Journal of Optoelectronics and Advanced Materials Vol. 2, No. 4, December 2000, p. 365 - 370

MAGNETIC EXCHANGE COUPLINGS IN THE HIGH-TEMPERATURE SUPERCONDUCTORS: ESR POINT OF VIEW[1]

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Using the electron spin resonance of Gd^{3+} - spies introduced in $YBa_2Cu_3O_{7-\delta}$ oriented powders the spin-spin interactions between Gd ions and the coupling of localised spins to the conduction electron spin system has been studied. The data give evidence for an exchange interaction between these paramagnetic ions. By analysing the spin dynamics in terms of the metal theory the exchange integrals between localised f - moments and the conduction electrons were evaluated. Different contributions to the exchange interaction are also discussed.

(Received July 15, 2000; accepted November 15, 2000)

Keywords: Exchange interaction, ESR, High temperature superconductors

1. Introduction

The substitution of most rare-earth ions (RE = Gd, Er, etc.) into Yttrium site of $YBa_2Cu_3O_{7-\delta}$ (YBCO) compounds has no significant influence on the superconducting properties. It was suggested that this substitution may even favour superconductivity contrasting the destructive influence of paramagnetic ions in conventional superconductors [1]. This behaviour can be explained by arguing that the interaction of the *f* electrons of the RE ions with the conduction electrons of the CuO_2 layers is weak because of the spatial separation in the crystal lattice. The presence of a weak magnetic interaction between the 4f-shell of the RE-ions and the conduction electrons was evidenced by ^{89}Y - NMR [2] and $^{170}Yb^{3+}$ - Mössbauer [3] measurements.

ESR spectroscopy of paramagnetic spies such as Gd^{3+} (S ground state, L=0, spin S=7/2) doped into high - T_c superconductors (HTC) is a powerful tool in the study of the magnetic interactions which could play a role in the mechanism of superconductivity [4].

In order to obtain further insight into the mechanism related to the magnetic exchange interactions in the normal state of HTC superconductors, an ESR investigation of oriented powders $Gd_xY_{1-x}Ba_2Cu_3O_{6.85}$ (GYBCO) was carried out. The simplest scenario that models the exchange interactions involves two subsystems, namely the Gd^{3+} spins and the conduction electrons from CuO_2 planes.

2. Experimental

A series of $GYBCO_{6.85}$ samples with x = 0.75, 0.50 and 0.25 ($T_c \cong 86$ K) were prepared by the standard solid state reaction method [5]. The powder grains, thoroughly grinded, were mixed with epoxy resin and oriented in a 7 T magnetic field at room temperature as previously described [6].

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[1] Paper presented at Romanian Conference on Advanced Materials, Bucharest, Romania, October 23-25, 2000

ESR measurements were carried out using a Bruker X-band spectrometer operating with a TE_{102} cavity. A Lorentzian lineshape, of our oriented samples was found throughout the investigated temperature range, $T > T_c$. In order to evaluate the ESR-parameters the derivative spectra were fitted with the known Lorentzian lineshape the fit parameters being the half width at half height (HWHH) $\delta B_{1/2}$ of the corresponding absorption line and the resonance field B_0 (or g-factor).

3. Theoretical considerations

The theory of Gd^{3+} - ESR in metallic systems has been reviewed thoroughly [7] and here we restrict ourselves to those aspects important for our ESR-investigation. We consider that in GYBCO samples two weakly interacting subsystems are present: the Gd-spins and the conduction electrons from the CuO_2-plane [6]. The Hamiltonian of the localised Gd-moments in an applied field can be written

$$H = H_{dd} + H_{ex,Gd} + H_{ion} + H_{eL} + H_{sf} \tag{1}$$

H_{dd} is the secular part of the dipolar Hamiltonian and can be expressed as:

$$H_{dd} = \sum_{j,k} \frac{\mu_o}{4\pi} (g\mu_B)^2 B_{jk} S_{z,j} S_{z,k} \tag{2}$$

where

$$B_{jk} = \frac{3}{2}\left(\frac{1-3\cos^2\Theta_{jk}}{r_{jk}^3}\right) \tag{3}$$

The exchange interaction between two nearest-neighbouring *Gd* spins could be given by:

$$H_{ex,Gd} = -\sum_{i,j} 2J_{ij} S_i S_j \tag{4}$$

in which an isotropic exchange coupling is assumed, i.e. $2J_{ij} = 2J$, if i and j label nearest-neighbour ions, and 0 otherwise.

H_{ion}, the Hamiltonian of the Gd^{3+}-ion in an axial crystal field appropriate for GYBCO compounds assuming an isotropic g-factor is given by:

$$H_{ion} = g\mu \vec{B}\cdot\vec{S} + \sum_{l,m\le l} B_l^m O_l^m \,, \tag{5}$$

where the first term is the usual Zeeman interaction and the second one represents a series expansions of the crystalline electric field in terms of the crystal field spin operators O_l^m as tabulated in Ref.[10]. As shown by Rockenbauer et al. [9] and Shaltiel et al. [10] terms up to l = 6 are relevant and even the off-diagonal element B_4^4 yield a large contribution to the crystal field splitting. Due to the fine structure splitting (S = 7/2, 7 lines) and the higher-order terms, the Gd-ESR spectra are very anisotropic both in cubic and axial systems. In GYBCO-samples for Gd-concentrations exceeding 25% only a single line is observed with an axial anisotropy in resonanace field and line width. For this unresolved fine structure the moment analysis of the single line yields $M_{1,\,CF}$ describing the temperature and frequency dependence of the resonance field and $M_{2,\,CF}$ contributing an additional broadening, respectively [6].

H_{eL}, the Hamiltonian of conduction electron spin-lattice interaction. In metallic systems the corresponding relaxation rate is generally of order of 10^{11} - 10^{13} s^{-1} [7] and can easily be modified by addition of non-magnetic impurities.

For Y (Gd) spins no direct overlap with atoms in CuO_2 plane occurs. Along the lines of Mila-Rice model [11], the NMR hyperfine interaction seen by ^{89}Y spins is caused by so-called transferred hyperfine interaction which is mainly isotropic [12]. The transfer is expected to occur via the less distant and more extended oxygen π -orbitals rather than through the copper d-orbitals. Obviously, the coupling between Gd-4f-spin subsystem and the conduction electrons of the CuO_2 - planes arises from a transferred exchange interaction. Assuming an isotropic exchange interaction the interaction Hamiltonian can be written as [7].

$$H_{sf} = -2\, J_{sf}\, \boldsymbol{S} - \boldsymbol{s} \tag{6}$$

where **S** and **s** are the Gd-spin and the spin of the conduction electrons, respectively and J_{sf} the exchange coupling constant.

This transferred exchange interaction gives rise to the Gd - ESR Knight shift, ${}^{Gd}K_s = \Delta g/g_i$, and to a relaxation of the Gd localised spins to the conduction electron spins.

In terms of the reduced spin susceptibility $\chi(0)$ of the conduction electrons at the wave vector q = 0 (in eV^{-1}) given by $\chi(0) = \chi_e / g_e^2 \mu_B^2$ and in the isothermal regime, non-bottleneck situation, ${}^{Gd}K_s$ can be expressed as [13]

$${}^{Gd}K_s = [2g_e\, J_{sf}(0)\, \chi(0)] / g_i \tag{7}$$

where $J_{sf}(0)$ is the exchange integral for q=0 and $g_i = 1.9901$ corresponds to the Gd^{3+} g-factor for zero spin susceptibility as resulting from high frequency ESR investigations [4]. In a simple two - component exchange model developed for metallic systems $J_{sf}(0)$ can be written as [7].

$$J_{sf}(0) = J_{at} + J_{cm} \tag{8}$$

where J_{at} is the positive intra-atomic exchange integral between the magnetic 4f-orbital and the conduction electrons and J_{cm} represents the negative interband mixing (covalency) term. Here, it is accepted that the covalent mixing of the Gd - 4f-shell with a d-like conduction band is larger than the mixing with an s-p-like one. It could lead to a negative effective exchange, if the corresponding contribution outweighs the direct exchange.

Therefore, the ${}^{Gd}K_s$ in the unbottlenecked regime can be considered as a sum of the positive s - p and negative d-contributions arising from f - s (p) and f - d -exchange interaction, respectively.

Concerning the spin dynamics one has to remember that in the presence of strong antiferromagnetic correlations in the CuO_2 - planes the relaxation rates are enhanced by spin fluctuations [12]. However, such fluctuations due to the symmetry of the lattice, geometrically cancel at the Gd - (or Y-) site. Therefore, we assume that the Korringa-like behaviour dominates the relaxation of the Gd-spins. In the non-bottleneck limit, the corresponding relaxation rate - the Korringa rate - is expressed as [13]

$${}^{Gd}T_1^{-1} = \frac{32\pi^2 K_B}{h}[\langle J_{sf}(q)\rangle \chi(0)]^2\, T \tag{9}$$

where now $< J_{sf}(q) >$ represents the exchange integral between the localised f-moments and the conduction electrons averaged over all q -vectors spanning the Fermi surface. Here, and in Eq.(4), the conduction electrons enhancement factors are not included.

The homogeneous contribution to the with is proportional to the relaxation rate ${}^{Gd}T_1^{-1}$ and one expects a linear temperature dependence of the width, the Korringa broadening ${}^{Gd}\delta B_K$ given by

$${}^{Gd}\delta B_K = \frac{4\pi k_B}{g_e \mu_B}[\langle J_{sf}(q)\rangle \chi(0)]^2\, T \tag{10}$$

where ${}^{Gd}\delta B_K$ is expressed in field units (*T*) and for the unbottlenecked regime considered above, it is independent of Gd-concentration.

Experimentally one observes a residual linewidth $\delta B_{1/2}^0$ mainly attributed to dipol-dipol interaction. Therefore the Gd-ESR linewidth in the normal state can be described in a first approximation by

$$\delta B_{1/2,\exp} = \delta B_{1/2}^0 + bT \tag{11}$$

where $b = \delta B_K / T$

We wish to point out that NMR investigations have shown that for oxygen - depleted $YBCO_x$ compounds, the normal state temperature dependence of $\chi(0)$ can well be described by [12]:

$$\chi(0) = \chi_0\left[1 - \tanh^2(\Delta / 2T)\right] \tag{12}$$

where Δ is the spin-gap energy. It means that in accordance with Eq. (2), $^{Gd}K_s$ in the isothermal regime should have the same temperature dependence and should be independent of the Gd-concentration. For highly doped state ($YBCO_7$), χ (0) is fairly temperature independent (Pauli like) and one would expect $^{Gd}K_s$ to be independent of both, concentration and temperature.

4. Experimental results and discussion

The effective g - values of Gd^{3+} are temperature independent in the normal state ($g_{eff} = 2.01 \pm 0.005$). By substracting a crystal field correction [13], we estimate for $^{Gd}K_s$ in the normal state of $GYBCO_{6.85}$ a value of $^{Gd}K_s \approx 5000$ ppm for B││c. The recently reported 245 GHz ESR - data in the range 100 - 160 K for $YBCO_7$, x = 0.01 and B││c give $^{Gd}K_s \approx 3260$ ppm. In comparison with the above shift, our $^{Gd}K_s$ value for GYBCO $_{6.85}$ is overestimated. This consideration is based on the experimental facts that in X - band and at higher temperatures we are dealing with large linewidths which increase the uncertainty in the values of B_o measured and thus in $^{Gd}K_s$.

The thermal broadening of the linewidth upon increasing the temperature could be attributed to a Korringa - like mechanism. A linear fit with the Eq.(8) of the normal state data for $GYBCO_{6.85}$ give the corresponding rate of $^{Gd}\delta B_K/T = 0.035 \pm 0.002$ mT/T, independent of Gd - concentration. Based on the above results we assume the presence of the unbotlenecked behaviour in the Korringa - like mechanism at least in the range of concentrations under investigation. The corresponding spin-lattice relaxation rate amounts to $^{Gd}(T_1\,T)^{-1} = 6.2 \times 10^{6}\ s^{-1}\ K^{-1}$. It could be compared with the value of $^{Gd}(T_1\,T)^{-1} = 8.6 \times 10^{6}\ s^{-1}\ K^{-1}$ found in the high temperature range of a $GdBaCuO_{6.85}$ sample by using a direct method of measuring short electronic T_1 [14].

The residual linewidth $\delta B^{0}_{1/2}$ in Eq.(11) is determined by the dipolar couplings among Gd spins, which is narrowed by the Gd-Gd exchange interaction. Comparing the theoretically exchange narrowed linewidth as function of x and orientation of external field, using a universal linewidth formula [12],

$$\delta B_{1/2} = \frac{h}{g\mu_B}\sqrt{\frac{\pi}{2}}\left[\frac{M_2}{\mu - 1.87}\right]^{1/2}, \tag{13}$$

with the experimental one, an effective exchange coupling constant between Gd - spins, $2J_{Gd\text{-}Gd} \cong 5\ \mu eV$, was recently determined by us [13]. In the above relation M_2 represents the second moment of the resonance line, while $\mu = M_2^2 / M_4$, with M_4 the corresponding fourth moment. This exchange energy must be compared with the typical dipolar energies ranging from 6 μeV for x = 0.1 up to 30 μeV for x = 1.

As it was shown before, Eq (7) and Eq (9) are valid only when the conduction electron subsystem is in thermal equilibrium with the lattice - isothermal regime - corresponding to a non - bottlenecked behaviour of the Gd - relaxation mechanism. The experimental results obtained so far on $GYBCO_x$ superconductors indicate that the above situation applies at least in the range of high Gd concentrations (x = 1 ÷ 0.05) [13-15]. Unfortunately no comparative data are available at low x but one could assume that the bottleneck effects are negligible since the conduction electron spin relaxation to the lattice is evidently strong. Second, a close agreement between the linewidth at 9.16 and 245 GHz was found in $Gd_{0.01}$ $YBCO_{6.75}$ oriented samples [4]. It proves that the Gd -ESR- line is homogenously broadened in the normal state. Therefore, the increase of the linewidth is predominantly due to an increase of the spin-lattice relaxation rate. This observation also supports our interpretation ascribing the observed thermal broadening in $GYBCO_{6.85}$ - samples to a Korringa - like process. Third, all the 9.4 GHz Gd - ESR investigations on spin dynamics in $GYBCO_{6.85}$ having a slightly underdoped composition show that the Gd -spin lattice relaxation rates, $^{Gd}T_1^{-1}$, as deduced from the thermal broadening of the linewidth, have a linear temperature dependence - Korringa - like relaxation [13,15]. One has to remember that the above behaviour was clearly evidenced by analysing the Gd -relaxation rate for 7/2 ↔ 5/2 fine transition line [15]. It was thus possible to avoid the difficulties encountered by us [13] and Janossy et all [4] concerning the overlap of the central and satellite fine lines. The finding of a Korringa - like relaxation mainly prove an interaction of Gd - spins with a Fermi liquid. For the underdoped systems only by using high frequency ESR [4] or the Atsarkin's method [14] the temperature variation of the relaxation rates as described by Eq. (9) in combination with the spin - gap expression (Eq. (12)) could be evidenced.

In order to estimate the exchange coupling parameters the spin susceptibility of our GYBCO$_{6.85}$ compounds has to be evaluated. We have developed two approaches to infer χ (0) from the Yttrium NMR Knight - shifts, ^{89}K, and the macroscopic susceptibilities, χ_m, for different oxygen concentrations, respectively [13]. Following this procedure the spin susceptibility of Gd$_{0.01}$YBCO$_{6.75}$ sample has also been evaluated in order to get o more reliable J_{sf} (0) value from the reported high - frequency ESR data [4].

Table 1 gives a comparison of the effective exchange integrals, J_{sf} (0) and < J_{sf} (q) >, evaluated by means of Eqs. (7) and (10) with other 4$f^{\,n}$ RE ions doped in HTSC.

Table 1. The normal state values of the exchange integrals J_{fs} (0) and <J_{fs} (q)> between RE – 4f ^{n} electron orbitals and conduction band carriers in different HTSC.

Compound	Gd^{3+}(4f ^{7})		Er^{3+}(4f ^{11})		Yb^{3+}(4f ^{13})	
	J_{fs}(0) (meV)	<J_{fs} (q)> (meV)	J_{fs}(0) (meV)	<J_{fs} (q)> (meV)	J_{fs}(0) (meV)	<J_{fs} (q)> (meV)
GYBCO$_{6.85}$	3.2	1.5	-	-	-	-
GYBCO$_{6.75}$	1.9	1	-	-	-	-
LSCO	-	2.5	-	4.3*	-	-
ErBCO$_7$	-	-	-	6.0*	-	-
YB(Cu,Zn)O$_7$	-	-	-	-	-	4.5*

* The <J_{fs}(q)> - values were derived by us from the reported thermal broadening of the ESR or Mössbauer linewidths and the appropriate density of states.

In order to account for the observed difference between J_{fs}(0) and < J_{fs}(q) > we introduced the Korringa scaling factor $^{Gd}S_k$ which contains both the static and dynamic spin susceptibility [13]. The similarity between $^{Gd}S_k$ and $^{89}S_k$ values suggests that the electron spins are uncorrelated as seen from the Gd(Y) - site, i.e. for q ≈ 0 fluctuations. Therefore, the above mentioned difference is most likely associated with a different q - space averaging of the exchange parameters.

There are some theoretical and experimental results which give strong evidence for a RKKY (Ruderman-Kasuya-Kittel-Yoshida) interaction among Re^{3+} moments in REBa$_2$Cu$_3$O$_7$ and how this occurs via the conduction electrons [17]. The exchange integral < J_{fs}(q) > obtained from our investigation makes it possible to evaluate, in principle, the integral of RKKY interaction, J^{RKKY} of the Gd^{3+} ions in GYBCO$_{6.85}$. Based on the RKKY indirect exchange model in two - dimensional superconductors [17],

$$J(R) \;=\; \frac{n_e^2 J_{sf}^2}{\varepsilon_F}\,\frac{(\sin 4\pi k_F \cdot R)}{(4\pi k_F \cdot R)^2} \tag{14}$$

we estimate J^{RKKY} ≈ 0.1 - 0.01 μeV [18]. It is approximately two orders of magnitude less than effective Gd - Gd exchange coupling constant, 2 $J_{Gd\text{-}Gd}$ ≅ 5 μeV found in GYBCO$_{6.85}$ [3]. It could imply that only a small part of the effective Gd - Gd exchange interaction could be mediated by the conduction electrons giving rise to an indirect exchange.

As shown in Section 2 two processes can contribute to an effective exchange between Gd - 4f shell and the conduction bands. In what follows, we assume the two - component exchange interaction model to be good enough for the normal state of YBCO superconductors. In the simplest scenario, the so - called " t - J - model ", the Cu - d$_{x^2-y^2}$ orbitals are strongly hybridised with the oxygen p - orbitals giving rise to d* and p* - bands [12]. The d - like band (negative covalent mixing with the 4f -shell) could then be responsible for the reduced value of J_{sf} (0). However, the s(p) - f - exchange interaction dominates over the d-f one since a positive value for the effective J_{sf}(0) is observed. Therefore, we assume a net s - p - type transferred exchange interaction detected by ESR at Gd - site in GYBCO. Moreover, the above assumption is further supported by the mechanism of ^{89}Y transferred isotropic hyperfine interaction. The indirect coupling occurs via the electron spins in the eight neighbouring oxygen p - orbitals rather than through the copper d - orbital [12].

5. Conclusions

The exchange interaction processes between Gd $^{3+}$ ions and the localised f - moments and the conduction carriers were investigated by ESR in the normal state of GYBCO$_{6.85}$ oriented powders.

We have found that in GYBCO samples two weakly interacting subsystems are present: the Gd - spins and the conduction electrons from the CuO$_2$ - plane. The corresponding coupling is due to a transferred exchange interaction.

The experimental results and theoretical analysis result in $2J^{Gd\text{-}Gd} = 5\mu eV$, $J_{sf}(0) \approx 3.2$ meV and $< J_{sf}(q) > = 1.5$ meV for the Gd-Gd exchange integral and the exchange integrals between Gd - 4f - orbital and conduction electrons, respectively. Since $J_{sf}(0) > 0$ we suggest a net s - p - type transferred exchange interaction detected by Gd $^{3+}$ - ESR. The above values are two orders of magnitude smaller than the corresponding quantities observed in intermetallic type II superconductors. It could explains the small effect of the RE ions on T_c in HTC superconductors.

The effective exchange coupling constant between Gd-ions is three orders of magnitude less than the exchange coupling between Gd - spin and the spin of the conduction electrons evaluated in the present investigations. It implies that only a small part of the Gd spin-spin exchange coupling could be mediated by the carriers giving rise to an indirect exchange process.

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