Normal-state transport and magnetic properties of RNi$_2$B$_2$C (R=Y, Ho, La)

I. R. Fisher and J. R. Cooper
IRC in Superconductivity, The University of Cambridge, Madingley Road, Cambridge, CB3 OHE, United Kingdom

R. J. Cava
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 13 July 1995)

Magnetic susceptibility, resistivity, thermoelectric power, and Hall effect measurements have been made for RNi$_2$B$_2$C, R=Y, Ho, La. The Y and Ho containing compounds are superconducting, with transition temperatures of 15 and 7.5 K, respectively. The La containing compound is nonsuperconducting down to 1.5 K. A distinct linear term is seen in the susceptibility of YNi$_2$B$_2$C, which is not seen in the nonsuperconducting LaNi$_2$B$_2$C. The two superconducting compounds have a linear resistivity at high temperatures, with a definite downward curvature below 300 K, while that of LaNi$_2$B$_2$C is linear up to 600 K (the limits of this study.) There seems to be an extra scattering process in the superconducting compounds which freezes out below 300 K. The thermopowers of the two superconducting compounds are identical, being small and negative, while that of LaNi$_2$B$_2$C is also negative, but is greater in magnitude. Analysis of the thermopower data reveals that LaNi$_2$B$_2$C has a factor of 2 larger electron diffusion term than the Y and Ho containing compounds, and that the latter values are nearly a factor of 10 smaller than expected from band theory. The Hall coefficient for all three materials is negative, small and shows some temperature dependence. At 300 K the carrier density for YNi$_2$B$_2$C is estimated to be 1.7 electrons per formula unit.

INTRODUCTION

The recent discovery of the class of quaternary intermetallic borocarbide superconductors[1,2] has sparked a great deal of research, though as yet very little in the way of normal-state transport measurements. They have relatively high transition temperatures for intermetallic compounds,[2] reaching 21 K for related thorium-palladium-based compounds[3,4] and 23 K for YPd$_5$B$_3$C$_{0.3}$.[5] Although the materials have a layered-type structure,[6,7] suggesting that they may share the strongly anisotropic properties of the cuprates, band structure calculations[8–11] indicate that the electronic structure is much more three dimensional. Within this framework superconductivity in these materials can be described by a conventional phonon mechanism, with the relatively high transition temperatures due to a van Hove–like peak in the density of states at ε_F.[8] Nickel substitution studies[12,13] provide some experimental evidence for this peak in the density of states, while specific heat measurements[14] and a substantial boron isotope effect[15] support the classification of these compounds as electron-phonon-mediated superconductors.

It has been shown that the transition temperature of the rare-earth borocarbides (R=Lu, Y, Tm, Er, Ho, Dy, Tb) scales with the de Gennes factor[16] $(g-1)^2J(J+1)$. This implies that T_c of the Ho compound is reduced from 15 K (T_c of the nonmagnetic Y compound) to 7.5 K as a consequence of spin-flip scattering of the conduction electrons from the Ho^{3+} magnetic moments. The strong magnetic moment carried by the Ho^{3+} ions also results in an interesting competition between magnetism and superconductivity at low temperatures.[16–22] Although LaNi$_2$B$_2$C is nonmagnetic, the compound is not superconducting down to 1.5 K and will be referred to as nonsuperconducting. It has been suggested that this is due to the large size of the La^{3+} ion, resulting in a flattening of the NiB$_4$ tetrahedra[23] and an increased Ni-Ni distance in the layered structure.[24]

Normal-state measurements are often helpful in understanding the underlying mechanisms which result in superconductivity. The present study compares the magnetic susceptibility, thermoelectric power, resistivity, and Hall effect of LaNi$_2$B$_2$C, YNi$_2$B$_2$C, and HoNi$_2$B$_2$C, finding some properties which are common to all three of these materials and some common only to the two superconducting ones.

All three compounds used in this study were prepared from pure elements by a standard arc-melting and annealing procedure, described in Ref. 2, and checked to be phase pure by powder x-ray diffraction. All samples were polycrystalline.

RESULTS

dc magnetic susceptibility measurements were made on all three compounds using a commercial superconducting quantum interference device (SQUID) magnetometer. A field of 50 000 G was used for the Y- and La-containing compounds. The Ho containing compound was measured in a field of 1000 G below 50 K and 2000 G above. Checks for linear magnetization with field were made for all samples at 20 and 300 K. The susceptibility measurements were repeated several times and, in the case of YNi$_2$B$_2$C, on two different samples. The normal-state susceptibility of HoNi$_2$B$_2$C is well fitted by a Curie law, with an effective moment of $10.4\mu_B$ per cell. This is in good agreement with the moment of trivalent Ho ions. The normal-state magnetic susceptibility of YNi$_2$B$_2$C and LaNi$_2$B$_2$C is shown in Fig. 1. Both curves are best fitted by a constant term, a small Curie

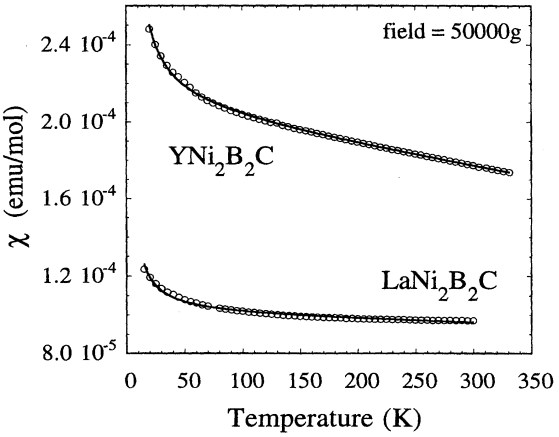

FIG. 1. dc magnetic susceptibility of YNi_2B_2C and $LaNi_2B_2C$. Line shows fit to $\chi=A+BT+C/T$, with $A=(2.056\pm0.003)\times10^{-4}$ and $(0.995\pm0.004)\times10^{-4}$ emu/mol, $B=(-1.05\pm0.01)\times10^{-7}$ and $(-3.0\pm0.6)\times10^{-9}$ emu/mol K, and $C=(9.3\pm0.1)\times10^{-4}$ and $(4.0\pm0.1)\times10^{-4}$ emu K/mol, respectively, for the two compounds. 1 mol≡1 formula unit.

term, and a linear term. The Curie term varies slightly between samples, but the constant and linear terms are sample independent.

Figure 2 shows the thermopower for all three compounds to be negative and small. YNi_2B_2C and $HoNi_2B_2C$ have a very similar thermopower, while that of $LaNi_2B_2C$ is larger. For temperatures greater than 280 K in the case of $LaNi_2B_2C$ and 230 K in the case of the superconducting materials, the data can be fitted by standard electron diffusion and phonon drag terms. This analysis reveals all three materials to have a similar phonon drag contribution (of between −450/T and −550/T μV/K), while the electronic thermopower of $LaNi_2B_2C$ [(-0.0134 ± 0.0001)T μV/K] is twice that of the superconducting Y- and Ho-containing compounds.

Resistivity data were taken for all three compounds up to

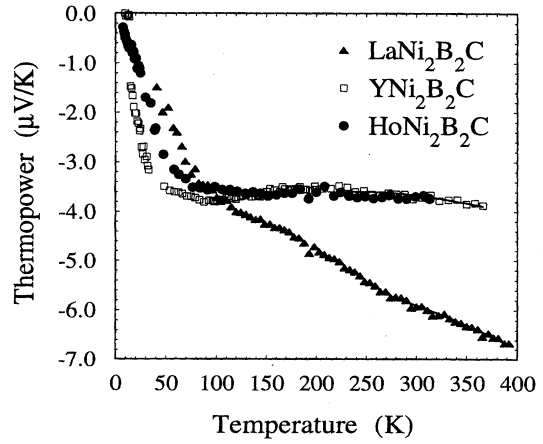

FIG. 2. Thermoelectric power of YNi_2B_2C, $HoNi_2B_2C$, and $LaNi_2B_2C$. Lines show the fit to electron diffusion and phonon drag contributions, $S=AT+B/T$. The fit is made for temperatures greater than 280 K for $LaNi_2B_2C$ and 230 K for YNi_2B_2C.

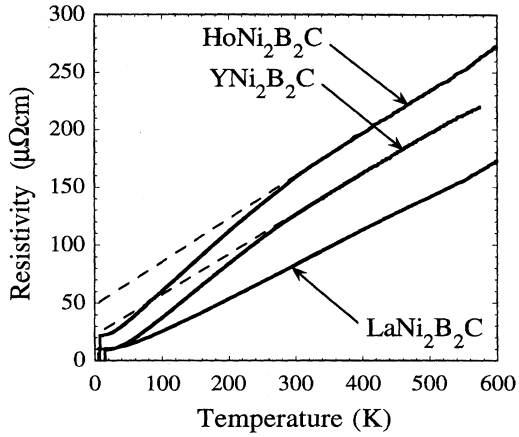

FIG. 3. Resistivity of YNi_2B_2C, $HoNi_2B_2C$, and $LaNi_2B_2C$. Dashed lines indicate the deviation from linearity of the superconducting samples.

600 K and are presented in Fig. 3. The residual resistivity of all three is slightly sample dependent, though typically between 10 and 20 μΩ cm. Below 30 K, $LaNi_2B_2C$ follows a power law $\rho=\alpha+\beta T^n$ with n between 4 and 5, crossing over to a linear behavior which extends to 600 K. The two superconducting materials follow the same power law over a limited temperature range from T_c to 22 K and only have a linear resistivity above 300 K, with ρ showing a significant downward curvature below this temperature. Within experimental uncertainty, the linear high-temperature section of the two superconducting compounds has the same slope as that of $LaNi_2B_2C$: 0.3 μΩcm/K.

The Hall coefficient was measured in a field of 10 T and results are presented in Fig. 4. Data for $HoNi_2B_2C$ were only taken down to 100 K. All three compounds have a negative and small Hall coefficient, showing some temperature dependence.

DISCUSSION

Assuming that contributions from core states ($\approx-0.4\times10^{-4}$ emu/mol, estimated using standard tables[25])

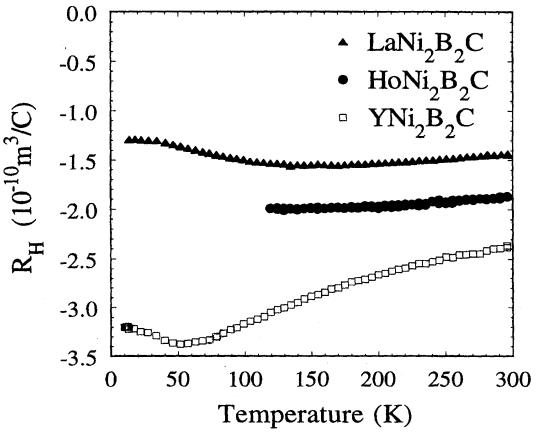

FIG. 4. Hall coefficient of YNi_2B_2C, $HoNi_2B_2C$, and $LaNi_2B_2C$ measured in a field of 10 T.

and Van Vleck terms approximately cancel, then the constant term in the magnetic susceptibility of YNi_2B_2C and $LaNi_2B_2C$ results from Pauli paramagnetism and the density of states at the Fermi surface, $n(\varepsilon_F)$, can be estimated. This gives values of 6.4 states/eV cell for YNi_2B_2C and 3.0 states/eV cell for $LaNi_2B_2C$, comparing well with values of 3–7 states/eV cell from band structure calculations for YNi_2B_2C (Ref. 8) and $LuNi_2B_2C$.[9–11] The Curie term is small, slightly sample dependent, and is most likely to arise from magnetic impurities on the rare-earth site. In the case of YNi_2B_2C, this could be just 0.3% of Ni with a moment of 1.7 μ_B ($s=1/2$) or even less of a magnetic rare earth (for example, 70 ppm of Ho^{3+}). The most striking feature of Fig. 1 is the linear term in the susceptibility. This term is very small for $LaNi_2B_2C$ ($-3.0\pm0.6\times10^{-9}$ emu/mol K), but is much larger for YNi_2B_2C ($-1.05\pm0.01\times10^{-7}$ emu/mol K). (The Curie term for $HoNi_2B_2C$ is so large that this linear term would not be observable.) There is no obvious explanation for this linear term that appears strongly in the superconducting sample and only weakly in the nonsuperconducting material. It could possibly arise from a strongly energy- or temperature-dependent density of states or perhaps from magnetic (spin) fluctuations.

The low magnitude of the electron diffusion thermopower of the superconducting compounds indicates a slowly varying density of states at the Fermi surface. Band structure calculations show a sharp peak in $n(\varepsilon_F)$,[8–11] which, according to the standard electron diffusion formula

$$S=\frac{\pi^2 k_B^2 T}{3e}\left(\frac{d\ \ln\ \sigma}{d\varepsilon}\right)_{\varepsilon=\varepsilon_F}$$

would result in a thermopower of 20–30 μV/K, ignoring any energy dependence in the scattering lifetime. This is a factor of 10 greater than we observe for YNi_2B_2C or $HoNi_2B_2C$. The larger electron diffusion thermopower of $LaNi_2B_2C$ indicates that the nonsuperconducting material has a more rapidly varying $n(\varepsilon_F)$ than its superconducting analogs. The small electron diffusion thermopower of YNi_2B_2C and $HoNi_2B_2C$ is perhaps a consequence of these materials sitting at the very top of the peak in the density of states predicted by band structure calculations,[8–11] rather than just to one side. The larger electron thermopower of $LaNi_2B_2C$ perhaps arises from ε_F being away from this peak, giving a small $n(\varepsilon_F)$, but a larger energy dependence.

The resistivity data are particularly interesting. Previous measurements[2,24,26] missed the distinct curvature seen in the resistivity of the superconducting samples because the data were only taken to 300 K. Since this curvature does not continue to a higher temperature, but rather flattens off to a linear behavior above 300 K, it is unlikely to be due to the onset of a saturation in the resistivity (a consequence of the mean free path becoming comparable to the size of the unit cell) as is seen in the $A15$ intermetallic superconductors.[27] Such curvature away from a linear high-temperature behavior is also seen in the underdoped cuprates.[28–30] In the cuprates this behavior is associated with the opening of a pseudogap in the density of states[31–33] and a decrease in the spin susceptibility, which is not observed here. The results in Fig. 3 indicate that above 300 K the same scattering process may be responsible for $d\rho/dT$ in all three compounds. However, for the superconducting ones there seems to be an extra T-independent scattering term which gradually freezes out below 300 K. Hence, above 300 K, the resistivity of $HoNi_2B_2C$ and YNi_2B_2C is greater than that of $LaNi_2B_2C$, but is parallel to it. Below 300 K this unknown scattering process freezes out, giving rise to the deviation from linear behavior in the Y- and Ho-containing compounds. The resistivity of nonsuperconducting $LaNi_2B_2C$ appears more like that of a regular metal, following a power law close to T^5 at low temperatures, crossing over to a linear high-temperature behavior. This behavior is consistent with electron-phonon scattering dominating the resistivity of the nonsuperconducting compound. The superconducting samples require an additional, as yet unknown, scattering process to understand their resistivity behavior. Phonons in conjunction with a small energy scale, perhaps the van Hove–like peak in the density of states at ε_F, might produce this kind of behavior.

Using published lattice parameters,[7] we find that YNi_2B_2C has a Hall number of 3.4 carriers per unit cell at 300 K (1.7 carriers per formula unit). It may be coincidental that this value is in good agreement with results of muon spin resonance (μSR) measurements, namely, 1.9 carriers per formula unit.[34] $LaNi_2B_2C$ has a smaller Hall coefficient than the superconducting compounds, but in a metallic system this does not necessarily indicate a greater carrier density.[35] The Hall coefficient of YNi_2B_2C has a stronger temperature dependence than that of $LaNi_2B_2C$, possibly as a consequence of the additional scattering process described above. Approaching 300 K, the temperature dependence (dR_H/dT) of YNi_2B_2C is similar to that of $LaNi_2B_2C$ although the magnitudes of R_H remain very different.

CONCLUSIONS

The results presented in this paper for nonsuperconducting $LaNi_2B_2C$ are entirely consistent with what is expected from electron-phonon scattering. However, there are some interesting differences in the normal-state properties of the superconducting and nonsuperconducting compounds. Associated with superconductivity, there is a linear term in the magnetic susceptibility and a distinct downward curvature from a linear high-temperature resistivity. These may indicate that the superconductivity in YNi_2B_2C and $HoNi_2B_2C$ is caused by phonons in conjunction with a small energy scale (responsible for the unusual T dependence of the resistivity and susceptibility) or even a nonphonon mechanism.

ACKNOWLEDGMENTS

We are grateful to W. F. Peck, Jr. for preparing the samples, to S. C. Smith for technical support, and to Dr. N. E. Hussey and Dr. A. P. Mackenzie for helpful discussions. Work in the UK was supported by EPSRC.

[1] R. Nagarajan *et al.*, Phys. Rev. Lett. **72**, 274 (1994).
[2] R. J. Cava *et al.*, Nature **367**, 252 (1994).
[3] H. W. Zandbergen *et al.*, Physica C **232**, 328 (1994).
[4] J. L. Sarrao *et al.*, Physica C **229**, 65 (1994).
[5] R. J. Cava *et al.*, Nature **367**, 146 (1994).
[6] T. Siegrist *et al.*, Nature **367**, 254 (1994).
[7] B. C. Chakoumakos and M. Paranthaman, Physica C **227**, 143 (1994).
[8] J. I. Lee *et al.*, Phys. Rev. B **50**, 4030 (1994).
[9] L. F. Mattheiss, Phys. Rev. B **49**, 13 279 (1994).
[10] R. Coehoorn, Physica C **228**, 331 (1994).
[11] W. E. Pickett and D. J. Singh, Phys. Rev. Lett. **72**, 3702 (1994).
[12] A. K. Gangopadhyay, A. J. Schuetz, and J. S. Schilling, Physica C **246**, 317 (1995).
[13] S. L. Bud'ko *et al.*, Physica C **243**, 183 (1995).
[14] S. A. Carter *et al.*, Phys. Rev. B **50**, 4216 (1994).
[15] D. D. Lawrie and J. P. Franck, Physica C **245**, 159 (1995).
[16] H. Eisaki *et al.*, Phys. Rev. B **50**, 647 (1994).
[17] P. C. Canfield *et al.*, Physica C **230**, 397 (1994).
[18] M. El Massalami *et al.*, Physica C **244**, 41 (1995).
[19] H. Schmidt and H. F. Braun, Physica C **229**, 315 (1994).
[20] A. I. Goldman *et al.*, Phys. Rev. B **50**, 9668 (1994).
[21] Q. Huang *et al.*, Phys. Rev. B **51**, 3701 (1995).
[22] T. E. Grigereit *et al.*, Phys. Rev. Lett. **73**, 2756 (1994).
[23] L. F. Mattheiss, T. Siegrist, and R. J. Cava, Solid State Commun. **91**, 587 (1994).
[24] C. C. Lai *et al.*, Phys. Rev. B **51**, 420 (1995).
[25] *Atom und Molekularphysik*, Landolt-Börnstein, Band 1, Parts 1–5 (Springer-Verlag, Berlin, 1950).
[26] C. Godart *et al.*, Phys. Rev. B **51**, 489 (1995).
[27] Z. Fisk and G. W. Webb, Phys. Rev. Lett. **36**, 1084 (1976).
[28] H. Takagi *et al.*, Phys. Rev. Lett. **69**, 2975 (1992).
[29] A. Carrington *et al.*, Phys. Rev. B **48**, 13 051 (1993).
[30] T. Nishikawa *et al.*, J. Phys. Soc. Jpn. **63**, 1441 (1994).
[31] J. W. Loram *et al.*, Physica C **235–240**, 134 (1994).
[32] B. Bucher *et al.*, Phys. Rev. Lett. **70**, 2012 (1993).
[33] T. Ito, K. Takenaka, and S. Uchida, Phys. Rev. Lett. **70**, 3995 (1993).
[34] R. Cywinski *et al.*, Physica C **223**, 273 (1994).
[35] C. M. Hurd, *The Hall Effect in Metals and Alloys* (Plenum, New York, 1972).