# Crystal-field and exchange interactions of dilute $Gd^{3+}$ ions in $Eu_2CuO_4$

D. Rao, M. Tovar,* and S. B. Oseroff
*Physics Department, San Diego State University, San Diego, California 92182*

D. C. Vier and S. Schultz
*Physics Department, University of California, San Diego, La Jolla, California 92093*

J. D. Thompson, S-W. Cheong, and Z. Fisk
*Los Alamos National Laboratory, Los Alamos, New Mexico 87545*
(Received 19 May 1988)

We have measured the electron-spin-resonance spectrum of $Gd^{3+}$ ions substituting for Eu ions in $Eu_2CuO_4$. The fine structure of the spectrum was partially resolved at room temperature and the individual transitions were completely separated below 100 K. The spectrum is described with a crystal-field effective Hamiltonian of tetragonal symmetry. The values obtained at low temperatures for the corresponding parameters are $b_2^0 = -486(7)\times10^{-4}$ cm$^{-1}$, $b_4^0 = -32(2)\times10^{-4}$ cm$^{-1}$, and $|b_4^4| = 790(50)\times10^{-4}$ cm$^{-1}$. These parameters are only weakly temperature dependent. The measured effective $g$ value is shifted from the free-ion value $g = 1.992$, indicating the existence of antiferromagnetic exchange interactions with the ions of the host.

The recent discovery of superconductivity at high temperatures[1] in copper-based oxides with planar Cu-O structures has focused attention on the physical properties of a large series of metallic and insulating compounds with similar crystalline structures. Among them, the $(R)_2CuO_4$ series, with $R$ = Pr, Nd, Sm, Eu, Gd, ..., form in a tetragonal structure[2] related to the orthorhombic structure of $La_2CuO_4$. These materials are nonmetallic and show interesting magnetic properties. While $Eu_2CuO_4$ is a Van Vleck paramagnet[2,3] with possible antiferromagnetic ordering[4] around 200 K, $Gd_2CuO_4$ shows weak ferromagnetism at room temperatures.[4] It is of interest then to study the interactions of individual $R$ ions with the rest of the lattice. In this paper we report experimental evidence of these interactions, particularly crystal-field effects, obtained through the analysis of the electron-spin-resonance (ESR) spectrum of dilute Gd ions in the $Eu_2CuO_4$ host. The samples were single-crystal platelets ($\sim 2\times2\times0.1$ mm$^3$) grown from a PbO flux. The crystal structure is tetragonal[5] with lattice constants $a = 3.910(1)$ Å and $c = 11.925(3)$ Å. In all cases the $c$ axis was found to be oriented perpendicular to the plates.

The ESR experiments were performed at 9 and 35 GHz. The spectra were centered around $g \cong 2$, as expected for the ground state of $Gd^{3+}$ ions ($4f^7$; $^8S_{7/2}$). A partially resolved fine structure was observed at room temperature, and below 100 K the individual lines were completely separated. This structure is strongly dependent on the relative orientation of the applied magnetic field and the crystalline axes. The maximum splitting of the spectra was obtained for the magnetic field aligned parallel to the $c$ axis. Assuming that $Gd^{3+}$ ions enter the $Eu_2CuO_4$ lattice, substituting for $Eu^{3+}$ ions, the corresponding spin Hamiltonian for tetragonal symmetry ($C_{4v}$) is

$$H_{CF}(\mathrm{Gd}) = g_{\parallel}\mu_B H_z S_z + g_{\perp}\mu_B (H_x S_x + H_y S_y) + (b_2^0/3)O_2^0 + (b_4^0/60)O_4^0 + (b_4^4/60)O_4^4 , \quad (1)$$

where $O_n^m$ are Stevens operators and $b_n^m$ are the corresponding crystal-field parameters. Sixth-order terms have not been included since we have found that their effect, if any, is below our present experimental resolution. In Figs. 1 and 2 we show the spectra obtained with the magnetic field parallel to the $c$ axis, measured at 9 and 35 GHz, respectively. For this orientation, only the diagonal terms $O_2^0$ and $O_4^0$ contribute in first order to the fine-structure splitting. Seven spectral lines are expected for $S = \frac{7}{2}$, corresponding to $M_S \leftrightarrow M_S - 1$ electronic transitions, but only six of these lines were observed at each of the two microwave frequencies used. In the case of 35 GHz the $\frac{7}{2} \leftrightarrow \frac{5}{2}$ transition was beyond the maximum magnetic field of our spectrometer and, for 9 GHz, the $-\frac{5}{2} \leftrightarrow \frac{7}{2}$ transition was not detected. This fact is consistent with the values obtained for $g_{\parallel}$, $b_2^0$, and $b_4^0$ given in Table I. The crystal-field splitting associated with these parameters is relatively large in comparison with the microwave energy at 9 GHz, and prevents the observation of the $-\frac{5}{2} \leftrightarrow -\frac{7}{2}$ transition for any applied magnetic field. In Figs. 1 and 2 we give the spectra obtained with the magnetic field parallel to the $c$ axis, measured at 9 and 35 GHz, respectively. For this orientation, only the diagonal terms $O_2^0$ and $O_4^0$ contribute in first order to the fine-structure splitting. The absolute signs for $b_2^0$ and $b_4^0$ were determined from the relative intensities of the ESR lines at low temperatures. An estimate of the absolute value of $b_4^4$ was obtained from the second-order perturbation shift of the spectral line. For the magnetic field oriented perpendicular to the $c$ axis the fine-structure lines move towards the central field, as expected for the proposed Hamiltonian. This results in strong superposition of the spectral lines, and therefore it was not possible to follow the angular dependence of the spectra and to derive values for the parameter $b_4^4$ and the $g_{\perp}$ factor.

The measured $g$ value for $\mathbf{H} \| c$ is shifted from the free-ion value $g = 1.992$. As shown in Table I, this shift is

 

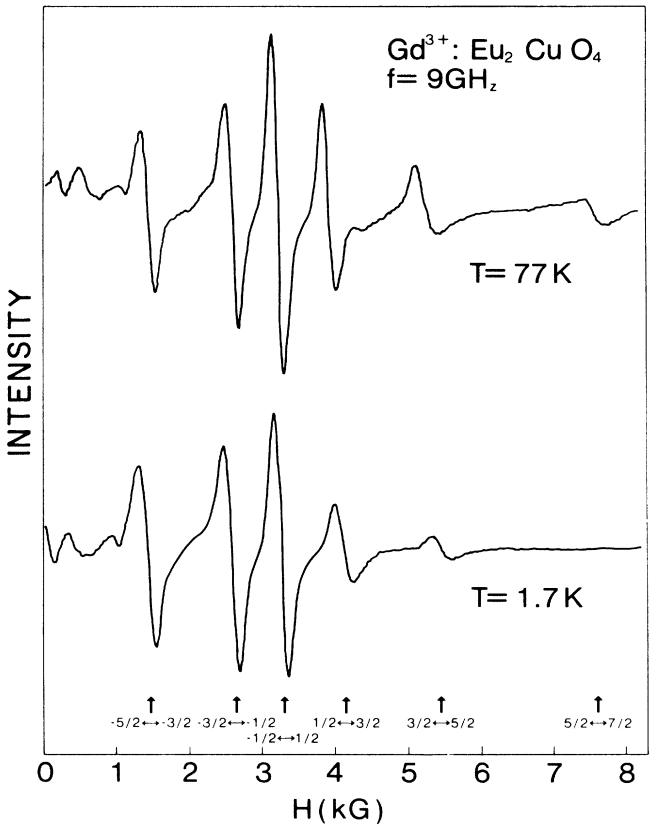


FIG. 1. ESR spectra of $Eu_2CuO_4$ doped with 1.5 at.% Gd, taken at 9 GHz with the external magnetic field parallel to the $c$ axis. Notice the reduced intensity of the high-field fine-structure lines at 1.7 K. Also, notice that due to the large crystal-field splitting, the $-\frac{7}{2} \leftrightarrow -\frac{5}{2}$ transition cannot be observed at this frequency.

small at room temperature and increases significantly when the temperature is lowered. It is possible to interpret it in terms of exchange interaction[6] with neighboring Eu ions. This interaction can then be described with a Hamiltonian of the form

$$H_{ex} = -\sum_k J_k \mathbf{S}_{Gd} \cdot \mathbf{S}_{Eu}^{(k)} , \tag{2}$$

coupling the spin of the $Gd^{3+}$ ions to the spin of the neighboring $Eu^{3+}$ ions. These ions have a singlet ground state ($^7F_0$) and they behave as Van Vleck paramagnets.[7] The admixture of the $^7F_1$ wave function into the ground state through the Zeeman interaction gives rise to a nonzero magnetic moment for the $Eu^{3+}$ ions proportional to the applied magnetic field. The exchange interaction can then be described in the mean-field approximation with an effective Hamiltonian:[4]

$$H_{ex} = \Delta_g \mu_B \mathbf{S}_{Gd} \cdot \mathbf{H} ,$$

where the $g$ shift $\Delta_g$ is defined by

$$\Delta g \mu_B \mathbf{H} \equiv -\sum_k J_k \langle \mathbf{S}_{Eu}^{(k)} \rangle .$$

The mean value of the Eu spins $\langle \mathbf{S}_{Eu}^{(k)} \rangle$, related to the measured magnetic susceptibility of the undoped

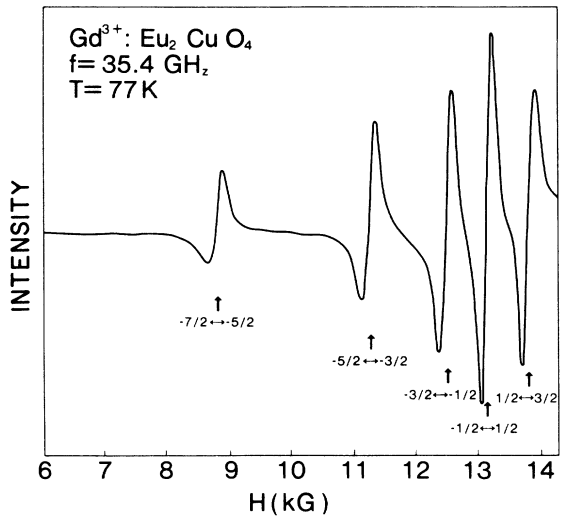


FIG. 2. ESR spectrum of $Eu_2CuO_4$ doped with 1.5 at.% Gd, taken at 35 GHz with the magnetic field parallel to the $c$ axis. Notice that at this frequency we do observe the low-field $-\frac{7}{2} \leftrightarrow -\frac{5}{2}$ fine-structure line.

$Eu_2CuO_4$ compound, and for the $z$ component of the applied magnetic field parallel to the $c$ axis, is

$$\chi_{\parallel}(Eu_2CuO_4) H_z = -N_A \mu_B \langle S_{Eu,z}^{(k)} \rangle .$$

Thus,

$$\Delta g = \left[ \sum_{NN} J_k \right] [\chi_{vv}(Eu)/N_A \mu_B^2] ,$$

where the sum over $k$ can generally be restricted to nearest neighbors.

The measured $g$ shift for the magnetic field parallel to the $c$ axis is temperature dependent as seen in Table I. Its average value in the temperature range 4–77 K is $\Delta g_{\parallel} = -0.12(5)$. If we use the measured value[3] of the magnetic susceptibility, $\chi_{\parallel} = +8.6(4) \times 10^{-3}$ emu/(mol Eu), we obtain a value for the coupling constant between $Gd^{3+}$ and $Eu^{3+}$ ions, $\sum_{NN} J_k = -0.48(20)$ meV. The negative sign indicates that the coupling has antiferromagnetic character.

However, the variation of the $g$ shift does not follow the same temperature dependence of the Van Vleck susceptibility of $Eu_2CuO_4$, which remains almost constant below

TABLE I. Crystal-field parameters and $g_{\parallel}$ values for dilute $Gd^{3+}$ ions in $Eu_2CuO_4$.

| Temperature (K) | $b_2^0$ ($10^{-4}$ cm$^{-1}$) | $b_4^0$ ($10^{-4}$ cm$^{-1}$) | $g_{\parallel}$ | Frequency (GHz) |
|---|---|---|---|---|
| 5 | −486(7) | −32(2) | 1.82(1) | 9.25 |
| 30 | −492(7) | −32(2) | 1.84(1) | 9.25 |
| 84 | −509(7) | −37(2) | 1.90(1) | 9.25 |
| 77 | −502(7) | −37(2) | 1.91(1) | 9.00 |
| 77 | −524(10) | −40(2) | 1.94(1) | 35.4 |
| Room temperature | −505(10) | −40(2) | 1.95(1) | 35.4 |

100 K. This fact suggests that other magnetic interactions may also be present, possibly with magnetic moments associated to the Cu-O planes. In this case the $g$ shift may be due to coupling to the antiferromagnetic order that seems to appear[4] around 200 K in pure $Eu_2CuO_4$.

In conclusion, we have determined $g$ values and crystal-field parameters for $Gd^{3+}$ ions substituting for $Eu^{3+}$ ions in $Eu_2CuO_4$. The measured crystal-field parameters indicate a splitting of the ground state of about 0.8 K. The observed $g$ values for $H \| c$ indicate antiferromagnetic interactions. If we associate these interactions with induced magnetic moments on Eu ions, an average coupling constant of $\sum_{NN} J_k = -0.48(20)$ meV is derived. However, the possibility of magnetic interactions with Cu-O ions cannot be ruled out.

We wish to acknowledge partial support from the Comisión Nacional de Energía Atómica (Argentina), National Science Foundation through Grant No. DMR 86-13856, and U.S. Department of Energy, Los Alamos National Laboratory.

*Permanent address: Centro Atómico Bariloche, 8400 Bariloche, Argentina.

[1]G. J. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2]R. Saez Puche, M. Norton, T. R. White, and W. S. Glausinger, J. Solid State Chem. **50**, 281 (1983), and references therein.

[3]M. Tovar, D. Rao, J. Barnett, S. B. Oseroff, J. D. Thompson, S-W. Cheong, Z. Fisk, D. C. Vier, and S. Schultz, Phys. Rev. B (to be published).

[4]M. Tovar, D. Rao, J. Barnett, K. Hovey, S. B. Oseroff, J. D. Thompson, S-W. Cheong, Z. Fisk, D. C. Vier, and S. Schultz (unpublished).

[5]Kimberly A. Kubat-Martin and R. R. Ryan (private communication).

[6]C. Rettori, D. Davidov, A. Grayevskey, and W. M. Walsh, Phys. Rev. B **11**, 4450 (1975).

[7]J. H. Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford Univ. Press, London, 1932), p. 248.