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Published in:

DOI:
10.1007/BF01318273

Citation for published version (APA):
Magnetic phase diagram and crystal fields of superconducting ErNi$_2$B$_2$C

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Received: 12 October 1994/Revised version: 22 November 1994

Abstract. We have measured the specific heat $C_p$ in magnetic fields and the resistance of the antiferromagnetically ordered borocarbide superconductor ErNi$_2$B$_2$C. From our data we show that the superconductivity at 10.6 K coexists with antiferromagnetic order beginning at 5.8 K, and we determine the magnetic $B$–$T$ phase diagram. The specific heat in zero field gives additional information about the crystalline electric field (CEF) splitting. We show that the low-temperature specific heat is dominated by several low-lying CEF doublets with the first excited level at about 10 K, while the splitting of the next two levels is about 50 to 100 K.

PACS: 74.70.Hk; 75.40.Cx

1. Introduction

Since the discovery of the borocarbide superconductors [1, 2] their metallurgical and physical properties have been the subject of many investigations [3–6]. Most of these works focussed on the determination of the superconducting parameters of the new intermetallic compounds. Presently there are only a few studies of the magnetic properties for the system RNi$_2$B$_2$C with $R =$ Ho, Er, Tm. Eisaki et al. [7] determined $B_{c2}$ of RNi$_2$B$_2$C; $R =$ Ho, Er, Tm, and they found peculiar anomalies in the $B_{c2}$ vs. $T$ curves, which they related to the onset of magnetism in these systems. Movshovich et al. [8] reported on the specific heat of single crystalline YNi$_2$B$_2$C and TmNi$_2$B$_2$C. They observed that the normal-state specific heat of TmNi$_2$B$_2$C contained CEF contributions, which they fitted with a Schottky anomaly having a value of 39 K for the first excited CEF doublet. Measurements of the specific heat and magnetization on single-crystalline HoNi$_2$B$_2$C performed by Canfield et al. [9] revealed also in this system small CEF splittings. Le et al. [10] performed a μSR-study of RNi$_2$B$_2$C; $R =$ Ho, Er and Tm, that proved the coexistence of magnetism and superconductivity on a microscopic level.

In order to obtain more information on the magnetic and the normal-state properties of these materials and their crystal-fields, we have measured the specific heat $C_p$ and its field dependence for ErNi$_2$B$_2$C. This system has been reported to be a magnetic superconductor with a $T_c$ of 10.5 K and $T_N$ of 5.5 K [2, 7]. Here we will (i) confirm the coexistence of superconductivity and magnetism, (ii) derive the CEF splitting of Er in ErNi$_2$B$_2$C and (iii) determine the magnetic $B$–$T_N$ phase diagram and its connection to the superconducting $B_{c2}$ – $T_c$ phase diagram.

We note that similar specific heat measurements on ErNi$_2$B$_2$C have been presented at two recent conferences by Michor et al. [11] and Hilscher et al. [12]. In both works it was stated, that the overall crystal-field splitting in ErNi$_2$B$_2$C is small. However, these measurements only extended over a small temperature range ($\leq 50$ K) and the corrections for the lattice contribution of ErNi$_2$B$_2$C were, as we will show, insufficient. Therefore, no quantitative estimate of the CEF scheme could be done. In these works it was also speculated that an anomaly at about 2 K in $C_p$ is indicative of the ordering of Ni moments. We will present evidence that this anomaly is due to the CEF contributions. Furthermore, the magnetic phase diagram and its relation to the superconductivity has not been derived in those works.

2. Metallurgy and experimental techniques

A polycrystalline sample of ErNi$_2$B$_2$C has been formed by arc-melting the constituents in stoichiometric ratio (Er: 4N, Ni: 4N, B: 3N and C: 3N) under argon atmosphere in a water-cooled copper crucible. The sample has been remelted seven times, after flipping over the ingots each
time. The weight loss during the melting was less than 0.1\%. The sample has been examined by X-ray diffraction and electron probe micro analysis (EPMA). The metallurgical analysis proves the sample to be homogeneous with the expected ErNi$_2$B$_2$C-stoichiometry apart from \( \approx 1\% \) second phase of composition Er$_2$Ni$_3$B$_5$. From the X-ray analysis the lattice parameters of the tetragonal structure are determined to \( a = 3.502 \) Å and \( c = 10.561 \) Å.

The superconducting and magnetic properties of ErNi$_2$B$_2$C have been examined via specific heat and resistance. The specific heat \( c_p \) has been determined by a conventional adiabatic technique, at temperatures from 2.5 to 20 K in fields up to 6 T and in zero field up to 180 K. The resistance \( R \) was measured with a four-probe ac-technique in zero field from 1.3 to 300 K. The same sample has been used in the \( \mu SR \)-measurements of Le et al. [10].

In order to correct the specific heat for lattice contributions a YNi$_2$B$_2$C single crystal was also measured. This large crystal was grown by the travelling-solvent floating-zone method in a NEC double-ellipsoid dual-lamp infrared image-furnace. As starting material stoichiometric melts were cast to a cylinder of 9 cm length and 6 mm diameter, for solvent a small disc of nominal composition Y:Ni:B:C 1:4:3:1 was prepared by arc-melting. As a seed a polycrystalline ingot of YNi$_2$B$_2$C was used. The growth was performed in a purified argon atmosphere monitored by a quadrupole mass-spectrometer. Seed and feed were counter-rotating at each 30 rpm and the seed-feed-translation were each adjusted at 0.5 mm/h. The average power input was about 650 W per lamp. The total growth process took approximately one week. Inspection of the grown boule by X-ray Laue and EPMA revealed that it consists of large grains of YNi$_2$B$_2$C separated by small amounts of Ni$_2$B flux, with a grain size varying between 10 and 100 mm$^3$. For the physical measurements these single crystalline grains were separated by spark cutting. More details on the crystal growth with this novel technique will be published elsewhere [13].

3. Results

The resistance measurement of ErNi$_2$B$_2$C reveals a superconducting transition at \( T_c \) = 10.6 K, defined as the midpoint of the transition with \( \Delta T_c = 0.5 \) K (see insert Fig. 1). There was no reappearance of resistivity below the \( \Theta_N \) temperature (\( T_N = 5.8 \) K, see below), hence the superconductivity coexists with the magnetic state.

The overall behavior of \( c_p/T \) and \( c_p \) vs. \( T \) in zero field for the Er and Y compounds is shown in Figs. 1 and 2. For both compounds our data of the specific heat are in good agreement with the measurements of other groups [5, 8, 11, 12] in the overlapping temperature ranges. The superconducting transition of YNi$_2$B$_2$C is clearly observable at \( T_c = 14.7 \) K determined via entropy balance. On the contrary, the superconducting transition of ErNi$_2$B$_2$C only appears as a small kink in \( c_p \) depicted in the inset of Fig. 2. The large background \( c_p \) impedes the resolution of this superconducting jump. A second anomaly can be seen in ErNi$_2$B$_2$C at about 12 K. This anomaly is only visible in the specific heat and does not appear in the resistance or susceptibility. A similar anomaly, although two to three times larger than that in our measurement, has also been observed by other groups [11, 12]. Because EPMA proves our sample to contain only about 1% second phase of Er$_2$Ni$_3$B$_5$, we believe this kink to represent the magnetic phase transition in \( c_p \) of this second phase.

The large background specific heat surrounding \( T_c \) is caused by magnetic and CEF effects. At \( T_N = 5.8 \) K there is a very strong \( \lambda \)-like anomaly denoting the magnetic ordering, and further the CEF strongly contributes to \( c_p/T \) below 100 K. To gain more information on the crystalline electric field a correction for the lattice contribution must be made. However, due to the significant mass difference of Y (atomic weight 88.9) and Er (atomic weight 167.3) the specific heat of YNi$_2$B$_2$C cannot simply be subtracted from ErNi$_2$B$_2$C.

\( c_p \) of YNi$_2$B$_2$C has already been described by Hilscher et al. [14] using Debye- and Einstein-contributions. In a similar way we have fitted the normal state specific heat of YNi$_2$B$_2$C with an expression \( c_p = \gamma T + c_{p,d}(Y) + c_{p,d}(B,C) \) with \( c_{p,d}(X) \) representing...
the specific heat of the element X calculated via Debye- and Einstein-formula, respectively. We applied a fit with the full Debye- and Einstein-integrals calculated by an interpolation scheme for temperatures above $T_c$. We are aware that especially for higher temperatures the results obtained by these functions are only approximate. However, it is the best possible approximation and we could describe this way the normal state specific heat of YNi$_2$B$_2$C using an electronic contribution $\gamma = 18.2$ mJ/mole K$^2$ (referred to as $\gamma_Y$). Debye-temperatures $\Theta_D$ of 287 K for Y and 382 K for Ni and an Einstein-temperature $\Theta_E = 745$ K for B and C. The electronic specific heat coefficient $\gamma_Y$ is in good agreement with previously published data [5,8], and the Debye- and Einstein-temperatures are in agreement with the mass relations between the different participating atoms. We stress that with a lower number of fit parameters we could not reproduce the normal state specific heat of YNi$_2$B$_2$C.

In order to compare our data with the data of other groups we used also the approach of Hilscher et al. [14]; they used two Einstein-temperatures and one Debye-temperature to fit their data. Thus, we got values of $\Theta_D = 210$ K, $\Theta_E(B,C) = 746$ K and $\Theta_E(B,C) = 309$ K in good agreement with the data of Hilscher et al. ($\Theta_D = 239$ K; $\Theta_E(B,C) = 680$ K; $\Theta_E(B,C) = 299$ K). However, the agreement between experiment and fit was better in our own approach.

Using the value of $\gamma_Y$, the ratio $\Delta c_p/\gamma Y T_c = 1.75 \pm 0.25$ can be calculated. This number is in agreement with the reported values of 1.59 [5] and 1.77 [8] and, as has been pointed out [5,8], classifies YNi$_2$B$_2$C as a modestly strong-coupling superconductor.

A similar calculation for ErNi$_2$B$_2$C is unreliable, since the jump $\Delta c_p$ has a large error due to the small anomaly in the specific heat (see inset Fig. 2). Further no reasonable value of $\gamma$ for ErNi$_2$B$_2$C (referred to as $\gamma_{Er}$) can be derived. Simple extrapolation of $c_p$ from 14 and 20 K leads to $\gamma_{Er} = 220$ mJ/mole K$^2$. This value is far too large, because the contributions of the crystal field excitations and short-range magnetic order greatly affect the result. However, $\gamma_{Er}$ should not be drastically different from $\gamma_Y$. If the f electrons of Er are fully localized, they do not contribute to $\gamma_{Er}$ and the value of $\gamma_Y$ would be a reasonable estimate. If some f electron character exists at the Fermi level, then $\gamma_{Er}$ will increase with respect to $\gamma_Y$. In the first case the superconducting jump should be similar to that of YNi$_2$B$_2$C, in the second case it should be even more pronounced than in YNi$_2$B$_2$C. We clearly observe a decrease in jump height of the superconducting transition of ErNi$_2$B$_2$C (if we calculate the ratio $\Delta c_p/\gamma Y T_c$ using for $\gamma$ the value of the Y-system of 18.2 mJ/mole K$^2$ we obtain 0.3, thus a value 6 times smaller than for YNi$_2$B$_2$C). Such a decrease in jump height for magnetic superconductors compared to their nonmagnetic allotropes is not uncommon and has been observed for e.g. ErRh$_4$B$_4$ [15]. Obviously, although the magnetism is not affecting superconductivity dramatically regarding transition temperatures, it does have an influence on the distribution of the superconducting entropy and the specific heat.

We have attempted to scale $c_p$ of YNi$_2$B$_2$C by multiplying $\Theta_D = 287$ K of Y by $\sqrt{m_Y/m_{Er}}$, giving a value of 209 K for Er. This scaled specific heat $c_p$ with $\Theta_D$ of Er = 209 K, $\Theta_D$ of Ni = 382 K and $\Theta_E(B,C) = 745$ K is taken as the lattice contribution and has been subtracted from the measured $c_p$ of ErNi$_2$B$_2$C. Our procedure is different from the lattice correction performed by Hilscher et al. [12], who simply subtracted the specific heat of YNi$_2$B$_2$C from ErNi$_2$B$_2$C. In Fig. 3 we show this “corrected” specific heat which we call the 4f-specific heat, or $c_p^{4f}$, plotted as $c_p/T$ vs. $T$. The main features of $c_p^{4f}/T$ are the antiferromagnetic anomaly at $T_N$ and the broad bump centered around 20 K indicating the crystal-field levels.

Using the 4f-specific heat and an extrapolation of $c_p^{4f}$ to $T = 0$ as indicated in Fig. 3 we can calculate the entropy, which is plotted in the inset of Fig. 3. The entropy calculations serve here as a check for the accuracy of the lattice correction we performed. For Er with $J = 15/2$ the entropy should saturate at $\ln(16) = 4R\ln(2)$. But in our case the entropy reaches about 6R ln(2), thus we have underestimated the subtracted contribution. We note that, if we would not perform the scaling of the lattice contribution by the factor $\sqrt{m_Y/m_{Er}}$, we would obtain even higher entropy values of more than 8R ln(2) at 180 K. The error in the determination of the entropy has three possible sources:

- Firstly we did not consider differences between $\gamma_{Er}$ and $\gamma_Y$.
- The second inaccuracy in the evaluation of the 4f-specific heat is the relatively strong dependence of $c_p^{4f}$ on the scaling of $\Theta_D$ from Y to Er. Further, at the highest temperatures still increasing entropy indicates differences in the Einstein contributions between YNi$_2$B$_2$C and ErNi$_2$B$_2$C, since at these temperatures the specific heat is mainly governed by the optical modes. The influence of these effects is illustrated by the fact that an ad hoc chosen $\Theta_D$ of Er (about 170 K instead of 209 K and a $\Theta_E(B,C)$ of about 600 K instead of 745 K) lead to a saturating entropy of less than 4R ln(2) at 180 K. The solid line in the inset of Fig. 3 shows the entropy calculated with $\Theta_D$ of Er = 170 K.
and \( \Theta_x(B, C) = 600 \text{ K} \). Obviously the main dependence of the result for the entropy on \( \Theta_D \) and \( \Theta_E \) appears at higher temperatures.

A third source of error comes from the extrapolation of \( c_p^J \) to \( T = 0 \). We estimated the low temperature part below the lowest measured point by \( \alpha T + \beta T^3 \) with \( \alpha = 600 \text{ mJ/mole K}^2 \). The parameter \( \alpha \) represents not only the electronic contribution to the specific heat, but as we will show, its value is influenced by low-lying crystal-field levels. Therefore, at the lowest temperatures we expect a decrease of the coefficient linear in temperature. However, we disregarded this error source as minor one (the contribution of the extrapolated temperature range to the entropy is about 0.3Rln(2)).

At any rate, with all these difficulties in evaluation of absolute values for \( c_p^J \), the overall features of the 4f-specific heat, i.e., the antiferromagnetism and the crystal field anomalies, remain qualitatively unaffected. This is because the largest error in the correction appears at higher temperatures, whereas at low temperatures, where the magnetic and crystal field anomalies in \( c_p \) occur, the lattice contribution is small.

Therefore, we can make several statements about the crystal-field scheme. In a tetragonal Er-system, in principle, 8 doublets have to be taken into account. The ground state without magnetic field and without magnetic ordering should be a Kramers doublet. In our case with magnetic ordering a singlet results. The entropy of the system above \( T_N \), at about 15 K, is already 2Rln(2), indicating that the first excited doublet should be at a rather low temperature of 10–20 K. And further we have the indication of a Schottky anomaly with the maximum in \( c_p^J/T \) at 20 K, an adjacent shoulder at 40 K, and an entropy of 3Rln(2) at 38 K which suggests two further doublets have become important. Accordingly, we propose a crystal-field scheme with a doublet ground state split into two closeby singlets due to magnetic ordering, a first excited doublet at about 10 K and two further doublets with energy splittings of about 50 K and 100 K, respectively. The four other doublets must be situated at higher energies and we cannot identify them from the specific heat measurement. Following this scheme we fitted \( c_p^J \) (represented by the solid line in Fig. 3), where we used energy splittings of 12 K, 63 K and 100 K. We remark that such a fit can only give an estimate of the general situation and absolute values have to be taken with care. Within this scheme the specific heat anomaly at about 2 K observed in ErNi_2B_2C by Michor et al. [11] and Hilscher et al. [12] would not be due to ordering of Ni moments, as they speculated, but represent contributions to the specific heat of the lowest lying CEF level. These contributions only appear as small structure in \( c_p \), since the main body of the Schottky anomaly is hidden by the specific heat of the magnetic transition (see Fig. 3). Only at lowest temperatures, where the specific heat of the Schottky anomaly becomes comparable of magnitude to the magnetic specific heat, the Schottky anomaly reveals itself by influencing the general shape of \( c_p(T) \) and forming the shoulder in \( c_p(T) \).

In Fig. 4 we show our measurements of the specific heat \( c_p \) in field of ErNi_2B_2C. The measurements can be divided into two different areas, those done in low field (\( \leq 2 \text{ T} \)) and those performed in high field (\( \geq 4 \text{ T} \)). In the low field regime clearly an anomaly at \( T_N \) is observed, although the transition peak although the transition peak smears out with increasing field. At high fields, on the contrary, the peak is so smeared out that no magnetic anomaly can be detected anymore and the concomitant entropy is shifted to higher temperatures. The broadening of the anomaly in field is probably related to the splitting of the low-temperature crystal-field-levels with field. We note that in the measurements of \( c_p \) in field no superconducting anomaly could be seen anymore. This is to be expected, since B_{c2} is probably, as in case of HoNi_2B_2C, strongly anisotropic [9] leading to a smeared out transition.

With our measurements in field we can complete the magnetic phase diagram (Fig. 5). The B_{c2}-curve has been taken from Eisaki et al. [7]. From our measurements of \( c_p(B) \) we determined the antiferromagnetic phase line. This line intersects the minimum of the anomaly in B_{c2}, and thereby confirms the magnetic origin of the anomaly.

![Figure 4](image_url)

**Fig. 4.** The field dependence of the specific heat of ErNi_2B_2C. The measurements have been made at 0 T (●), 1 T (△), 2 T (▽), 4 T (○) and 6 T (●). Also plotted is the specific heat in zero field of YNi_2B_2C (+).

![Figure 5](image_url)

**Fig. 5.** The magnetic phase diagram of ErNi_2B_2C. The B_{c2}-curve has been taken from Eisaki et al. [7]. The borderline of the magnetic phase transition we derived from our specific heat measurements.
4. Conclusion

We have performed measurements of the specific heat and resistance of $\text{ErNi}_2\text{B}_2\text{C}$. With our data we confirm the coexistence of superconductivity and magnetism. Further we determine the basic features of the CEF splitting of Er in $\text{ErNi}_2\text{B}_2\text{C}$. It turns out that in $\text{ErNi}_2\text{B}_2\text{C}$ similar to $\text{HoNi}_2\text{B}_2\text{C}$ and $\text{TmNi}_2\text{B}_2\text{C}$ the low-temperature specific heat is governed by CEF contributions. Finally, we complete the magnetic and superconducting $B-T_N$ and $T_c$ phase diagram. Thus, we can prove the magnetic origin of the anomaly in $B_{c2}$, as has been suggested by Eisaki et al. [7].

We acknowledge fruitful discussions with G.M. Eliahasberg. This work was partially supported by the Stichting voor Fundamenteel Onderzoek der Materie (FOM).

References


13. Brück, E. Menovsky, A.A.: (to be published)
