High-pressure effects in single crystals: $R\mathrm{Ni_2B_2C}$ ($R=\mathrm{Dy, Pr}$)

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We report electrical resistivity studies for two magnetic borocarbides $\mathrm{DyNi_2B_2C}$ and $\mathrm{PrNi_2B_2C}$ single crystals under quasihydrostatic pressure, using a diamond anvil cell. The superconducting critical temperature for $\mathrm{DyNi_2B_2C}$ decreases in linear form with pressure at a rate $dT_C/dP = -0.7$ K/GPa up to about 1.8 GPa, above this pressure T_C decreases drastically. Measurements of resistivity versus pressure in $\mathrm{DyNi_2B_2C}$ show that the feature related with the antiferromagnetic order remain almost unchanged. At 5.3 GPa, $\mathrm{PrNi_2B_2C}$ does not show evidence of a superconducting transition. From the resistivity data due to spin disorder we have calculated the exchange-interaction strength between rare-earth ions as a function of pressure.

The quaternary intermetallic borocarbides $R\mathrm{Ni_2B_2C}$ with $R=\mathrm{Dy, Ho, Er, Tm, Lu, Sc, Y, or Pd}$ (Refs. 1–4) are superconducting, whereas with $R=\mathrm{Pr, Gd, Tb, Yb}$ (Refs. 5–8) they are only magnetic. All these compounds crystallize in a body centered tetragonal (bct) structure with space group $I4/mmm$. They can be visualized as a framework of alternating RC atoms and $\mathrm{Ni_2B_2}$ layers stacked along the c direction.[9] Some present helical magnetism, heavy-fermion behavior[9,10] and other kinds of magnetism or superconductivity.[2,11]

In this paper we focussed on the study of $\mathrm{DyNi_2B_2C}$ and $\mathrm{PrNi_2B_2C}$ in which we performed high-pressure resistivity measurements using a diamond anvil cell. $\mathrm{DyNi_2B_2C}$ is unique among the $R\mathrm{Ni_2B_2C}$ compounds in that the antiferromagnetic transition temperature T_N is above the superconducting temperature T_C, in this case $T_N = 10.3$ K and $T_C = 6.2$ K.[12] The onset of superconductivity takes place in a magnetically ordered state. The magnetic structure at low temperature ($T<T_N$) consists of the R moments ordered ferromagnetically in the $a-b$ plane, with adjacent layers aligned in the opposite direction along the c axis.[13]

The second system that we studied, $\mathrm{PrNi_2B_2C}$, does not superconduct when measured at about 0.3 K. Several authors[5,14,15] have investigated this absence and the matter is still controversial. Neutron-diffraction measurements in polycrystalline samples of $\mathrm{PrNi_2B_2C}$ have shown an antiferromagnetic transition at $T_N = 4$ K.[13] Takeya and Kuznietz[16] have observed two magnetic transitions, one at $T\sim1.8$ K and other at $T=15$ K, the latter they believe to be of antiferromagnetic nature. Recently, single crystals of $\mathrm{PrNi_2B_2C}$ have been grown by our group.[17] Magnetic measurements performed in those crystals show two magnetic transitions, one at about 4 K another at about 15 K. Resistivity measurements also show another anomaly at about 8 K that we associated with a decreasing of magnetic scattering due to Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between d and f electron population.[18]

It is important to recognize that these two compounds have identical ordered structures in the ground state. However, both present different magnetic and superconducting properties. The magnetic interaction in these intermetallic compounds is mainly governed by the $4f$-$4f$ RKKY indirect exchange-interaction[18,19] mediated by the conduction electronic band.

The main idea of the high-pressure experiments described in this report is the fact that under quasihydrostatic pressure, the rare earth-ions can change their magnetic interactions, and thus also the overall electronic properties of the compound under study. Therefore, we have performed measurements of the electrical resistivity of the two single crystals at different pressures, and evaluated the RKKY exchange-interaction strength as a function of pressure. We point out that the pressure experiments were carried out several times for each sample and the results were reproducible. The results are reported below.

Single crystals of the $R\mathrm{Ni_2B_2C}$ ($R=\mathrm{Dy, Pr}$) compounds were obtained by the cold copper crucible method and characterized as described elsewhere.[17] Four-lead electrical resistance measurements were carried out over the temperature range from 2 to 300 K at various pressures. The quasihydrostatic pressure was generated using a diamond anvil cell (piston-cylinder type Be-Cu cell) (Ref. 20) consisting of two diamonds, each of 0.7 mm culet size. A steel gasket was preindented and a 200 μm diameter hole was drilled at the center. The samples used have dimensions of approximately $100\times100\times40$ μm^3 and were placed in the steel gasket hole. This was filled previously with pyrophyllite powder as the transmitting pressure medium. The metallic gasket was electrically insulated, pressing over it $\mathrm{Al_2O_3}$ powder of 1 μm grain size. Four gold wires of 10 μm diameter were used as electrical leads. A thin foil of aluminum was placed under the gold wires to prevent ruptures during the experiment. A thin Mylar film was used in order to prevent motion of the sample and of the electrical leads when pressure was applied. T_C was determined in $\mathrm{DyNi_2B_2C}$ when the electrical resistance was equal to zero. The high-pressure cell was calibrated at low temperature by using a Pb manometer.[21]

In order to obtain a quasihydrostatic environment, we packed the sample in pyrophyllite, a soft powder as the transmitting pressure media which develops shear stress at about $0.25\times P$, where P is the applied pressure.[22] Particularly, we do not discard that shear stresses might be present in our
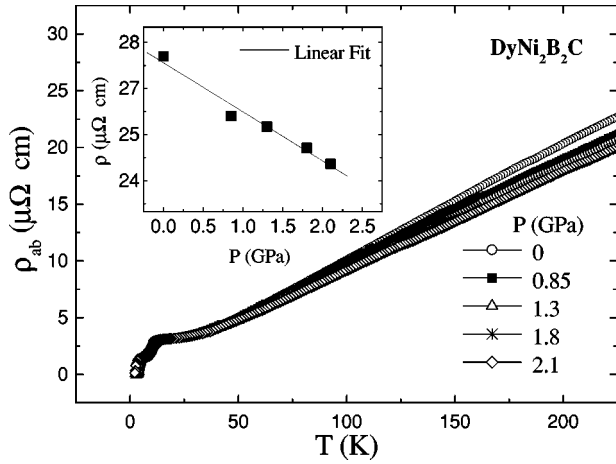
FIG. 1. Temperature and pressure dependence of the in-plane resistivity of $DyNi_2B_2C$ single crystal. Note that linearity of the resistivity from 50 to 300 K is not modified by pressure. The inset shows the linear variation of $\rho(P)$ at room temperature.

samples. However assuming that the bulk modulus of the $PrNi_2B_2C$ and $DyNi_2B_2C$ are similar to those of YNi_2B_2C and $HoNi_2B_2C$ which is about 200 GPa,[23,24] we think that the effects of the shear stress in our samples, could be not very substantial. As a probe of this assumption we examined the samples under optical microscopy after the pressure measurements, and they were intact, free of cracks, and fractures. Plots of the in-plane resistivity (ρ_{ab}) as a function of temperature and pressure for $DyNi_2B_2C$ are given in Figs. 1 and 2. At ambient pressure the $\rho_{ab}(T)$ curve reveals a linear behavior from room temperature down to about 50 K. At about $T = 10.8$ K it shows a change in the resistivity which is identified as the antiferromagnetic transition.[12] The onset of the superconducting transition occurs at 5.8 K and is completed at 4.8 K. In the high-pressure regime we found no significant change in the overall behavior of the resistivity curves above 50 K (see Fig. 1). At room temperature, the resistivity as a
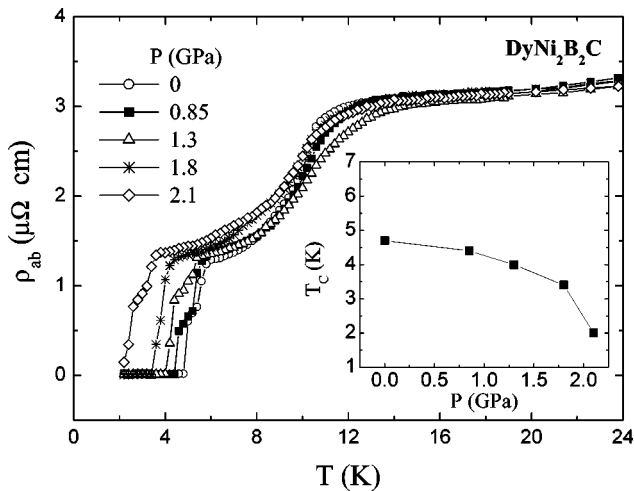

FIG. 2. A zoom view of the pressure effects in the superconducting and antiferromagnetic transitions of a $DyNi_2B_2C$ single crystal. Inset shows the change of T_C with pressure, which is almost linear from about 0 to 1.8 GPa.

function of pressure shows a linear dependence, decreasing at a rate $d\rho_{ab}/dP = -1.59$ $\mu\Omega$ cm/GPa (inset of Fig. 1), indicating that no structural transition is present. The effect of pressure on the resistivity at room temperature is to reduce it for about 12.5% at a pressure of about 2.1 GPa. The inset of Fig. 2 shows the pressure dependence of the superconducting critical temperature. In the pressure range from 0 to 1.8 GPa it seems a linear variation in the $T_C - P$ curve. This dependence was determined to be $dT_C/dP = -0.7$ K/GPa. At a pressure of 2.1 GPa a relatively strong change occurs in the superconducting transition (see Fig. 2). Although the transition to the superconducting state was not completed when measured down to 2 K such change suggests a quadratic behavior of $T_C(P)$ above 1.8 GPa, instead of the linear one. A quadratic decreasing of $T_C(P)$ dependence also has been reported in YNi_2B_2C, $HoNi_2B_2C$, $ErNi_2B_2C$, and $TmNi_2B_2C$ systems.[25]

It should be pointed out that all the superconducting systems RNi_2B_2C possess negative rates dT_C/dP (Refs. 25,26,24) except $LuNi_2B_2C$. The latter showed a small positive value on dT_C/dP.[19] Nevertheless, it is worth mentioning that in single crystals of $ErNi_2B_2C$ (Ref. 25) and polycrystalline $HoNi_2B_2C$ (Ref. 27) samples positive rates for dT_C/dP have been reported, but in polycrystalline $ErNi_2B_2C$ (Ref. 19) and in single crystal $HoNi_2B_2C$ (Ref. 25) the dT_C/dP rates have been found to be negative. Another observation is that the feature related with the antiferromagnetic transition in the $\rho(T)$ curves at 0, 0.85, 1.8 and 2.1 GPa seems to remain independent of the applied pressure, and only one curve (1.3 GPa) shows a lightly flattened onset. In order to know if T_N is indeed changed with the applied pressure, measurements of susceptibility at high pressure and low temperature will be necessary.

The second system studied was $PrNi_2B_2C$; compared with the $DyNi_2B_2C$ single crystal, the effective magnetic moment of Pr^{3+} ($3.58\mu_B$) is smaller than Dy^{3+} ($10.63\mu_B$), and we expected therefore that the interaction between spins of the rare earth will be weaker for $PrNi_2B_2C$. This weak magnetic interaction simply means that the system is more favorable for the emergence of the superconducting state. Our experiments indicate [see Fig. 3(a)] that this is not the case. At a pressure of about 5.3 GPa the crystal remains nonsuperconducting. It is important to mention that the pressure does not alter the general behavior of resistivity from room temperature to low temperature. At ambient pressure and low temperature, we observed a noticeable decrease in the slope of the curve at about 8 K. As the temperature decreases the change seems to be more pronounced, although it is not abrupt. We think that this anomaly could correspond to a decreasing of the scattering process due to the ordering of the spin structure, which is originated by the RKKY interaction between d and f electron population.[18] On the other hand, specific heat measurements on polycrystalline $PrNi_2B_2C$ have revealed a moderated heavy fermion behavior.[28,29]

Recently magnetic measurements in $PrNi_2B_2C$ single crystals have shown a decreasing of the magnetic moment of Pr ion in the c direction.[30] Consequently the experiments performed in $PrNi_2B_2C$ polycrystalline[29] and those in our single crystals allow us to think that spin screening effects
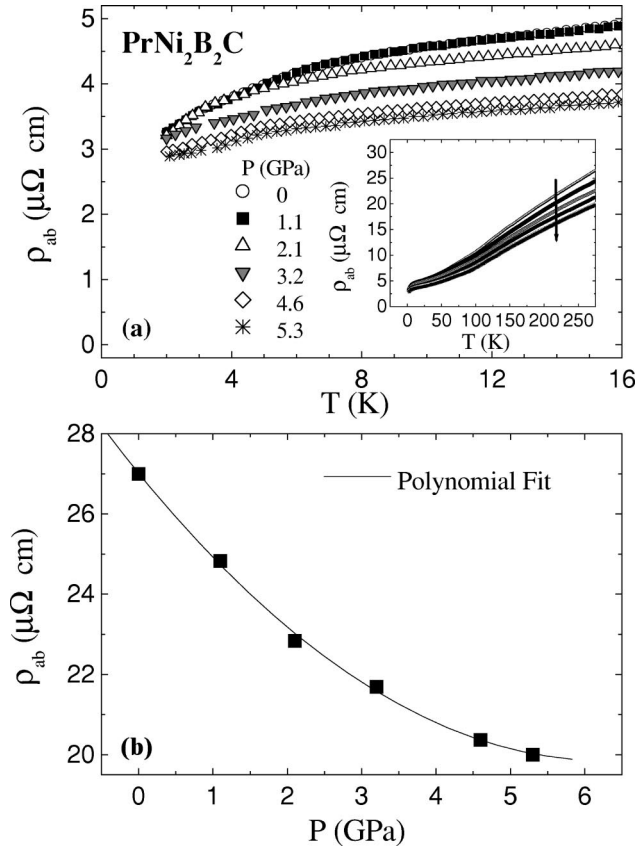
FIG. 3. (a) Pressure dependence of $\rho(T)$ for a $PrNi_2B_2C$ single crystal. Note that the resistivity drop at low temperature decreases with pressure. Inset shows the pressure effect on the overall behavior of $\rho(T)$. (The arrow indicates the increasing pressure.) (b) Pressure dependence of the electrical resistivity for a $PrNi_2B_2C$ single crystal at room temperature.

could be correlated with the resistivity change at low temperature (8 K). However, specific heat measurements on $PrNi_2B_2C$ single crystal are now in progress in order to understand more about this system.[30] Our group performed measurements of the magnetization and coercive forces, both as a function of the temperature for this system, and observed a magnetic transition at about 15 K, which might be ferrimagnetic in nature, instead of the antiferromagnetic one reported in the literature.[16] This transition is not manifested in resistivity measurements. It is important to note that in metallic praseodymium several structural transitions develop under pressure, one of them is particularly correlated with change of the valence.[31] In general such transitions are observed and manifested as changes in the resistivity-pressure measurements at room temperature. We made measurements of the resistivity as a function of pressure at room temperature in $PrNi_2B_2C$ and they shown a smooth parabolic behavior [Fig. 3(b)], which indicates that no structural transition is taking place. From the $\rho_{ab}(T)$ vs P curve we found that the resistivity decreases 13% at 2.4 GPa, which is bigger than that for $DyNi_2B_2C$. The width of the resistivity drop at low temperature decreases notably as the pressure increases, affecting the exchange interaction.

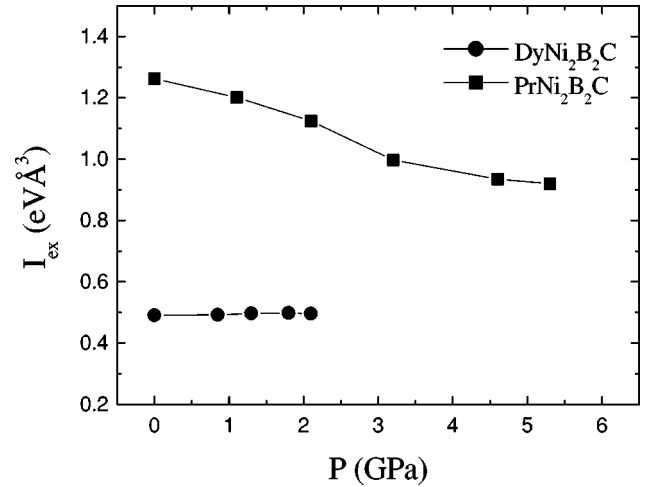As mentioned above, the magnetic interactions in these

FIG. 4. Exchange-interaction strength as a function of pressure for $DyNi_2B_2C$ and $PrNi_2B_2C$ single crystal. (Lines are guide to the eye.)

rare-earth compounds are mainly governed by the indirect RKKY exchange interaction. The strength of this interaction can be calculated from resistivity measurements. In the normal state, the resistivity as a function of temperature can be expressed as the sum of three terms: residual resistivity, resistivity due to electron-phonon scattering, and the magnetic contribution. The latter describes the scattering processes of the conduction electrons by the rare earth magnetic moments. The sum is therefore given by

$$\rho_T = \rho_0 + \rho_{ph}(T) + \rho_{spd}(T).$$

The exchange-interaction strength between the conduction electrons and the rare-earth ions can be calculated using the expression[18]

$$\rho_{spd}(T) = \frac{(3\pi N)I_{ex}^2(g-1)2J(J+1)}{\hbar e v_F^2},$$

where N is the number of rare-earth atoms per unit volume, v_F the Fermi velocity, g the Landé factor, and J the total angular momentum of the localized rare-earth ion R^{+3} in units of $\hbar$, according to Hund's rule ground state. The exchange-interaction strength I_{ex} is calculated from the measured value of the drop in resistivity due to the spin ordering ($\Delta\rho = \rho_{spd}$) at different pressures. For this calculation we assumed that v_F and J are not altered by pressure. The Fermi velocity v_F is expected to be close to the value $v_F = 3.6 \times 10^7$ cm/s calculated for $LuNi_2B_2C$.[32] In $DyNi_2B_2C$ the value we calculated for I_{ex} was about 0.5 eV $Å^3$ (3.8 meV) at ambient pressure. At high-pressure I_{ex} almost remains constant (with small increase at a rate of 3×10^{-3} eV $Å^3$/GPa). Thus, the interaction is not modified much by pressure (see Fig. 4). This result agrees well with the calculations for $HoNi_2B_2C$ and $ErNi_2B_2C$ already reported with values of I_{ex} of the order of 0.6 and 0.7 eV $Å^3$, respectively.[33] Accordingly, the magnitude of the exchange interaction is between the same values for these two compounds, even although the volume of the unit cell decreases from $DyNi_2B_2C$ to

$ErNi_2B_2C$. Thus, the small change for I_{ex} with pressure in $DyNi_2B_2C$ seems very reasonable.

Considering that the variation of T_N and the exchange-interaction strength in $DyNi_2B_2C$ compound were not substantially altered with pressure, at first glance it will come to suggest that there is some correlation between them. This latter could reinforce the idea that in this system T_N is principally determined by the interlayer coupling, because it is inferred to be of the RKKY type.[34] On the other hand, we conclude that the decreasing of T_C with pressure is not correlated with the RKKY exchange. Accordingly the superconducting state does not appear to have some relation with the magnetic order in this system as it has been suggested by Lynn.[15] For $PrNi_2B_2C$ the exchange-interaction strength was calculated at different pressures taking the resistivity drop between 8 and 2 K. At atmospheric pressure $\Delta\rho \sim 1\,\mu\Omega$ cm and I_{ex} was found to be 1.26 eV Å^3 (9.23 meV), which is bigger than for $DyNi_2B_2C$. From the viewpoint of the interlayer separation this value could be expected to be greater than for $DyNi_2B_2C$, because the unit cell of $PrNi_2B_2C$ has the smaller spatial separation between magnetic sheets along the c axis than $DyNi_2B_2C$. However, the variation of I_{ex} with pressure (see Fig. 4) shows a linear form with a rate $dI_{ex}/dP = -0.069$ eV Å^3/GPa, whose absolute value is larger than for $DyNi_2B_2C$. Considering the magnitude of I_{ex} in (Dy, Ho, Er) Ni_2B_2C, the negative rate dI_{ex}/dP in

$PrNi_2B_2C$ then indicates an anomalous behavior of the exchange interaction with the pressure.

In summary, electrical resistivity as a function of temperature and pressure were measured for two single crystals $DyNi_2B_2C$ and $PrNi_2B_2C$. For the system $DyNi_2B_2C$ under pressure, T_C at first decreases linearly, but above 1.8 GPa a drastic change occurs with resulting nonlinear behavior. On the other hand, the feature related with the antiferromagnetic order, seems to remain almost constant with the pressure. From the exchange-interaction strength as a function of pressure for $DyNi_2B_2C$ we conclude that the decreasing of T_C with pressure is not correlated with the RKKY interaction. The smooth change of the resistivity at about 8 K of the nonsuperconducting compound $PrNi_2B_2C$ (Ref. 14) is not modified with the applied pressure. Finally the pressure dependence of the exchange-interaction strength in this system shows an anomalous behavior.

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