Interaction between localized and conduction-electron spins in the high-T_c superconductor Gd:EuBa$_2$Cu$_3$O$_{6+x}$

D. Shaltiel
Racah Institute of Physics, Hebrew University, Jerusalem, Israel
and Department of Physics, Monash University, Clayton, Victoria 3168, Australia

C. Noble, J. Pilbrow, and D. Hutton
Department of Physics, Monash University, Clayton, Victoria 3168, Australia

E. Walker
Department of Physics, University of Geneva, Geneva, Switzerland
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This work studies the spin-spin interaction between the conduction electrons and localized spins in high-T_c superconductors. We report the ESR at 9.74 GHz of low concentration of Gd substituting the Eu in single crystals of EuBa$_2$Cu$_3$O$_{6+x}$ ($x\approx 0.85$). At low temperatures just above T_c, the Gd ESR spectra in the c axis direction is almost resolved. With increasing temperature, exchange effects narrow most of the spectrum into a line close to $g=2.00$ except the $7/2\leftrightarrow 5/2$ transition, which remains partially resolved. This transition has a Dysonian line shape and shows a Korringa behavior. The narrowing of the spectra and the Korringa behavior indicate an exchange coupling between the conduction electrons and the Gd spin systems, and can be analyzed by the Barnes-Plefka theory. From the linewidth broadening of the $7/2\leftrightarrow 5/2$ transition and the Barnes-Plefka theory we obtain a Korringa constant $\Delta H_K/T=0.5$ G/K. From this value we calculated the exchange interaction J_{Ss} between the Gd spins, S, and the conduction electrons, s, using reported values for conduction electron susceptibility. We obtain $J_{Ss}=0.5\pm 0.1\times 10^{-3}$ eV, a value that is two or three orders of magnitude smaller than those observed in metals. It explains the small effect of magnetic ions on the T_c in the RBa$_2$Cu$_3$O$_{6+x}$ compounds. (R = rare earth). From the angular dependent spectra of Gd:EuBa$_2$Cu$_3$O$_{6+x}$ we obtain zero field terms of $b_2^0=-1800$ MHz, $b_4^0=-180$ MHz, and $b_4^4=+600$ MHz. These values are not significantly different from those obtained for Gd in YBa$_2$Cu$_3$O$_{6+x}$. [S0163-1829(96)00617-1]

INTRODUCTION

The study of the spin-spin interaction between the conduction electrons and localized spins gives significant information about the properties of the conduction-electron system.[1] It is important to apply it in the investigation of high-T_c superconductors where the conduction electrons play a decisive role in the superconducting properties and the high superconducting transition temperatures.

In this work we report the ESR measurements of small amounts of Gd in EuBa$_2$Cu$_3$O$_{6+x}$ ($x\approx 0.85$). ESR of the localized moments in metals has been very effective in the study of the spin-spin interaction with the conduction electrons. Gadolinium has the advantage over other localized magnetic atoms in that its ground state is an almost pure $S=7/2$ state and therefore its interaction with the lattice is sufficiently weak enabling one to observe the ESR even above room temperatures. It has also the advantage in the case of EuBa$_2$Cu$_3$O$_{6+x}$ that it goes substitutionally in the lattice replacing the europium. Furthermore its effect on the superconducting properties is small as reflected in the small change of T_c even when all the Eu is replaced by Gd.[2]

The 123 compounds consist of two sets of double Cu planes. The element in the 1 site, such as rare earth elements or Y, are located between these two sets of Cu planes. As the conductivity resides mostly within each of the Cu plane sets their interaction with the elements in site 1 was found to be small. This explains the small effect of most of the magnetic rare earth atoms on T_c. Interactions between the elements in site 1 and the conduction electrons was investigated mostly by the NMR of Y (Refs. 3 and 4) and also by the ESR of Gd (Refs. 5–7) partially substituting a nonmagnetic element such as Y or Eu. The NMR and most of the ESR measurements were carried out either in powders[5] or in powders aligned along the c axis.[7] Shaltiel *et al.*[6] have investigated the ESR spectra of Gd in single crystals of YBa$_2$Cu$_3$O$_{6+x}$. They reported the observation of a resolved fine spectrum at temperatures close to but above T_c and a Korringa relaxation of an exchanged narrowed line. Janossy *et al.*[8] reported the observation of the ESR spectrum of Gd:YBa$_2$Cu$_3$O$_{6+x}$ in oriented powders measured in the c direction. Their results show both the Korringa relaxation and g shift of the $1/2\leftrightarrow -1/2$ transition at 245 GHz. NMR of Y in YBa$_2$Cu$_3$O$_{6+x}$ shows a very small Knight shift and small Korringa behavior[3,4] that varies with temperature and oxygen concentration.[4]

In this work we report the Korringa behavior above T_c of the $7/2\leftrightarrow 5/2$ transition of a Gd spin probe in a single crystal of a 123 compound. The use of the $7/2\leftrightarrow 5/2$ transition removes the uncertainty in assigning various contributions to the linewidth that may be present when the central $1/2\leftrightarrow -1/2$ line is used. This is particularly the case when

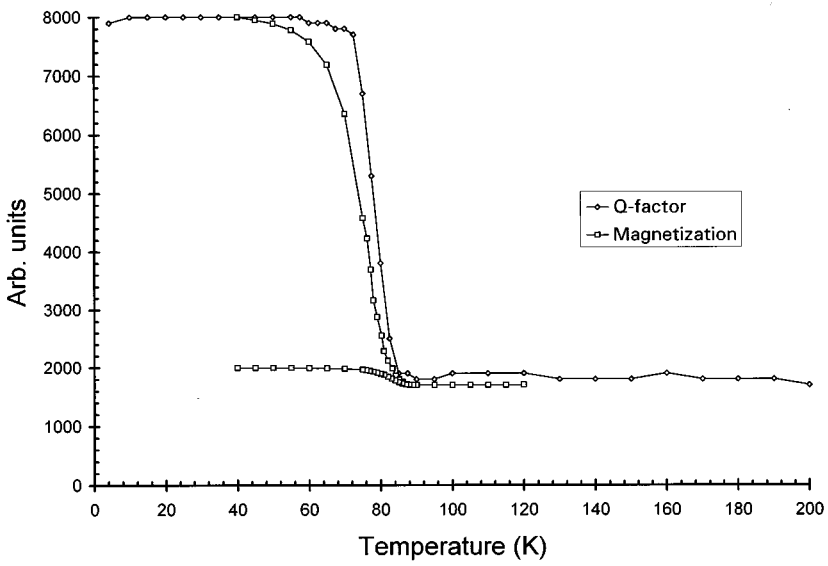

FIG. 1. Q factor of the sapphire resonator as a function of temperature, with the Gd:$EuBa_2Cu_3O_{6+x}$ sample. Also shown is the magnetization of the sample measured in a squid magnetometer. The sample was initially cooled with no applied field. A field of 50 G (the same field at which the Q factor measurements were performed) was then applied and the magnetization was then measured as the temperature was raised above T_c and then lowered. This curve was arbitrarily scaled to compare with the Q factor measurements.

the Korringa relaxation is fast at high temperatures and when the experiment is performed at X band. Under these conditions it is unlikely that the spectra will be fully resolved and an additional exchange narrowed component will be present in the same field position as the $1/2 \leftrightarrow -1/2$ transition. Most importantly the $7/2 \leftrightarrow 5/2$ transition will remain resolved at temperatures where the other transitions are obscured by this process.

This method enabled us to obtain linewidth measurements at X band over a wide temperature range above T_c. These results allowed us to calculate the spin-spin exchange interaction J_{Ss} between the local Gd spins and the conduction electrons in a 123 compound. In contrast to NMR so far reported, we do not observe above 110 K deviation from a simple linear broadening with temperature. Our results indicate similar behavior to that observed in metals indicating an interaction with a Fermi liquid.

EXPERIMENTAL RESULTS

A few single crystals of $EuBa_2Cu_3O_{6+x}$, $x \approx 0.85$, with a nominal concentration of 5% Gd replacing the Eu atoms were investigated. The crystals were grown in Geneva using the flux method. Some of these crystals were heat treated in an oxygen atmosphere for 7 days at 400 °C to alter the oxygen content. The work reported here however was carried out on a $2 \times 3 \times 0.1$ mm crystal which was not heat treated after being removed from the flux. The value of T_c was determined by magnetization measurements using a squid magnetometer. The Gd ESR was measured with a Bruker ESP380e spectrometer at 9.74 GHz using either a dielectric resonator or a rectangular cavity. The dielectric resonator was introduced into a helium flow dewar that enabled variation of the temperature from 4.2 K to room temperature. In the rectangular cavity the temperature control system consists of a quartz dewar insert that passes through the cavity and a temperature controlled nitrogen gas system that feeds the nitrogen through the quartz dewar. It allowed the variation of the temperature from 110 to 330 K and thus a total temperature range of 4.2 to 330 K was possible.

The crystals with a platelet form had the c axis perpendicular to the platelet plane. To avoid possible damage due to moisture the crystals were sealed in a 3 mm diameter quartz tube in helium atmosphere with the c axis and either the a or the b axis perpendicular to the tube axis. The quartz tube axis was perpendicular to the direction of the magnetic field. Rotating the quartz tube enabled to change the magnetic field in the c-a plane or c-b plane. We did not determine which of the a or b direction was in the plane. As the monitoring thermocouple was outside the quartz tube, and therefore not in direct contact with the sample, the absolute accuracy of the temperature measurements for the nitrogen flow system is estimated to be ± 2 K. In the sapphire resonator the absolute accuracy was even lower. However, differences in temperatures of ± 0.1 K could be measured when desired; this was the case when measuring the ESR spectra just above T_c. Here T_c can be determined by the ESR spectrum of the sample itself. ESR is a very sensitive technique to determine the onset of superconductivity, from both changes in the Q factor of the cavity and the onset of vortex noise. We used the change in the Q factor of the cavity as function of the temperature to determine the superconducting transition. This is shown in Fig. 1 with a sharp transition width of less than 3 K evident. This indicates a fairly homogeneous sample.

Figure 2 shows the ESR spectra for different angles θ between the c axis and the magnetic field for a temperature just above T_c [Fig. 2(a)]. The theoretical field positions that correspond to $\Delta M = \pm 1$ transitions as a function of the angle θ are also shown in Fig. 2(b). At room temperature only two lines are observed: the $7/2 \leftrightarrow 5/2$ transition and a line around $g = 2.00$. At 81 K in the c direction more transitions are observed and the central line shows a certain amount of structure. Along this direction the highest field line is the $7/2 \leftrightarrow 5/2$ transition followed by the $5/2 \leftrightarrow 3/2$ and the $3/2 \leftrightarrow 1/2$ transitions at lower fields. As seen from Fig. 2(a) by rotating the crystal away from the c axis, the $7/2 \leftrightarrow 5/2$ transition shifts to lower fields and after crossing the $5/2 \leftrightarrow 3/2$ transition, the two lines become unresolvable and a single line is then observed. The same is observed when θ is further increased and this line encounters the $3/2 \leftrightarrow 1/2$ tran-

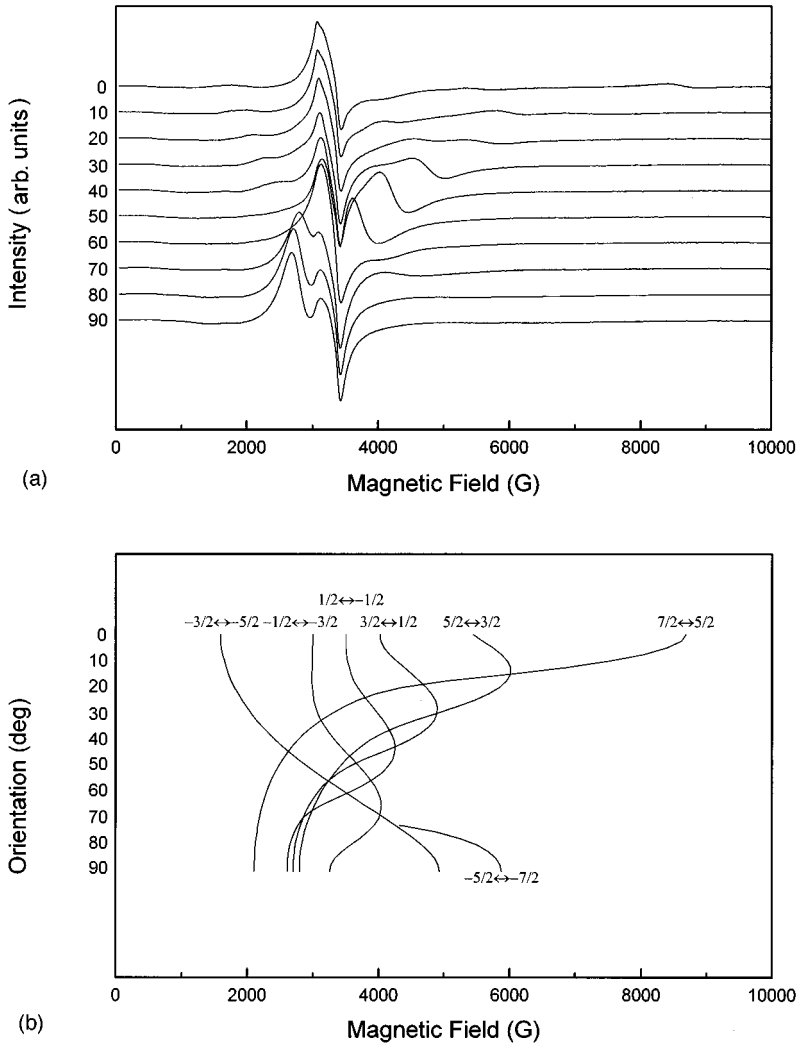

FIG. 2. (a) ESR spectra of a single crystal of Gd in $EuBa_2Cu_3O_{6+x}$ for orientations between 0 and 90° of the applied magnetic field relative to the c axis in the c-a plane at $T=81$ K. (b) Calculated angular dependence of the most strongly allowed transitions of a single crystal of Gd in $EuBa_2Cu_3O_{6+x}$ over the same range of orientations as in part (a). These values were calculated by numerical diagonalization of the Hamiltonian given in Eqs. (1) and (2). The coefficients of the zero-field terms were chosen to best fit the data for the four resolved transitions in the c direction and the two resolved transitions perpendicular to the c axis.

sition and only one line remains resolved. This behavior is an indication of a weak exchange narrowing effect that becomes effective when adjacent transitions begin to interact via the Korringa process.

This exchange narrowing is also evident as a collapsing of the fine structure when the temperature is increased. At $T=81$ K and $B\perp c$ the central line shows two superimposed lines separated by about 500 G whilst at room temperature only one line is observed. A similar effect is shown in Fig. 3 for the evolution of the spectra in the c direction with in-

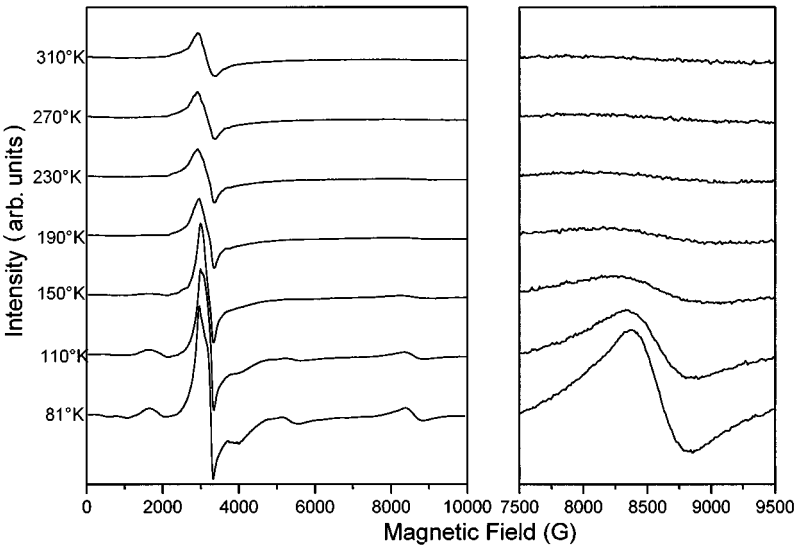

FIG. 3. The ESR spectra of Gd in a single crystal of $EuBa_2Cu_3O_{6+x}$ with the applied field parallel to the c axis in the temperature region 81 to 310 K. The spectra between 7500 and 9500 G is shown enlarged on the right. The 7/2↔5/2 transition is just discernable at this scale at the highest temperature.

creasing temperature. At 81 K with the magnetic field in the c direction the spectrum is well resolved. Increasing the temperature, the semi resolved spectra of the central line coalesces into a single line at 110 K. The peak to peak intensity of most transitions decreases, with respect to the central line, as the temperature is increased. At 230 K none could be observed even for the highest amplification of the spectrometer.

The most important result was, that in contrast to the other lines, the $7/2 \leftrightarrow 5/2$ transition did not disappear and could be observed even at 330 K. The position of this transition (within the experimental error introduced by the linewidth) did not change with temperature. The linewidth of this transition as a function of temperature shows a linear behavior with a slope of 3.5 G/K (Fig. 4).

THEORETICAL CONSIDERATIONS

The temperature and angular behavior of the spectra indicate that in addition to the zero field splitting of the Gd $S=7/2$ ground state an exchange narrowing mechanism is present.[1] The origin of the exchange interaction is the interaction with the conduction carriers and can be written as $J_{Ss}(\mathbf{S}\cdot\mathbf{s})$, where J_{Ss} is the exchange interaction between the Gd spins $\mathbf{S}$ and the spin of the conduction carriers $\mathbf{s}$.

The total Hamiltonian is written as

$$\mathscr{H}=g\mu_B\mathbf{B}\cdot\mathbf{S}+\mathscr{H}_{\rm zf}+J_{Ss}(\mathbf{S}\cdot\mathbf{s}), \tag{1}$$

where the zero field Hamiltonian can be approximated by

$$\mathscr{H}_{\rm zf}=b_2^0O_2^0+b_4^0O_4^0+b_4^4O_4^4, \tag{2}$$

where O_2^0, O_4^0, and O_4^4 are the spin operators reflecting the symmetry of the Gd ion environment. In this approximation we neglect terms higher than fourth order which have little influence on the observed spectra when compared with the uncertainties in the line positions. The parameters b_2^0, b_4^0, and b_4^4 are then sufficient to describe the angular dependence of the observed transitions.

The ESR spectra for a system of Gd spins and conduction electrons will depend on the Gd concentration, the conduction-electron spin system, the spin relaxation between the two systems, and the spin relaxation of each system to the lattice. The behavior of such a system has been calculated by Hasegawa[9] for $\mathbf{S}=1/2$. The more complicated system where $\mathbf{S}>1/2$ is given by the Barnes-Plefka[10,11] theory. It has been shown that for metals such as Al (Ref. 12) or Pd (Ref. 13) and at ''high'' temperature, the seven fine structure lines of the Gd spectra collapse into a single line with $g=g_{\rm Gd}+\Delta g$, where $g_{\rm Gd}=1.993$ is the g value obtained in insulators and

$$\Delta g=J_{Ss}\eta=J_{Ss}\chi_{\rm ce}/g\mu_B^2N. \tag{3}$$

Here η is the density of states per spin at the Fermi surface, $\chi_{\rm ce}$ is the spin susceptibility of the conduction electrons per mole, N is Avogadro's number, and μ_B is the Bohr magneton.

The linewidth, ΔH, of this totally collapsed central line will follow the Korringa behavior

$$\Delta H=\Delta H_K+\Delta H_{\rm res}. \tag{4}$$

$\Delta H_{\rm res}$ is the residual linewidth and ΔH_K is the Korringa broadening given by

$$\Delta H_K=\frac{\pi k_BT}{g\mu_B}(J_{Ss}\chi_{\rm ce}/g\mu_B^2N)^2, \tag{5}$$

where k_B is the Boltzmann constant.

The case of complete collapse of the fine structure to a single central line can occur when the Korringa broadening is large compared to the zero field splittings. Under certain conditions, usually when the exchange constant is small, or at ''low'' temperatures, or when the zero field splittings are large a more complex behavior can be observed. At high temperatures the spectra collapse into a single line. However, when lowering the temperature the spectra begin to separate. Transitions that occur at magnetic fields where the Korringa interaction between adjacent transitions is small will be the first to become resolved. This is expected of the $\pm 7/2 \leftrightarrow \pm 5/2$ transitions which are isolated from the other transitions when the zero field splitting is large. As the temperature is further decreased a full fine structure spectrum is obtained. This has been demonstrated for Gd in Pd (Ref. 13) at low temperatures and Gd in LaSb,[14] where it was shown that the value of the exchange constant is small.

In a fully resolved spectrum we expect the temperature dependent broadening of the individual lines for completely resolved spectra to be given by[14]

$$\Delta H_K(M\leftrightarrow M+1)=\Delta H_K[S(S+1)-M(M+1)]. \tag{6}$$

Thus for the temperature broadening of the individual transitions we expect their linewidth to be enhanced by a factor of 16, 15, 12, and 7 with respect to the fully exchanged narrowed linewidth, for the transitions $1/2 \leftrightarrow -1/2, \pm 3/2 \leftrightarrow \pm 1/2, \pm 5/2 \leftrightarrow \pm 3/2$, and $\pm 7/2 \leftrightarrow \pm 5/2$, respectively. This equation is of course valid only when the applied magnetic field is parallel to the c axis in a highly anisotropic system such as this and therefore the only quantitative use will be restricted to this case.

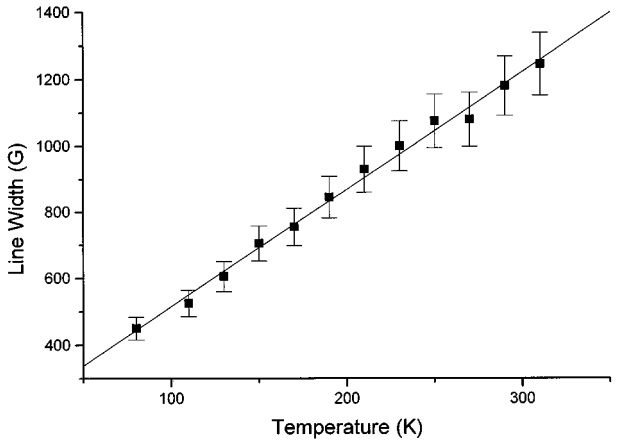

FIG. 4. Linewidth as a function of temperature of the $7/2 \leftrightarrow 5/2$ transition of Gd in single crystal of $EuBa_2Cu_3O_{6+x}$. The full line is a linear best fit to the data with a slope of 3.5 G/K.

ANALYSIS AND DISCUSSION

Our experimental results show behavior as predicted by the Barnes-Plefka theory. For the lowest temperature where the spectra could be measured just above T_c, and in the c direction [see Fig. 2(a)], an almost resolved spectrum is observed. However, when the crystal is rotated away from the c axis, so that two or more of the transitions begin to interact via the Korringa process, they merge into a single line. This has been observed in our results when $\theta \geqslant 25$ [Fig. 2(a)]. The temperature effect is also seen where spectral components that are resolved at 81 K collapses at 293 K. This is shown in detail for the spectra with the applied field in the c direction. The almost resolved spectrum just above T_c gradually collapses into the center line when the temperature increases (Fig. 3), except for the $7/2 \leftrightarrow 5/2$ transition which remains resolved at high temperatures.

This result by itself is strong evidence for the presence of the exchange narrowing mechanism in this system. Other transitions, most notably the $5/2 \leftrightarrow 3/2$ transition, should be at least a factor of 12/7 more intense and should be less susceptible to mosaic broadening than the $7/2 \leftrightarrow 5/2$ transition. Nevertheless these transitions are unresolved when the $7/2 \leftrightarrow 5/2$ transition is still observable. This is however easily understood when it is noted that this transition occurs at a field where the respective energy levels are separated by approximately twice the microwave frequency from all others and hence the exchange narrowing mechanism will have a much smaller effect. The effects of the Korringa process are still seen as its linewidth increases linearly with temperature (Fig. 4).

In addition to the qualitative results that show the existence of the exchange interaction between the Gd spins and the conduction electrons the linear increase of the width of the $7/2 \leftrightarrow 5/2$ transition permits us to obtain quantitative results. From the slope of the linewidth with temperature of 3.5 G/K we calculate the Korringa broadening using Eq. (4) to be 0.5 G/K. To calculate J_{Ss} from Eq. (5), $\chi_{\rm ce}$ has to be evaluated. The total susceptibility χ_m of $YBa_2Cu_3O_{6+x}$ has been measured by Parkin *et al.*[15] and was found to depend on both the temperature and the oxygen concentration. It includes the negative diamagnetic contribution $\chi_{\rm dia}$ and the Van Vleck susceptibility $\chi_{\rm VV}$. Thus $\chi_m = \chi_{\rm ce} + \chi_{\rm dia} + \chi_{\rm VV}$.

From the T_c of 80 K we estimate the oxygen concentration to be 6.85.[16] The magnitude of $\chi_{\rm dia}$ and $\chi_{\rm VV}$ are approximately equal but of opposite sign and thus cancel each other,[4] therefore $\chi_m \approx \chi_{\rm ce}$. From the results of Parkin *et al.* and using an average value for the small variation with temperature we obtain $\chi_m = 2.56 \times 10^{-4}$ emu/mole. Using Eq. (5) we obtain for $J_{Ss} = 0.6 \times 10^{-3}$ eV. This value is two orders of magnitude smaller than the corresponding quantity observed in metals.[12] It again explains the small effect of the rare earth on T_c in the 123 compounds. From the linewidth, it is not possible to obtain the sign of the exchange interaction. Using Eq. (3) and the value of J_{Ss} we calculate $|\Delta g| = 0.5 \times 10^{-3}$ with respect to $g = 1.993$ of Gd; this value of Δg lies inside the experimental spread of the g values of Gd in insulators and therefore it will be difficult to obtain the sign of interaction from such a measurement.

Using Eqs. (1) and (2) and the experimental results shown in Fig. 2(a) we calculated the angular dependence of the transitions with $\Delta M = \pm 1$. The parameters used are $b_2^0 = -1800$ MHz, $b_4^0 = -180$ MHz, and $b_4^4 = +600$ MHz. These parameters are close to those of Gd in $YBa_2Cu_3O_{6+x}$ (Ref. 7) and we assume the sign of b_2^0 to be negative to be consistent with their low temperature measurements. A more accurate fit was not possible in the present case due to the difficulties in assigning transition positions in the partially resolved spectra.

In conclusion in this work we were able to obtain the Korringa broadening of the $7/2 \leftrightarrow 5/2$ fine structure transition of a Gd spin probe in a 123 high-T_c compound. This enabled us to use ESR spectra where exchange narrowing is present, to derive the exchange interaction between the localized spins and the conduction electrons, in a straightforward way. This method avoids any ambiguity that one may encounter when obtaining the Korringa slope from the central line in a spectrum where an exchange narrowed component may also be present. The similar zero field parameters of Gd for Eu and Y in the 123 compounds show the distances of the atoms surrounding the Gd atoms in these two compounds are almost the same. Our results indicate similar behavior to that observed in metals indicating an interaction with a Fermi liquid.

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