}_2\text{C}$ and $\text{LaIr}_2\text{B}_2\text{C}$

R. J. Cava, T. Siegrist, and B. Batlogg

*AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974*

H. Takagi and H. Eisaki

*Institute of Solid State Physics, University of Tokyo, 7-22-1, Roppongi, Minato-ku, Tokyo 106, Japan*

S. A. Carter, J. J. Krajewski, and W. F. Peck, Jr.

*AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974*

(Received 10 June 1994)

The crystal structures, magnetic susceptibilities, and electrical resistivities of the quaternary intermetallic compounds  $\text{LaRh}_2\text{B}_2\text{C}$  and  $\text{LaIr}_2\text{B}_2\text{C}$  are reported. Although isostructural with the recently reported superconductors  $\text{LNi}_2\text{B}_2\text{C}$  and  $\text{LPt}_2\text{B}_2\text{C}$  ( $L = \text{La}$  and  $\text{Y}$ ), they are not superconducting at temperatures above 1.4 K. The magnetic-susceptibility measurements reveal densities of states at the Fermi level intermediate to the Ni- and Pt-based compounds.

The recent discovery of superconductivity at temperatures up to 23 K in quaternary intermetallic borocarbides<sup>1-4</sup> has sparked renewed interest in searching for superconductivity in intermetallic materials. Compounds with the  $\text{LuNi}_2\text{B}_2\text{C}$  structure type<sup>5</sup> have been shown to be responsible for the superconductivity in Ni- and Pt-based borocarbides, and the same structure type, or a non-stoichiometric variation of it, has been proposed to be superconducting at 23 K in  $\text{Y-Pd-B-C}$ .<sup>6,7</sup> The structure consists of tetrahedrally bonded, square  $T_2\text{B}_2$  layers ( $T = \text{transition metal}$ ), separated by square rocksaltlike  $\text{LC}$  layers. Very strong boron-carbon bonds join the two layers. We have been exploring the extent to which this structure type forms, as the related  $\text{ThCr}_2\text{Si}_2$  structure type is found for many ternary intermetallic compounds. Investigations of compositions of the type  $\text{LT}_2\text{B}_2\text{C}$  with  $L = \text{La}$  and  $\text{Y}$ , and  $T = \text{Fe, Ru, Co, Rh, Ir, Cu, Ag, and Au}$ , showed the presence of the  $\text{LuNi}_2\text{B}_2\text{C}$  structure type in single-phase form only for  $\text{LaRh}_2\text{B}_2\text{C}$  and  $\text{LaIr}_2\text{B}_2\text{C}$ . In this report we briefly describe their synthesis, crystal structures, and elementary physical properties.

Starting materials were lanthanide metal shavings (99.99%), Rh and Ir powder (99.99%), and coarse C (99.99%) and B (99.6%) powder. Samples of 0.5-g total weight were first pressed into 0.25-in.-diam pellets. They were then arc melted under Ar on a standard water-cooled copper hearth. They were melted three times, with the button turned over between each melt. There was good crystal growth in the buttons, and  $\text{LaIr}_2\text{B}_2\text{C}$  and  $\text{LaRh}_2\text{B}_2\text{C}$  were essentially single phase as melted.

The arc-melted buttons were wrapped in Ta foil, sealed in evacuated quartz tubes, and annealed at 1050°C for several days.

As we found for the  $\text{LPt}_2\text{B}_2\text{C}$  analogs,<sup>4,8</sup> the stability of the  $\text{LuNi}_2\text{B}_2\text{C}$  structure type in  $\text{LIr}_2\text{B}_2\text{C}$  and  $\text{LRh}_2\text{B}_2\text{C}$  was best for the larger rare earths. Single-phase materials for  $L = \text{Y}$  could not be synthesized under our conditions. Preliminary experiments to determine the stability of the phase for intermediate rare-earth sizes were performed by arc melting and annealing samples of composition  $\text{La}_{1-x}\text{Y}_x\text{T}_2\text{B}_2\text{C}$ , for  $x = 0.25, 0.5, 0.75$ , and 1.0. For  $T = \text{Ir}$ , the Y solubility limit was lower than 0.25, probably close to  $x = 0.1$ , based on the small but significant shift in the unit-cell parameter for the  $\text{LuNi}_2\text{B}_2\text{C}$  type phase in the multiple-phase sample at  $x = 0.25$ , suggesting stability for the Ir-based analogs only for the largest rare earths. For the Rh-based samples, single-phase material of composition  $\text{La}_{0.75}\text{Y}_{0.25}\text{Rh}_2\text{B}_2\text{C}$  was obtained. The material of composition  $\text{La}_{0.5}\text{Y}_{0.5}\text{Rh}_2\text{C}$  was multiple phase, as were all samples at higher-Y contents. The  $\text{LuNi}_2\text{B}_2\text{C}$ -type pattern persisted even to the solely Y-containing material, where it accounted for approximately 50% of the sample. The lattice parameters were  $a_0 = 3.768$  and  $c_0 = 10.305$  Å, showing the decrease in  $a_0$  and increase in  $c_0$  on going from larger to smaller rare earth expected in this structure type<sup>5</sup> (for  $\text{LaRh}_2\text{B}_2\text{C}$ ,  $a_0 = 3.906$  and  $c_0 = 10.246$  Å). Annealing the  $\text{La}_{1-x}\text{Y}_x\text{Rh}_2\text{B}_2\text{C}$  samples for  $0.5 \leq x \leq 1.0$  at 1200°C overnight did not significantly change the phase purity. This suggests that either higher-temperature annealing

TABLE I. Crystal-structure parameters for  $\text{LaRh}_2\text{B}_2\text{C}$  and  $\text{LaIr}_2\text{B}_2\text{C}$ . For  $\text{LaRh}_2\text{B}_2\text{C}$ , the space group is  $I4/mmm$ ,  $a = 3.9019(2)$  Å,  $c = 10.2460(6)$  Å,  $Z = 2$ ,  $R = 0.022$ , and  $R_w = 0.026$  (391 independent reflections, 391 observed [ $I > 2.5\sigma(I)$ ], 11 parameters). For  $\text{LaIr}_2\text{B}_2\text{C}$ , the space group is  $I4/mmm$ ,  $a = 3.8965(10)$  Å,  $c = 10.454(3)$  Å,  $Z = 2$ ,  $R = 0.028$ , and  $R_w = 0.033$  (397 independent reflections, 397 observed [ $I > 2.5\sigma(I)$ ], 11 parameters).

	<i>x</i>	<i>y</i>	<i>z</i>	Biso (Å <sup>2</sup> )
<b><math>\text{LaRh}_2\text{B}_2\text{C}</math></b>				
La	0	0	0	0.529(10)
Rh	1/2	0	1/4	0.383(8)
B	0	0	0.3518(8)	0.86(16)
C	1/2	1/2	0	0.91(19)
<b><math>\text{LaIr}_2\text{B}_2\text{C}</math></b>				
La	0	0	0	0.517(13)
Ir	1/2	0	1/4	0.310(7)
B	0	0	0.3501(23)	1.1(4)
C	1/2	1/2	0	1.1(3)

conditions would be required to successfully obtain the complete La-Y solid solution in single-phase form or that some type of nonstoichiometry of the  $\text{LuNi}_2\text{B}_2\text{C}$  phase is occurring for the smaller rare earth, e.g., boron or carbon deficiency. We note that the  $\text{ThCr}_2\text{Si}_2$ -type phase  $\text{YRh}_2\text{B}_2$  has not been reported, although the Y-Rh-B system has been studied extensively,<sup>9</sup> and so the tetragonal body-centered phase observed in  $\text{YRh}_2\text{B}_2\text{C}$  is likely to indeed be a borocarbide.

Small single crystals of  $\text{LaRh}_2\text{B}_2\text{C}$  and  $\text{LaIr}_2\text{B}_2\text{C}$  were removed from the arc-melted and annealed boules for crystal-structure determination. Data were collected on an Enraf-Norius diffractometer using graphite-monochromated Mo  $K\alpha$  radiation. Lattice parameters were obtained by determining the absolute  $2\theta$  values at

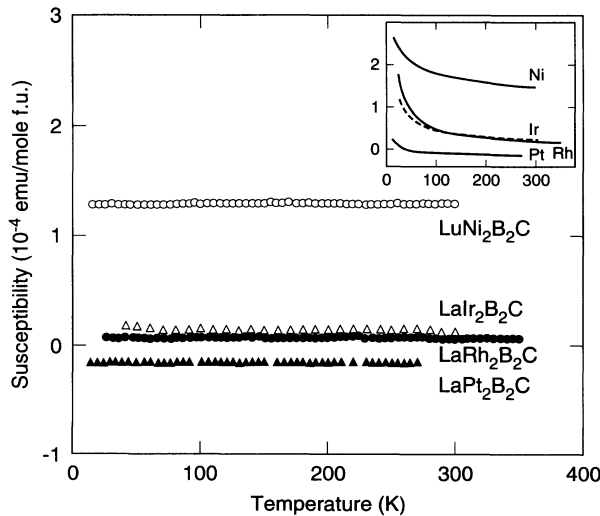


FIG. 1. Temperature dependence of the magnetic susceptibilities for various  $LT_2B_2C$  compounds. The inset shows raw data before subtraction of the contributions of small amounts of magnetic impurities.

TABLE II. Magnetic susceptibilities for  $\text{LnT}_2\text{B}_2\text{C}$ -type compounds ( $10^{-4}$  emu/mol formula unit).

Compound	$\chi_{\text{meas}}$	$\chi_{\text{core}}^a$	$\chi_{\text{ce}}^b$
$\text{LuNi}_2\text{B}_2\text{C}$	1.3(1)	-1.3(1)	2.6(2)
$\text{LaRh}_2\text{B}_2\text{C}$	0.07(3)	-0.84(20)	0.91(23)
$\text{LaIr}_2\text{B}_2\text{C}$	0.12(3)	-1.15(25)	1.27(28)
$\text{LaPt}_{1.7}\text{Au}_{0.3}\text{B}_2\text{C}$	-0.15(1)	-1.05(15)	0.90(15)

<sup>a</sup>Core electron susceptibility estimated from standard tables.

<sup>b</sup>Conduction electron susceptibility  $\chi_{\text{ce}} = \chi_{\text{meas}} - \chi_{\text{core}}$ .

high angles of 35 reflections. A Gaussian integration absorption correction was applied to the intensity data, and the structure was refined using the NRCVAX programs.<sup>10</sup> The results for both  $\text{LaRh}_2\text{B}_2\text{C}$  and  $\text{LaIr}_2\text{B}_2\text{C}$  are summarized in Table I. The crystal structures are of the ideal  $\text{LuNi}_2\text{B}_2\text{C}$  type. Consistent with the fact that excellent-quality single-phase polycrystalline materials can be synthesized at the ideal  $\text{LaT}_2\text{B}_2\text{C}$  stoichiometry, there is no indication of nonstoichiometry for either phase in the structural refinements.

The temperature dependence of the magnetic susceptibility for both materials was measured between 4.2 and 300 K in a commercial superconducting quantum interference device magnetometer. The magnetic moments  $M$  were measured in a series of fields, up to 40 kOe, to ensure that the susceptibilities were derived from linear  $M(H)$  relationships. The raw data measured in this way are presented in the inset to Fig. 1, with data also presented for the superconducting single-phase materials  $\text{LuNi}_2\text{B}_2\text{C}$  and  $\text{LaPt}_{1.7}\text{Au}_{0.3}\text{B}_2\text{C}$ .<sup>8</sup> Small amounts of magnetic impurity phases are present in the samples and give rise to slight upturns of  $\chi(T)$  at low temperatures. The main panel of Fig. 1 presents intrinsic magnetic susceptibilities for all the materials, obtained by subtracting the contributions of the magnetic impurities. The observed temperature-independent magnetic susceptibilities are the sum of the susceptibilities from the core electrons ( $\chi_{\text{core}}$ ), Van Vleck-type paramagnetism ( $\chi_{\text{vv}}$ , here considered to be negligible), and conduction electron paramagnetism ( $\chi_{\text{ce}}$ ). The values of  $\chi_{\text{ce}}$  determined from the experimen-

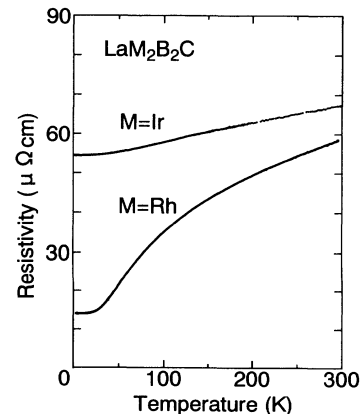


FIG. 2. Temperature dependence of the resistivities of polycrystalline samples of  $\text{LaIr}_2\text{B}_2\text{C}$  and  $\text{LaRh}_2\text{B}_2\text{C}$ .

tal susceptibilities and  $\chi_{\text{core}}$  obtained from standard tables are shown in Table II. Comparison of  $\chi_{\text{ce}}$  and the electronic density of states measured by specific heat in  $\text{LuNi}_2\text{B}_2\text{C}$  and  $\text{LaPt}_{1.7}\text{Au}_{0.3}\text{B}_2\text{C}$  (Ref. 11) has shown that the values for  $\chi_{\text{ce}}$  are a good measure of the electronic density of states for each material, i.e., the ratio of  $\chi_{\text{ce}}$  and the Sommerfeld constant  $\gamma$  is very close to the free electron value. The new materials  $\text{LaRh}_2\text{B}_2\text{C}$  and  $\text{LaIr}_2\text{B}_2\text{C}$ , therefore, have densities of states intermediate to those of the superconducting analogs.

Temperature-dependent resistivities for  $\text{LaRh}_2\text{B}_2\text{C}$  and  $\text{LaIr}_2\text{B}_2\text{C}$  are presented in Fig. 2, measured in the standard four-probe geometry on polycrystalline pieces. Although the resistivities are comparable ( $60\text{--}70\ \mu\Omega\text{ cm}$ ) at room temperature, the Rh sample has a considerably better resistance ratio, reaching a resistivity of approximately  $10\ \mu\Omega\text{ cm}$  at 4 K. The shapes of  $\rho(\tau)$ , especially when compared to  $\text{Ni}_3$ , suggest a tendency to resistivity saturation at higher temperatures, perhaps due to less perfect crystal quality in the present materials.

In conclusion, investigation of the range of occurrence of the  $\text{LuNi}_2\text{B}_2\text{C}$  structure type for transition metals in

columns VIII A and I B indicated that the structure type is stable for materials based on Rh and Ir for the large rare earths. A related phase was also observed for  $\text{LaCo}_2\text{B}_2\text{C}$ , but the material was not obtained in single phase form. Due to the fact that  $\text{LaCo}_2\text{B}_2$  occurs in the  $\text{ThCr}_2\text{Si}_2$  structure type,<sup>12,13</sup> there exists the possibility that a  $\text{LaCo}_2\text{B}_2\text{C}_x$  solid solution series could form: further investigation will be necessary to clarify the stoichiometry of the borocarbide phase. Although their densities of states at the Fermi level are comparable to those of the superconducting materials of the same structure type,  $\text{LaRh}_2\text{B}_2\text{C}$  and  $\text{LaIr}_2\text{B}_2\text{C}$  are not superconducting down to our lowest measurement temperature, 1.4 K. This may be due to the significantly different band filling expected: band-structure calculations suggest that the Fermi level would fall in a different position in the electronic band scheme.<sup>14</sup> More detailed comparison of superconducting and nonsuperconducting materials in the new  $\text{LuNi}_2\text{B}_2\text{C}$  structure type will help elucidate the roles played by the differing electronic, magnetic, and structural components in the microscopic mechanism for superconductivity.

<sup>1</sup>R. J. Cava, H. Takagi, B. Batlogg, H. W. Zandbergen, J. J. Krajewski, W. F. Peck, Jr., R. B. van Dover, R. J. Felder, K. Mizuhashi, J. O. Lee, H. Eisaki, and S. Uchida, *Nature (London)* **367**, 148 (1994).

<sup>2</sup>R. Nagarajan, C. Mazumdar, Z. Hossain, S. K. Dhar, K. V. Golpakrishnan, L. C. Gupta, C. Godart, B. D. Padalia, and R. Vijayaraghavan, *Phys. Rev. Lett.* **72**, 274 (1994).

<sup>3</sup>R. J. Cava, H. Takagi, H. W. Zandbergen, J. J. Krajewski, W. F. Peck, Jr., T. Siegrist, B. Batlogg, R. B. van Dover, R. J. Felder, K. Mizuhashi, J. O. Lee, H. Eisaki, and S. Uchida, *Nature (London)* **367**, 252 (1994).

<sup>4</sup>R. J. Cava, B. Batlogg, T. Siegrist, J. J. Krajewski, W. F. Peck, Jr., S. Carter, R. J. Felder, H. Takagi, and R. B. van Dover, *Phys. Rev. B* **49**, 12 384 (1994).

<sup>5</sup>T. Siegrist, H. W. Zandbergen, R. J. Cava, J. J. Krajewski, and W. F. Peck, Jr., *Nature (London)* **367**, 254 (1994).

<sup>6</sup>H. W. Zandbergen, W. G. Sloof, R. J. Cava, J. J. Krajewski, and W. R. Peck, Jr., *Physica C* **226**, 365 (1994).

<sup>7</sup>H. Fujii, S. Ikeda, T. Kimura, S. Arisawa, H. Hirata, H. Kumakara, K. Kadowaki, and S. Togano, *Jpn. J. Appl. Phys.* **33**, L590 (1994).

<sup>8</sup>R. J. Cava, B. Batlogg, J. J. Krajewski, W. F. Peck, Jr., T. Siegrist, R. M. Fleming, S. A. Carter, H. Takagi, R. J. Felder, R. B. van Dover and L. W. Rupp, Jr., *Physica C* **226**, 170 (1994).

<sup>9</sup>P. D. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (ASM International, Materials Park, Ohio, 1991), pp. 1623–1624.

<sup>10</sup>E. J. Gabe, Y. LePage, J.-P. Charland, F. L. Lee, and P. S. White, *J. Appl. Crystallogr.* **22**, 348 (1989).

<sup>11</sup>S. A. Carter, B. Batlogg, R. J. Cava, J. J. Krajewski, W. F. Peck, Jr., and H. Takagi, *Phys. Rev. B* **50**, 4216 (1994).

<sup>12</sup>K. Niihara, T. Shishido, and S. Yajima, *Bull. Chem. Soc. Jpn.* **46**, 1137 (1973).

<sup>13</sup>R. Rogl, *Monatsch. Chem.* **104**, 1626 (1973).

<sup>14</sup>L. F. Mattheiss, *Phys. Rev. B* **49**, 14 050 (1994).