ESR in the $Y_{1-x}Gd_xBa_2Cu_3O_y$ system

N. E. Alekseevskiĭ,[1)] I. A. Garifullin, N. N. Garif'yanov,
B. I. Kochelaev,[2)] A. V. Mitin,[1)] V. I. Nizhankovskiĭ,[1)]
L. R. Tagirov,[2)] and E. P. Khlybov[3)]
E. K. Zavoĭskiĭ Kazan' Physicotechnical Institute, Academy of Sciences of the USSR

(Submitted 24 August 1987)
Pis'ma Zh. Eksp. Teor. Fiz. **46**, No. 7, 292–295 (10 October 1987)

The ESR spectrum of Cu^{2+} and Gd^{3+} ions has been observed and identified in the superconducting system $Y_{1-x}Gd_xBa_2Cu_3O_y$. The integral of the exchange interaction of Gd^{3+} ions with conduction electrons is found: $J_{sf} = 7.4 \times 10^{-3}$ eV. The energy gap is estimated to be $2\Delta_0/k_BT_c \simeq 6.5$. The integral of the exchange interaction between Gd^{3+} ions is estimated to be $J_{GdGd} = 0.12$ K.

The discovery of superconductivity in the La-Ba-Cu-O system at temperatures above 30 K (Ref. 1) was followed quickly by the demonstration that a superconductivity arises at temperatures above 90 K in the Y-Ba-Cu-O system.[2] It has been found that when yttrium is replaced by other rare-earth atoms, the temperature of the superconducting transition depends only slightly on both their atomic number and their magnetic states.[3] The ESR method is extremely informative for studying the electronic and crystalline microstructure of paramagnetic centers and their effects on the superconducting properties of a material (Ref. 4, for example). In the present letter we are reporting a preliminary study of ESR in the $Y_{1-x}Gd_xBa_2Cu_3O_y$ system.

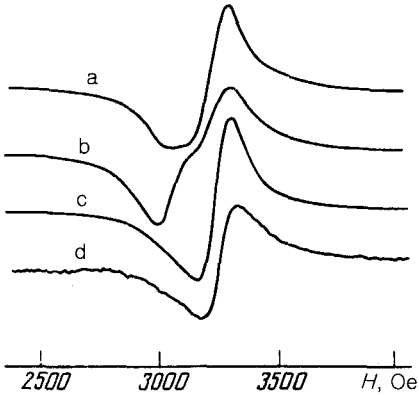

FIG. 1. a—ESR spectrum of Cu^{2+} at $T = 130$ K in a powdered sample of $YBa_2Cu_3O_y$; b—in an oriented powder, with $c \| H_0$, $T = 130$ K; c—$c \perp H_0$, $T = 130$ K; d—$c \perp H_0$, $T = 80$ K.

The test samples were synthesized by the known procedure from oxides of the elements, used in stoichiometric proportions in accordance with the formula $RBa_2Cu_3O_7$. An x-ray phase analysis showed that the host phase in the samples is accompanied by a small amount ($< 10\%$) of the phase R_2BaCuO_5. No other foreign phases were observed. The ESR measurements were carried out at a frequency of 9400 MHz over the temperature range 1.5–300 K. The samples were powders with a particle size of 50 μm, sealed in paraffin.

$YBa_2Cu_3O_y$. The derivative absorption curve, shown in Fig. 1a, has a shape characteristic of the ESR spectrum of powdered samples containing paramagnetic ions with an anisotropic g-factor. A satisfactory numerical simulation of this spectrum proved possible only by mixing the imaginary and real parts of the rf magnetic susceptibility, as is the usual case for conducting samples. The study yielded $g_\| = 2.20$ and $g_\perp = 2.06$. These are typical values for the ESR signal of Cu^{2+} ions with a ground state described primarily by the $d_{x^2-y^2}$ wave function. Rough estimates indicate that 10% of the copper ions in the sample are participating in the resonance.

To determine the positions of the localized moments of Cu^{2+}, we prepared an oriented powder with the help of a magnetic field. According to the data of an x-ray analysis, the crystallographic c axes of the powder turned out to be parallel to the orienting field. From the angular dependence of the ESR spectrum of these samples (Figs. 1b and 1c) we found that the z symmetry axis of the local surroundings of the Cu^{2+} ions is also parallel to the orienting field. Most probably, the paramagnetic Cu^{2+} centers are in the planes between barium ions containing rows of copper and oxygen ions. This conclusion is indicated by the instability of the oxygen ions in these planes, according to the results of an x-ray structural analysis[5] and our data on the correlation between the number of localized states and the particular type of heat treatment of the samples. A redistribution of oxygen atoms in the xy plane gives rise to two types of local surroundings for copper ions. When the vacant sites between rows are filled by oxygen atoms, the Cu^{2+} ions are in nearly octahedral surroundings. The relation $g_\| > g_\perp$ found experimentally indicates that the octahedra are elongated along the $z \| c$ axis, although in the ideal structure the Cu-O distance along the z axis would be

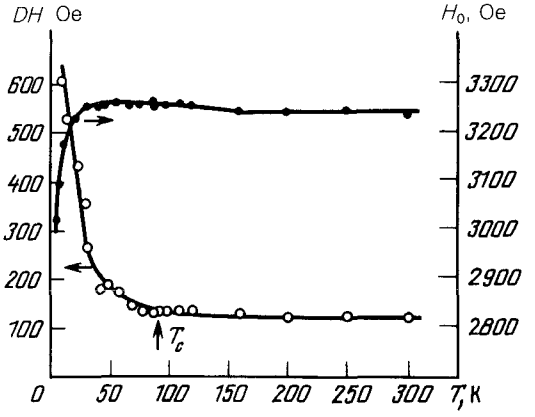

FIG. 2. Temperature dependence of the width of ESR line and of the Cu^{2+} resonant field for the orientation $c \perp H_0$.

shorter than the length of the Cu-O bonds in the xy plane. If oxygen atoms are lost from the rows, we would expect the ground state of the Cu^{2+} ion to be d_{z^2}, whose ESR spectrum we did not observe.

Figure 2 shows the temperature dependence of the linewidth and the resonant field for an oriented sample with an axis $c \perp H_0$. At $T > T_c$ the ESR linewidth is independent of the temperature, indicating that there is no contact between the observed Cu^{2+} ions and band electrons.

When the sample goes superconducting, the noise level increases sharply (Fig. 1d), while the integral intensity decreases, as we have seen previously in ordinary superconductors.[6] Moreover, there is no basis for asserting that the superconducting regions of the sample and the regions from which the ESR signal is observed are not spatially separated. At $T < 40$ K the ESR line begins to broaden rapidly and to shift toward a weaker magnetic field (Fig. 2), as would happen as a magnetic-ordering point was approached. Against the background of this broad line, we begin to detect a signal from Cu^{2+} ions of a "green" phase.

$GdBa_2Cu_3O_y$. At $T > T_c$ we observe a single isotropic line with $g = 2.03 \pm 0.02$, which we link with the ESR signal of Gd^{3+} ions. The linear temperature dependence observed for the width of the DH line, with $dDH/dT = 0.82$ Oe/K (Fig. 3), is apparently caused by a Corring relaxation of localized moments of gadolinium to conduction electrons:

$$DH_K(T) = \pi k_B (\rho_F J_{sf})^2 T/g\mu_B. \qquad (1)$$

Here ρ_F is the state density of conduction electrons at the Fermi level, and J_{sf} is the exchange integral for the interaction of localized f electrons with conduction electrons. The density ρ_F in (1) can be estimated from the electron specific heat $\gamma = 4.6 \times 10^{-3}$ $J/(\text{mole-Cu}) \cdot \text{K}^2$, found from our measurements of the upper critical field and the electrical resistivity. From the DH_K width we then find $J_{sf} = 7.4 \times 10^{-3}$ eV. Similar small values of J_{sf} have been observed previously for rare-earth ions in molybdenum chalcogenides.[7]

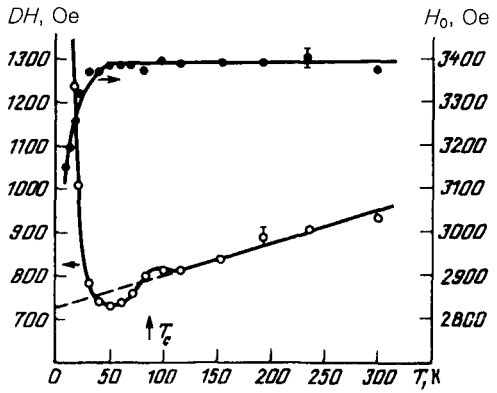

FIG. 3. Temperature dependence of the width of the ESR line and of the resonant field in a $GdBa_2Cu_3O_y$ sample. The arrow marks the T_c value measured by an inductive method.

Using the values found for J_{sf} and ρ_F, we can estimate the lowering of the superconducting transition temperature caused by the presence of localized moments of gadolinium ions[8]:

$$\delta T_c = -\pi^2 cS(S+1)\rho_F J_{sf}^2 / 8k_B . \qquad (2)$$

Here S is the spin of the localized states, and c their concentration. For $GdBa_2Cu_3O_y$, expression (2) yields $\delta T_c = -0.75$ K, in good agreement with the experimental observation that T_c depends only weakly on the magnetic state of the rare-earth ion in such systems.

The temperature-independent residual linewidth, which can be found through a linear extrapolation of $DH(T)$ to $T = 0$ K, turns out to be 720 Oe. An estimate puts the contribution of magnetic dipole-dipole interactions to this width on the order of 2500 Oe. To estimate the contribution of the unresolved fine structure, we carried out ESR measurements on a $Y_{0.98}Gd_{0.02}Ba_2Cu_3O_y$ sample. From the results we found the total range of the fine structure to be on the order of 3000 Oe. The observed residual linewidth of 720 Oe is thus smaller than these contributions to DH, indicating an exchange narrowing of the ESR line. An estimate based on the moment method puts the magnitude of the exchange integral between nearest gadolinium ions at $J_{GdGd} = 0.12$ K. From this value we can estimate the paramagnetic Curie temperature: $\Theta_p = S(S+1)J_{GdGd} \cdot z/3 = 2.4$ K for $z = 4$ nearest neighbors. This result agrees with the value of $\Theta_p = -5$ K which we obtained in direct measurements of the susceptibility in the normal phase.

After some broadening near the superconducting transition temperature, the ESR line contracts by about 75 Oe over the temperature interval 80–50 K (Fig. 3). The effect is qualitatively reminiscent of the temperature dependence of the Corring relaxation rate in an ordinary superconductor (Ref. 9, for example), where a nonmonotonic behavior of this sort is linked with the appearance of a gap in the spectrum of elementary excitations. The implication is that the gadolinium ions are interacting with the superconducting electrons. The observed temperature dependence of DH can be used

to plot the temperature dependence of the gap. Near T_c, the gap increases considerably more rapidly than it would in the BCS weak-coupling model, and the value of $2\Delta_0/k_B T_c$ turns out to be 6.5.

At temperatures below 50 K, the ESR line begins to broaden and shift toward a weaker magnetic field. This behavior apparently indicates a freezing of the exchange fluctuations and an elimination of the exchange narrowing, due to the approach to the point of magnetic ordering. Since the ESR line becomes unobservable below 7 K, without reaching a maximum width, we would expect that the temperature of the magnetic ordering satisfies $T_M < 7$ K. The latter result agrees with a result from Ref. 10, where data on the heat capacity of $GdBa_2Bu_3O_y$ were used to reach the conclusion $T_M = 2.24$ K.

[1)] Institute of Physical Problems, Academy of Sciences of the USSR, Moscow.
[2)] Kazan' State University.
[3)] Institute of High-Pressure Physics, Academy of Sciences of the USSR, Troitsk.

[1]J. G. Bednorz and K. A. Muller, Z. Phys. **64**, 189 (1986).
[2]M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Mehg, L. Gao, Z. Huang, Y. O. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).
[3]N. E. Alekseevskiĭ, E. P. Khlybov, V. V. Evdokimova, G. M. Kuz'micheva, A. V. Mitin, V. I. Nizhankovskiĭ, and A. I. Khar'kovskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. Supplement, 11 (1987).
[4]N. E. Alekseevskiĭ, I. A. Garifullin, B. I. Kochelaev, and É. G. Kharakhash'yan, Zh. Eksp. Teor. Fiz. **72**, 1523 (1977) [Sov. Phys. JETP **45**, 799 (1977)].
[5]R. M. Hazen, L. W. Funger, R. J. Angel, C. T. Prewitt, N. L. Ross, H. K. Mao, C. G. Hadidiacos, P. H. Hor, R. L. Meng, and C. W. Chu, Phys. Rev. B **35**, 7238 (1987).
[6]B. I. Kochelayev, E. G. Kharakhashyan, I. A. Garifullin, and N. E. Alekseevsky, in Proceedings of the Eighteenth AMPERE Congress, Nottingham, 1974, p. 23.
[7]R. Odermatt, Helv. Phys. Acta **54**, 1 (1981).
[8]A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960) [Sov. Phys. JETP **12**, 1243 (1961)].
[9]N. E. Alekseevskiĭ, I. A. Garifullin, B. I. Kochelaev, G. G. Khaliullin, and É. G. Kharakhash'yan, Zh. Eksp. Teor. Fiz. **82**, 1979 (1982) [Sov. Phys. JETP **55**, 1138 (1982)].
[10]J. O. Willis, Z. Fisk, J. D. Thompson, S.-W. Cheong, R. M. Aikin, J. L. Smith, and E. Zirngeiebl, JMMM **67**, L139 (1987).

Translated by Dave Parsons