Effect of hydrostatic and chemical pressure on the exchange interaction in magnetic borocarbide superconductors

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The investigation of pair-breaking effects in magnetic rare-earth nickel borocarbide superconductors reveals a considerable increase of the magnetic exchange integral $\mathcal{J}_{sf}$ by hydrostatic as well as chemical pressure. In both, $\mathcal{J}_{sf}$ is governed by the R-C distance (or lattice constant a) and is described quantitatively by a simple phenomenological model. Thereby, just two parameters $\mathcal{J}_{sf0} = 31$ meV and $\Delta\mathcal{J}_{sf}/\Delta a = 165$ meV/Å explain well the influence of chemical pressure upon the initial depression rates of T_c in solid solutions $R'_{1-x}R_x Ni_2 B_2 C$ with $R = $ Gd, Tb, Dy, Ho and $R' = $ Y and Lu.

In a first report on the coexistence of superconductivity and magnetism in $R Ni_2 B_2 C$ (with $R = $ Dy, Ho, Er, and Tm) Eisaki *et al.*[1] pointed out that the antiferromagnetic ordering temperatures as well as the depression of superconductivity due to the localized moments of the rare-earth sublattice roughly scale with the de Gennes factor $DG = (g_J - 1)^2 J(J+1)$, where g_J is the Landé factor and J is the total angular momentum of the rare-earth R^{3+} ion. More detailed investigations of solid solutions $Lu_{1-x}R_x Ni_2 B_2 C$ ($R = $ Gd, Dy) by Cho *et al.*[2], however, showed that significant deviations from de Gennes (DG) scaling occur for $T_N > T_c$ and even in the paramagnetic regime ($T_c > T_N$). As the largest pair-breaking effect with respect to the DG factor was observed for gadolinium they suggested that $J(J+1)$ of other R elements (e.g., Dy, Ho) may be reduced by crystalline electric field (CEF) effects to an effective value $[J(J+1)]_{eff}$. A numerical evaluation[2] of $[J(J+1)]_{eff}$ using the theory of Fulde and Peschl,[3] however, predicts a minor influence of the CEF upon the DG factor (see also Ref. 4). A breakdown of the linear relation between T_c and the fraction of magnetic ions was reported also for $Lu_{1-x}Ho_x Ni_2 B_2 C$, where $T_c > T_N$ across the whole series.[5]

It is the aim of this paper to analyze the influence of hydrostatic and chemical pressure upon pair-breaking in the borocarbide superconductors which serves as a probe for the s-f exchange interaction in the rare-earth ions.

Previous high-pressure studies on borocarbides with a nonmagnetic rare earth, e.g., on $YNi_2 B_2 C$, revealed a rather small effect upon T_c ranging from $dT_c/dp \simeq -90$ to $+32$ mK/GPa.[6–8] A small initial increase of T_c was also reported for $LuNi_2 B_2 C$ (see Ref. 6) showing that the pressure induced lattice stiffening of the borocarbide superconductors is small or perhaps compensated by electronic effects. Thus, magnetic $R Ni_2 B_2 C$ superconductors should be ideal compounds to study the effect of hydrostatic pressure upon the pair-breaking exchange interactions with the $4f$ electrons.

The reduction of T_c due to magnetic exchange with paramagnetic impurities is well described by the Abrikosov-Gor'kov (AG) pair-breaking theory[9] which provides the analytic relation

$$\ln\left(\frac{T_{c0}}{T_c}\right) = \Psi\left(\frac{T_{c0}}{2T_c}\rho + \frac{1}{2}\right) - \Psi\left(\frac{1}{2}\right), \tag{1}$$

where T_c and T_{c0} are the critical temperatures with and without magnetic impurities, Ψ is the digamma function, and ρ the pair-breaking parameter given by

$$\rho = \frac{cN(E_f)\mathcal{J}_{sf}^2(g_J-1)^2 J(J+1)}{k_B T_{c0}}, \tag{2}$$

i.e., by the concentration c of magnetic impurities, the density of states at the Fermi level, $N(E_f)$, the s-f exchange integral, $\mathcal{J}_{sf}$, and the DG factor. As hydrostatic pressure reduces interatomic distances, it increases the orbital overlap and may influence the exchange $\mathcal{J}_{sf}$ which should be visible by a change of the superconducting transition temperature. Investigations on the magnetic superconductor $HoNi_2 B_2 C$ (single crystal) by Uwatoko *et al.*[10] indeed showed a significantly enhanced effect of pressure upon T_c with $dT_c/dp \simeq -500$ mK/GPa. A similar result was reported for $TmNi_2 B_2 C$, too.[8] In a preceding investigation on polycrystalline $HoNi_2 B_2 C$, however, Carter *et al.*[11] found a significant increase of T_c by $dT_c/dp \simeq +700$ mK/GPa, i.e., just the opposite to the single-crystal result. On the other hand, both studies revealed a pressure induced increase of the Néel temperature T_N by $dT_N/dp \simeq +0.7$ K/GPa (Ref. 10) and $dT_N/dp \simeq +2.5$ K/GPa (Ref. 11). The significant sample dependence of these results may be explained by the close interplay of superconductivity with rather complex magnetic order phenomena which are easily modified by minor compositional changes.[12,13] To simplify the further interpretation we have studied magnetically dilute pseudoquaternary borocarbides which are closely related to the model of randomly distributed paramagnetic impurities in a superconductor solved analytically by Abrikosov and Gor'kov[9] [see Eq. (1)].

Resistivity measurements under hydrostatic pressure up to 1.3 GPa on $LuNi_2 B_2 C$, $Y_{1-x}Gd_x Ni_2 B_2 C$ with $x = 0$, 0.05, 0.15, and 0.2 and on $Y_{0.6}Dy_{0.4}Ni_2 B_2 C$ were performed in a liquid pressure cell (see Ref. 14). As a typical result the $Y_{0.85}Gd_{0.15}Ni_2 B_2 C$ data are shown in Fig. 1 where T_c was determined from the midpoint of the resistive transitions yielding $T_c(p)$ collected together in Fig. 2. As noted above, T_c of Y- and $LuNi_2 B_2 C$ is nearly pressure independent while there is a significant pressure effect in the dilute magnetic borocarbides revealing a correlation between the reduction of the transition temperature, $\Delta T_c = T_{c0} - T_c$, due to pair-
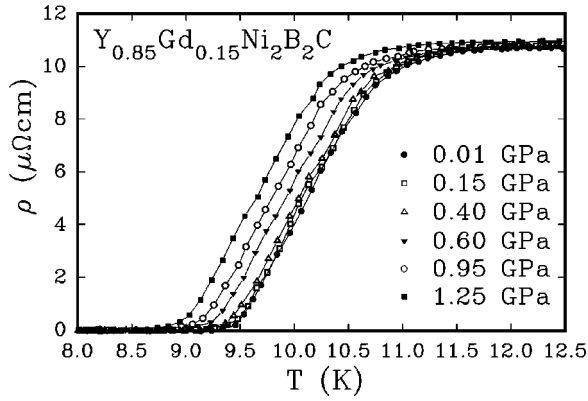
FIG. 1. The resistivity, $\rho(T)$, of $Y_{0.85}Gd_{0.15}Ni_2B_2C$ under hydrostatic pressure p as labeled.

breaking at ambient pressure and the reduction of T_c by hydrostatic pressure. Accordingly, the larger the pair-breaking parameter ρ the larger is dT_c/dp of these paramagnetic superconductors. Assuming a linear increase of the exchange integral $\mathcal{J}_{sf}$ with applied pressure allows a quantitative evaluation of $d\mathcal{J}_{sf}/dp$ because $T_{c0}(YNi_2B_2C)$ is almost independent of pressure. Furthermore, $N(E_f) \simeq 0.34$ states/(eV atom spin) is assumed to be constant as demonstrated by a systematic band structure study for the whole series of *heavy* rare-earth borocarbides.[15] The concentration of magnetic moments c is $x/6$. Thereby, the analysis of $T_c(p)$ by a modified AG relation (see Fig. 2) with two free parameters incorporated into the pair-breaking relation

$$\rho = \frac{cN(E_f)\left[\mathcal{J}_{sf}(0) + \dfrac{d\mathcal{J}_{sf}}{dp}p\right]^2 DG}{k_B T_{c0}} \quad (3)$$

yields a common set of parameters $\mathcal{J}_{sf}(0) \simeq 36$ meV and $d\mathcal{J}_{sf}/dp \sim 1.3$ meV/GPa describing the $Y_{1-x}Gd_xNi_2B_2C$ results and the same magnitude of $d\mathcal{J}_{sf}/dp$ for $Y_{0.60}Dy_{0.40}Ni_2B_2C$. The transition temperatures, mean suppression rates dT_c/dp and $\mathcal{J}_{sf}(p)$ results are collected in
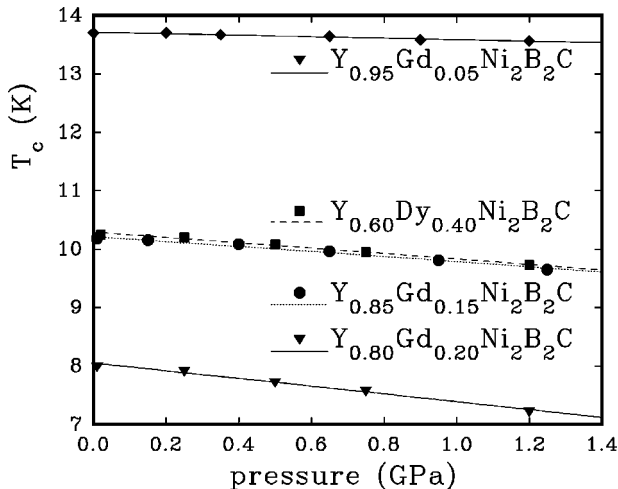

FIG. 2. The pressure dependence of the superconducting transition temperature of paramagnetic $Y_{1-x}R_xNi_2B_2C$ with R = Gd, Dy. The solid lines correspond to the fit by the modified AG relation [Eqs. (1) and (3)].

TABLE I. The transition temperature T_c at ambient pressure, dT_c/dp, the exchange integral $\mathcal{J}_{sf}(p=0)$ and its pressure dependence $d\mathcal{J}_{sf}/dp$ obtained by fitting the modified AG relation.

	$T_c(p=0)$ (K)	dT_c/dp mK/GPa	$\mathcal{J}_{sf}(0)$ meV	$d\mathcal{J}_{sf}/dp$ meV/GPa
$LuNi_2B_2C$	16.5	$\sim 0 \pm 80$		
YNi_2B_2C	15.5	$\sim 0 \pm 80$		
$Y_{0.95}Gd_{0.05}Ni_2B_2C$	13.7	$-120\,(50)$	36.8	1.22
$Y_{0.60}Dy_{0.40}Ni_2B_2C$	10.25	$-430\,(50)$	32.7	1.24
$Y_{0.85}Gd_{0.15}Ni_2B_2C$	10.2	$-430\,(50)$	36.0	1.26
$Y_{0.80}Gd_{0.20}Ni_2B_2C$	8.0	$-630\,(80)$	36.2	1.33

Table I. The absolute values given for $d\mathcal{J}_{sf}/dp \simeq 1.3$ meV/GPa are perhaps slightly overestimated because a minor reduction of T_c due to other effects may be present.

The results mentioned above indicate a rather systematic effect of hydrostatic pressure upon the exchange coupling. Thus, a variation of $\mathcal{J}_{sf}$ is anticipated also in the case of ''chemical pressure,'' i.e., when the lattice parameters change due to rare-earth substitution in the pseudoquaternary systems $R_xR'_{1-x}Ni_2B_2C$ with R' = Y or Lu. Investigations on the effect of rare-earth substitutions in heavy rare-earth borocarbides revealed a quite linear variation of the lattice constants showing neither a line broadening nor superstructure reflections in the x-ray-diffraction (XRD) patterns.[16] Across the series RNi_2B_2C with R from La to Lu there is a counteracting variation of the lattice constants a and c where the lanthanide contraction causes a reduction of a but an increase of c.[17] Hence, chemical pressure acts in an uniaxial manner. On the other hand, high-pressure XRD data by Oomi et al.[18] for YNi_2B_2C and by Jaenicke-Rössler et al.[19] for $TbNi_2B_2C$ revealed a reduction of both the lattice constant a and c. Thus, the lattice compression by hydrostatic pressure is much more isotropic than by chemical pressure. The compressibilities reported for YNi_2B_2C and $TbNi_2B_2C$ $\Delta V/\Delta p \simeq -0.8\,(1)$ Å^3/GPa and $\Delta a/\Delta p \simeq 6.2\,(2)$ mÅ/GPa are similar and shall hold approximately ($\pm 5\%$) also for the other RNi_2B_2C compounds as well as for the pseudoquaternaries $R_xR'_{1-x}Ni_2B_2C$. These compressibilities can be used to calculate the hydrostatic pressure required to reduce either the volume V or the lattice parameter a of YNi_2B_2C towards the smaller value of $LuNi_2B_2C$; hence, one obtains quite different values of 4.3 GPa and 9.8 GPa, respectively.

In order to analyze the effect of chemical pressure we compare the data available for the solid solutions $R'_{1-x}R_xNi_2B_2C$ with R = Gd, Tb, Dy, Ho, Er and R' = Y, Lu (for references see Table II). For each of them we evaluate $\mathcal{J}_{sf}$ using Eqs. (1) and (2) with $N(E_f) \simeq 0.34$ states/(eV atom spin) to fit the reported $T_c(x)$ data in the dilute paramagnetic limit, i.e., $x < 0.3$ and $x < 0.5$ for R = Gd, Tb and R = Dy, Ho, Er, respectively. The values thus obtained for $\mathcal{J}_{sf}$ and the relative difference between the ionic size of R and R' indicated by the change of the a-lattice constant, Δa, are collected in Table II. The comparison of $\mathcal{J}_{sf}$ with the relative compression of a (i.e., of the R-C bond for $x \to 0$) generally reveals larger $\mathcal{J}_{sf}$ values in the Lu systems and also an overall correlation of $\mathcal{J}_{sf}$ and Δa. Note, there is a good quantitative agreement for $\mathcal{J}_{sf}$

TABLE II. The exchange integral $\mathcal{J}_{sf}$ of the solid solutions $R_x R'_{1-x}\text{Ni}_2\text{B}_2\text{C}$ with $R = \text{Gd-Er}$ and $R' = \text{Y}$, Lu obtained by fitting the $T_c(x)$ data by the AG relation (for details see text) and $\Delta a = a_{x=1} - a_{x=0}$ the change in the lattice parameter a. The $T_c(x)$ data are taken from this work, El Massalami et al. (Ref. [20]), Cho et al. (Ref. [2]), Bitterlich et al. (Ref. [21]), Eversmann et al. (Ref. [22]), and Freudenberger et al. (Ref. [5]).

R	$R' = \text{Y}$		$R' = \text{Lu}$	
	$\mathcal{J}_{sf}$ (meV)	Δa (10^{-2} Å)	$\mathcal{J}_{sf}$ (meV)	Δa (10^{-2} Å)
Gd	38	5.5	48	11.6
Tb	36	2.7		8.8
Dy	33	0.9	39	7.0
Ho	31	−0.6	37	5.5
Er	33	−2.4	40	3.7

~ 37–38 meV in the Y/Gd and Lu/Ho series where $\Delta a \simeq 0.055$ Å is of the same magnitude. The significance of the $\mathcal{J}_{sf}$ values given for rare earths with small de Gennes factors (i.e., for Er with DG$=2.55$ compared to DG$=15.75$ for Gd) is, of course, reduced because other effects gain importance, e.g., a dip of about 1.5 K in $T_c(x)$ observed for $\text{Y}_{1-x}\text{Lu}_x\text{Ni}_2\text{B}_2\text{C}$.[16]

A simple quantitative estimation of the relative increase of "chemical pressure" in $\text{Lu}_{1-x}\text{Gd}_x\text{Ni}_2\text{B}_2\text{C}$ compared to $\text{Y}_{1-x}\text{Gd}_x\text{Ni}_2\text{B}_2\text{C}$ is obtained by replacing the above result $\mathcal{J}_{sf}=48$ meV for Lu/Gd by an expression $\mathcal{J}_{sf}$ ($=38$ meV in Y/Gd) $+ d\mathcal{J}_{sf}/dp (=1.3$ meV/GPa$) \times P_0^{chem}(1-x)$, where

the factor $(1-x)$ accounts for the gradual release of chemical pressure within the solid solution, $P^{chem}(x) = P_0^{chem}(1-x)$. Thereby, the relative "chemical pressure" in the Lu based solid solution compared to the Y based one, P_0^{chem}, is found to be about 10 GPa. We note that just the same magnitude of hydrostatic pressure is required to reduce the lattice parameter a of $\text{YNi}_2\text{B}_2\text{C}$ to that of $\text{LuNi}_2\text{B}_2\text{C}$ indicating that the key distance which modifies the s-f exchange in the R ion is the R-C bond length. The significant influence of this bond upon the intra-atomic exchange $\mathcal{J}_{sf}$ may be explained by its shortness and covalent character.[15]

In order to achieve a quantitative description of the effect of chemical pressure we propose a simple phenomenological relation for the pair-breaking parameter ρ. Thereby, we introduce a linear dependence of the exchange integral $\mathcal{J}_{sf}$ on the lattice parameter a

$$\rho = \frac{cN(E_f)\left[\mathcal{J}_{sf0} + \dfrac{d\mathcal{J}_{sf}}{da}\Delta a(1-x)\right]^2 \text{DG}}{k_B T_{c0}} \qquad (4)$$

with $\Delta a \equiv a_{x=1} - a_{x=0}$ and two parameters: $\mathcal{J}_{sf0}$ is the exchange integral of unalloyed $R\text{Ni}_2\text{B}_2\text{C}$, where the R-C distance corresponds properly to the individual R-ion size (i.e., $a = 3.588$ Å for $\text{GdNi}_2\text{B}_2\text{C}$, $a = 3.560$ Å for $\text{TbNi}_2\text{B}_2\text{C}$, and so forth; see Ref. [17]) and $d\mathcal{J}_{sf}/da$ accounts for the effect of chemical pressure due to R/R' substitution. These two parameters shall be valid for a set of pseudoquaternaries $R_x R'_{1-x}\text{Ni}_2\text{B}_2\text{C}$ with $R = \text{Gd-Ho}$ and $R' = \text{Y}$ and Lu. The solid solution without chemical pressure (i.e., $\Delta a \rightarrow 0$) is ap-
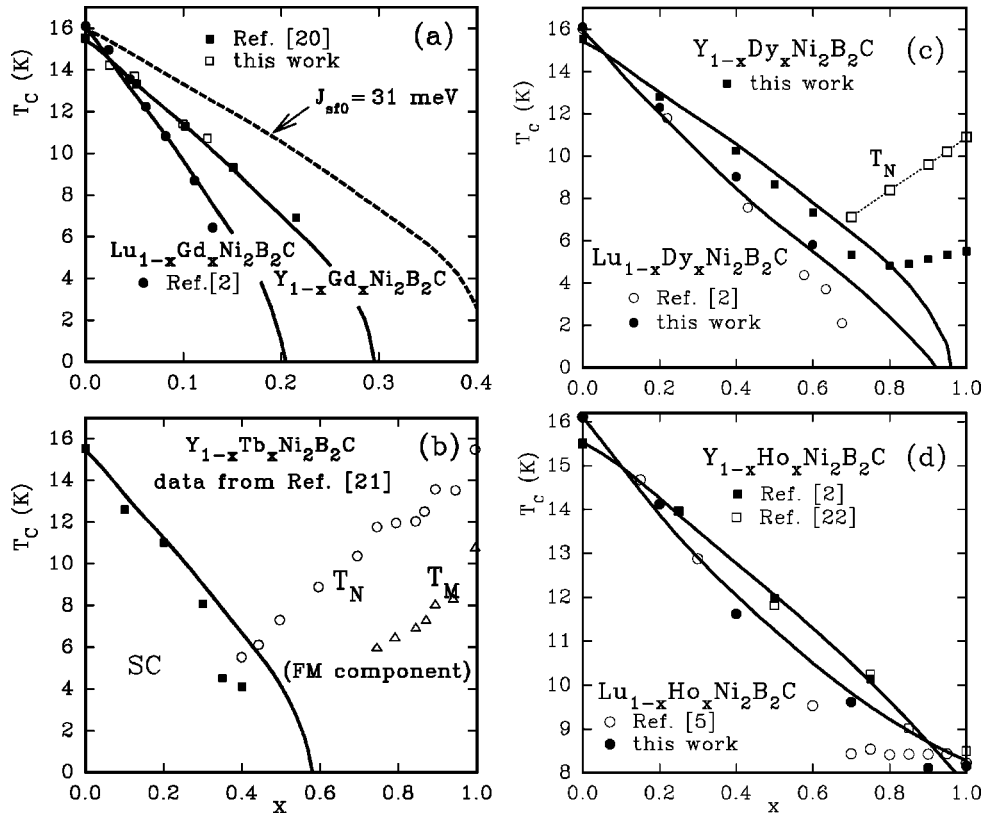

FIG. 3. Comparison of $T_c(x)$ calculated with Eqs. 1 and 4 (solid lines) and the experimental data as labeled. For $\text{Lu}_{1-x}\text{Gd}_x\text{Ni}_2\text{B}_2\text{C}$, the AG prediction for $\mathcal{J}_{sf0}=31$ meV without taking into account chemical pressure is shown by the dashed line.

proximately realized by $(Y,Ho)Ni_2B_2C$ yielding $\mathcal{J}_{sf0} = 31$ meV, which is assumed to be constant within the heavy rare-earth series RNi_2B_2C. The second parameter, $d\mathcal{J}_{sf}/da$, should be related to the pressure effect via the compressibility of the lattice constant a, i.e., $d\mathcal{J}_{sf}/da \simeq d\mathcal{J}_{sf}/dp \times dp/da$, but as we noted above $d\mathcal{J}_{sf}/dp = 1.2 - 1.3$ meV/GPa may be overestimated. In fact, a slightly reduced value of 1.0 meV/GPa times $(6.2 \text{ m\AA/GPa})^{-1}$ yielding $d\mathcal{J}_{sf}/da = 165$ meV/Å gives satisfactory agreement between the calculated $T_c(x)$ using Eqs. 1 and 4 [solid lines in Figs. 3(a)–(d)] and the experimental T_c values of the solid solutions $R'_{1-x}R_x Ni_2B_2C$ ($R =$ Gd, Tb, Dy, Ho and $R' =$ Y, Lu). Of course, a phenomenological approach based on the AG theory which eschews all magnetic correlations cannot account for the influence of long-range magnetic order when T_N exceeds T_c as, e.g., in $Y_{1-x}Dy_x Ni_2B_2C$ for $x > 0.6$ [see Fig. 3(c)]. Nevertheless, the comparison of the model curves with the experimental data demonstrates that the simple two parameter account for the chemical pressure describes reasonably well the initial suppression rates of T_c in the magnetically dilute limit ($x \rightarrow 0$). Even the pronounced curvature in $T_c(x)$ of $Lu_{1-x}Ho_x Ni_2B_2C$ can be traced back

to the release of chemical pressure within this series. The present approach explains a number of features of the phase diagrams in Figs. 3(a)–(d) showing that $\mathcal{J}_{sf0} \simeq 31$ meV is indeed constant within the heavy rare-earth series RNi_2B_2C and that the CEF influence upon $T_c(x)$ is small as predicted theoretically.[3]

In conclusion, we have shown that the reduction of T_c in solid solutions $Y_{1-x}R_x Ni_2B_2C$ by hydrostatic pressure is significantly enhanced compared to YNi_2B_2C. This enhanced reduction can be traced back to a pressure induced increase of the magnetic exchange integral $\mathcal{J}_{sf}$. The corresponding effect of ''chemical pressure'' arising from the change of the lattice parameter a due to rare-earth substitution is even quantitatively in line with that of hydrostatic pressure. This can be accounted for by a simple phenomenological model where $\mathcal{J}_{sf}$ increases linearly as the lattice parameter a shrinks with respect to that of unalloyed RNi_2B_2C.

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