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# Electron spin resonance of $\mathbf{Gd^{3+}}$ in the normal state of $\boldsymbol{R}\mathbf{Ni_2B_2C}$ $(\boldsymbol{R}\mathbf{=Y,Lu})$

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Electron spin resonance (ESR) of $Gd^{3+}$ in the normal state ($T>T_c$) of $R_{1-x}Gd_xNi_2B_2C$ ($R$=Y,Lu) is reported. The results show that the exchange coupling between the rare-earth localized magnetic moment and the conduction electrons depends on the conduction electrons momentum transfer ($|\mathbf{k}_F^{\mathrm{in}}-\mathbf{k}_F^{\mathrm{out}}|=q$), i.e., $J_{fs}(q)$. The temperature dependence of the ESR linewidth yields a value for one of the exchange parameters, $\langle J_{fs}^2(q)\rangle_{E_F}^{1/2}$, which is in agreement with that estimated from the slope of the initial linear decrease of $T_c$ by the $Gd^{3+}$ impurities. These results indicate that the $R_{1-x}Gd_xNi_2B_2C$ ($R$=Y,Lu) compounds behave as conventional BCS superconductors, in agreement with previous reports.

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## I. INTRODUCTION

The series of quaternary intermetallic rare-earth nickel borocarbides $R$Ni$_2$B$_2$C ($R$ = rare earth) compounds[1] have recently attracted great interest due to their relatively high superconducting temperatures ($T_c$=16.6 K for $R$=Lu and $T_c$=15.5 K for $R$= Y).[2] The magnetic anisotropy and coexisting superconductivity (SC) with the antiferromagnetic (AF) ordering associated to the magnetic rare-earths $R$ elements ($T_N \lesseqgtr T_c$),[3–5] have strongly motivated the scientific community to study these materials. The interplay between SC and magnetism in these materials resembles that of the ternary ErRh$_4$B$_4$ and HoMo$_6$S$_8$ compounds.[6] The incommensurate modulated magnetic structure shown by neutron diffraction experiments in HoNi$_2$B$_2$C (Ref. 7) at temperatures between T$_N\approx$5 K and T$_c\approx$7.5 K, and the suppression of SC by the substitution of Dy by Lu in DyNi$_2$B$_2$C,[8] were interpreted in terms of a *magnetic* pair breaking in the $R$Ni$_2$B$_2$C ($R$=Er,Dy) compounds. The structure of the $R$Ni$_2$B$_2$C compounds is a filled variant of the body-centered tetragonal (bct) ThCr$_2$Si$_2$ (space group $I_4/mmm$) with Ni layers perpendicular to the $c$ axis.[9] This structure is qualitatively similar to that of the layered cuprate high-$T_c$ superconductors. However, no local magnetic moment or AF spin correlations on the Ni sublattice have been found.[10] In addition, electronic band structure calculations suggest that the $R$Ni$_2$B$_2$C compounds are 3D $d$-band metals and that the SC is mediated by the conventional electron-phonon BCS mechanism.[11–13] Experimental support for this is given by tunneling spectroscopy[14] and boron isotope effect[15] measurements in these materials.

It is known that by means of electron spin resonance (ESR) of dilute rare-earth magnetic impurities (i.e., $Gd^{3+}$) in the normal state of BCS-type superconducting compounds, it is possible to determine the exchange parameters between the localized magnetic impurity and the conduction electrons (CE's).[16] It was also shown that the exchange parameter obtained from the thermal broadening of the ESR linewidth (Korringa rate), was comparable with that extracted from the slope of the initial linear decrease of $T_c$ by the magnetic impurities, as predicted by the Abrikosov Gorkov (AG) theory.[16,17] The present work's goal is to measure, by means of ESR, the exchange parameters between the localized magnetic moment of $Gd^{3+}$and the CE's in the normal state of the $R$Ni$_2$B$_2$C ($R$=Y,Lu) compounds, and to compare the value obtained from the Korringa rate with the one obtained from the reduction of $T_c$ by the $Gd^{3+}$ impurities.

## II. EXPERIMENT

Single crystals of Lu$_{1-x}$Gd$_x$Ni$_2$B$_2$C ($x\approx$0.005) were grown at the Ames Laboratory by the high-temperature flux growth method described elsewhere.[3,18] The Y$_{1-x}$Gd$_x$Ni$_2$B$_2$C ($x\approx$0.005) samples were made at the CBPF Laboratory in a polycrystalline form by the arc-melting technique.[19] The structure and phase purity were checked by x-ray powder diffraction and the crystals orientation determined by the usual Laue method. The ESR experiments were carried out in a conventional Varian ESR spectrometer using a TE$_{102}$ room-temperature cavity. The sample temperature was varied using a helium gas flux temperature controller. To increase the ESR signal to noise ratio, the temperature dependences of the spectra were taken in powdered samples. Magnetization measurements have been done in a Quantum Design dc superconducting interference device magnetometer. The temperature dependence of the magnetic susceptibility in the normal state was measured increasing the temperature, after zero field cooling (ZFC), in a field of 5 kOe. Table I gives the $Gd^{3+}$ concentration estimated from the fitting of the magnetic susceptibility data to a Curie-Weiss law.

## III. EXPERIMENTAL RESULTS

Figure 1 shows the $Gd^{3+}$ ESR powder spectra observed in the normal state at $T$=18 K for $R_{1-x}$Gd$_x$Ni$_2$B$_2$C ($R$

TABLE I. Experimental parameters for $Gd:(Lu,Y)Ni_2B_2C$.

| | $g$ | $a$ | $b$ | $c$ | $\gamma$ | $\beta$ | $\frac{\Delta T_c}{\Delta c}$ |
|---|---|---|---|---|---|---|---|
| | | Oe | Oe/K | % | $\frac{\text{mJ}}{\text{mol K}^2}$ | $\frac{\text{mJ}}{\text{mol K}^4}$ | K/% |
| $Lu_{1-x}Gd_xNi_2B_2C$ | 2.035(7) | 165(10) | 13(1) | 0.5(2) | 19(2) [a] | 2.67(10)X10$^{-4}$ [a] | $-0.65(4)$ [a] |
| $Y_{1-x}Gd_xNi_2B_2C$ | 2.03(3) | 830(30) | 11(2) | 2.1(2) | 18.7(5) [a] | 1.02(10)X10$^{-4}$ [a] | $\approx -0.43$ [a] |

[a] See Refs. 8,34,38,39.

$=$Y, Lu) compounds with $x \approx 0.005$ for $R=$Lu(T$_c \approx 16$ K) and $x \approx 0.02$ for $R=$Y(T$_c \approx 15$ K). The spectra show the usual Dysonian type of line shape,[20] characteristic of metallic sample particles of dimensions much larger than the skin depth. The dashed lines in Fig. 1 are the best fit of the experimental spectra to a Lorentzian admixture of absorption and dispersion derivatives.[21] From these fittings the linewidth $\Delta H$ and the $g$ value are obtained.

Figure 2 presents the temperature dependence of the $Gd^{3+}$ ESR linewidth for the samples of Fig. 1. The observed linear thermal broadening of $\Delta H$ indicates that the $Gd^{3+}$ localized magnetic moment relax to the lattice via an exchange coupling with the CE's, known as the Korringa mechanism.[16] The dashed lines are the best fit of the data to $\Delta H = a + bT$.

Several samples of Gd concentrations in the range between 0.5 to 2 % were measured. Within the accuracy of the measurements, the $b$ and $g$ values were concentration independent and the residual linewidth $a$ increases with the Gd concentration. The $g$ value was found to be temperature independent within the experimental error. Table I shows the experimental parameters obtained with $x \approx 0.005$ for the Lu-based sample and $x \approx 0.02$ for the Y-based sample.

We were unable to measure the ESR of $Gd^{3+}$ in the superconducting state ($T < T_c$) of the $R_{1-x}Gd_xNi_2B_2C$ ($R$ $=$Y,Lu) compounds. This is usually an extremely difficult measurement due to (i) the large change in the loaded cavity quality factor ($Q_l$) between the normal and superconducting state and (ii) the interaction between the vortices and the microwave magnetic field $h_{rf}$ in the superconducting state. That results in a large frequency drift and nonresonant microwave absorption in the ESR detector system.

## IV. ANALYSIS AND DISCUSSION

The exchange interaction $J_{fs}\mathbf{S}\cdot\mathbf{s}$ between a localized $4f$ electron spin ($\mathbf{S}$) on a solute atom ($Gd^{3+}$) and the free CE's spin ($\mathbf{s}$) of the host metal, cause $g$ shift (Knight shift)[22] and thermal line broadening (Korringa rate)[23] of the ESR spectra. Conduction electron-electron exchange enhancement[24,25] and the $q$-dependent exchange interaction $J_{fs}(q)$ (Ref. 26) are often used in the analysis of the ESR data.[27] $J_{fs}(q)$ is the Fourier transform of the spatially varying exchange coupling. In this case, and when "bottleneck" and "dynamic" effects are not present, the $g$ shift ($\Delta g$) and Korringa rate ($b$) can be written as[28]

$$\Delta g = J_{fs}(0)\frac{\eta(E_F)}{1-\alpha} \tag{1}$$

and

$$b = \frac{d(\Delta H)}{dT} = \frac{\pi k}{g\mu_B}\langle J_{fs}^2(q)\rangle_{E_F}\eta^2(E_F)\frac{K(\alpha)}{(1-\alpha)^2}, \tag{2}$$

where $J_{fs}(0)$ and $\langle J_{fs}^2(q)\rangle_{E_F}$ are the effective exchange parameters between the $Gd^{3+}$ local moment and the CE's in the presence of CE's momentum transfer ($q = |\mathbf{k}_F^{\text{in}} - \mathbf{k}_F^{\text{out}}|$

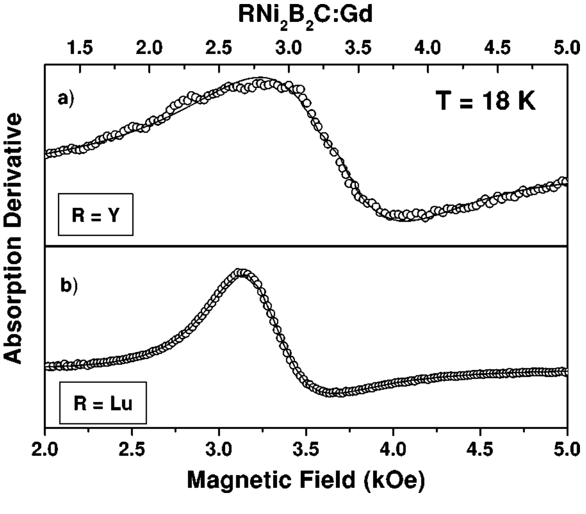

FIG. 1. ESR spectra of $Gd^{3+}$ in (a) $Lu_{1-x}Gd_xNi_2B_2C$ for $x \approx 0.005$ and (b) $Y_{1-x}Gd_xNi_2B_2C$ for $x \approx 0.02$ and $T = 18$ K.

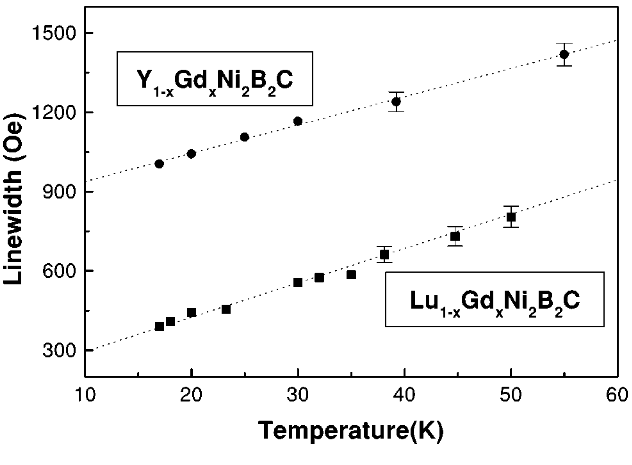

FIG. 2. Temperature dependence of the $Gd^{3+}$ ESR linewidth for the two samples shown in Fig. 1.

TABLE II. Extracted parameters for Gd:(Lu,Y)$Ni_2B_2C$.

| | $\eta(E_F)$ $\frac{\text{states}}{\text{eV mol spin}}$ | $\lambda$ | $\theta_D$ K | $\alpha$ | $K(\alpha)$ | $J_{fs}(0)$ meV | ESR $\langle J_{fs}^2(q)\rangle_{E_F}^{1/2}$ meV | SC $\langle J_{fs}^2(q)\rangle_{E_F}^{1/2}$ meV |
|---|---|---|---|---|---|---|---|---|
| $Lu_{1-x}Gd_xNi_2B_2C$ | 2.20(7) | $\approx 0.8$ [a] | $\approx 345$ [a] | $\approx 0.2$ [a] | $\approx 0.8$ [a] | 15(2) | 10(4) | 11(3) |
| $Y_{1-x}Gd_xNi_2B_2C$ | 2.05(6) | $\approx 0.9$ [a] | $\approx 489$ [a] | $\approx 0.3$ [a] | $\approx 0.7$ [a] | 13(2) | 9(3) | 10(2) |

[a] See Refs. 33,4,35,36.

$=k_F[2(1-\cos\theta)]^{1/2}$).[26] Under these assumptions the $Gd^{3+}$ $g$ shift measures the CE's polarization ($q=0$), and the Korringa rate the CE's momentum transfer ($0\leqslant q\leqslant 2k_F$) averaged over the Fermi surface.[26] $(1-\alpha)^{-1}$ and $K(\alpha)$ are the Stoner and the Korringa enhancement factors, respectively, due to the electron-electron exchange interaction.[27,29,30] $\eta(E_F)$ is the "bare" density of states for one spin direction at the Fermi surface, $k$ is the Boltzmann constant, $\mu_B$ is the Bohr magneton, and $g$ is the $Gd^{3+}$ $g$ value.

Equations (1) and (2) are appropriated for the analysis of ESR data of diluted rare earths in metallic hosts with appreciable CE's spin-flip scattering, i.e., the *unbottleneck* regime. We found in this work that the $g$ value and $b$ parameter do not depend on the $Gd^{3+}$ concentration. Hence, it is expected that the following relation would hold:[27,28]

$$b=\frac{d(\Delta H)}{dT}=\frac{\pi k}{g\mu_B}\frac{\langle J_{fs}^2(q)\rangle_{E_F}}{J_{fs}^2(0)}(\Delta g)^2K(\alpha). \tag{3}$$

In our analysis the contribution from different CE's bands will be neglected, because the measured thermal broadening of the linewidths are much smaller than those expected from the measured $g$ shifts.[31]

In a superconductor the electron-phonon interaction enhances the CE's effective mass, and in turn the density of states at the Fermi level. Thus, the Sommerfield's parameter is usually written as $\gamma=(2/3)\pi^2k^2(1+\lambda)\eta(E_F)$, where $\lambda$ is the electron-phonon coupling constant.[32] The $RNi_2B_2C$ ($R=$Y,Lu) compounds have been classified as intermediate coupled electron-phonon-mediate superconductors, with $\lambda_Y\approx 0.9$ (Ref. 33) and $\lambda_{Lu}\approx 0.8$.[34] The electronic contribution to the heat capacity $\gamma$ for the Lu- and Y-based compounds, were measured and their values are shown in Table I. Now, using the $\gamma$ and $\lambda$ values, the density of states at the Fermi level $\eta(E_F)$ can be estimated for the Y- and Lu-based compounds (see Table II). The extracted values for $\eta(E_F)$ are in good agreement with the theoretical ones obtained from band calculations.[35,36] In addition, electron-electron exchange enhancement is important in these systems and has been evaluated by NMR measurements[35] for the Y-based compound and from theoretical calculations for the Lu-based compound.[36] The values of $\alpha$, from the Stoner enhancement factor $(1-\alpha)^{-1}$ and $K(\alpha)$ are given in Table II.

Using in Eq. (3) the $g$ value of $Gd^{3+}$ in insulators as a reference, 1.993(2),[37] $\pi k/g\mu_B=2.34\times 10^4$ Oe/K, and the values of $\Delta g$, $b$, $\eta(E_F)$, $\alpha$, and $K(\alpha)$ from Tables I and II, the exchange parameters between the $Gd^{3+}$ local moment and the CE's in these two compounds were estimated. Table II summarizes these parameters for $Gd^{3+}$ in $RNi_2B_2C$ ($R=$Y,Lu). Notice that the ratios $\langle J_{fs}^2(q)\rangle_{E_F}^{1/2}/J_{fs}(0)$, are about the same for both systems. This suggests similar wave-vector dependence of the exchange interaction for isomorphic compounds.

It is interesting to compare the exchange parameter $\langle J_{fs}^2(q\rangle_{E_F}^{1/2}$ obtained in our ESR experiments and that obtained from the decrease of $T_c$ by adding $Gd^{3+}$ magnetic impurities, $\Delta T_c/\Delta c$. From the Abrikosov-Gorkov (AG) theory[17] we have that

$$\left|\frac{\Delta T_c}{\Delta c}\right|=(\pi^2/8k_B)\langle J_{fs}^2(q)\rangle_{E_F}\eta(E_F)(g_J-1)^2J(J+1). \tag{4}$$

The values of $\Delta T_c/\Delta c$, for both compounds, were taken from the literature[38,8] and are given in Table I. The values for $\langle J_{fs}^2(q)\rangle_{E_F}^{1/2}$ calculated using these data are in agreement with those obtained in this work (see Table II).

## V. CONCLUSIONS

We have shown that $R_{1-x}Gd_xNi_2B_2C$ ($R=$Y,Lu) dilute magnetic alloys behave as conventional three-dimensional superconductors as far as the ESR and superconducting results are concerned. Taking into account the CE mass enhancement due to the electron-phonon coupling $\lambda$ and the electron-electron exchange enhancement $\alpha$ we found comparable effective exchange parameters $\langle J_{fs}^2(q)\rangle_{E_F}^{1/2}$ from the thermal broadening of the $Gd^{3+}$ ESR linewidth (Korringa rate) and the decrease of $T_c$ by the $Gd^{3+}$magnetic impurities (AG). This shows that the exchange coupling between the $Gd^{3+}$ local moment and the CE's governs the impurity relaxation and pair-braking processes.

Our ESR results ($g$-shift and Korringa rate) show that the exchange interaction between the localized magnetic moments and the CE's involves only a single electronic conduction band. The exchange interaction is found to be strongly dependent on the CE's momentum transfer ($|\mathbf{k}_F^{\text{in}}-\mathbf{k}_F^{\text{out}}|=q$) and is of atomiclike $[J_{fs}(0)>0]$.

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