Crystal-field effects in the electron-spin resonance of Gd$^{3+}$ and Er$^{3+}$ in Pr$_2$CuO$_4$
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The low-temperature ($T < 300$ K) electron-spin-resonance (ESR) spectra of Gd$^{3+}$ and Er$^{3+}$ in Pr$_2$CuO$_4$ show symmetry properties appropriate to the crystal tetragonal symmetry. The completely resolved Gd$^{3+}$ spectra allowed us to measure, at $T = 2$ K, the principal $g$ values $g_\perp = 2.040(8)$, $g_r = 1.985(8)$, and the crystal-field parameters \[ b_2^0 = -399(2) \times 10^{-4} \text{ cm}^{-1}, \]
\[ b_4^0 = 33.1(7) \times 10^{-4} \text{ cm}^{-1}, \]
and \[ b_6^0 = 205(3) \times 10^{-4} \text{ cm}^{-1}. \] The large broadening of the ESR lines, observed above $T \sim 40$ K, is due to a relaxation via the thermally populated crystal-field excited Pr levels. For Er$^{3+}$ in Pr$_2$CuO$_4$ we observe a single ESR line corresponding to a ground-state doublet with $g_r = 17.94(5)$ and $g_r \leq 0.2$. The absence of any splittings of the ESR lines below the Neel temperature implies that the magnetostatic dipole field at the rare-earth-ion site due to the antiferromagnetically ordered Cu moments is $< 45$ Oe.

I. INTRODUCTION

The magnetic properties of the high superconducting transition temperature copper oxide materials have been intensively studied in order to determine whether the underlying superconducting mechanism has a magnetic origin.

Alternatively, even if the origin of the superconductivity does not involve magnetism, it may be possible to utilize magnetic probes to help elucidate the nature of the electronic system. We have undertaken a comprehensive study of the magnetic properties of the host insulating $T'$-phase materials (with symmetry $I4/mmm$) of the form $R_2$CuO$_4$ (where $R$ is one of several rare earths), using a variety of magnetically sensitive probes including dc and ac magnetization, microwave magnetoabsorption, and electron-spin resonance (ESR).

In general, we find that the $T'$-phase $R_2$CuO$_4$ compounds may be classified into two groups which show different types of magnetic behavior. One exhibits a remarkably rich set of magnetic features such as weak ferromagnetism, anisotropic microwave absorption signals, and an unusually large anisotropic shift of the Gd$^{3+}$ ESR field for resonance, while the other does not.

More recently, we have found there are also additional splittings of the crystal-field fine structure Gd$^{3+}$ ESR lines in Eu$_2$CuO$_4$, and the related $T'$-phase La$_2$CuO$_4$ doped with Gd. The compound Eu$_2$CuO$_4$ is a member of the group that does exhibit some of the unusual magnetic properties just mentioned (i.e., other than the extra splittings), while La$_2$CuO$_4$ forms in a different structure.

One of the properties found in the first group of materials is that all the unusual magnetic features are "turned off" above a characteristic temperature, termed $T_h$ which we have identified with the Neel temperature associated with the three-dimensional (3D) antiferromagnetic (AF) ordering of the planar Cu-O set of moments. However, neutron scattering and muon spin rotation (μSR) experiments also indicate a 3D-AF ordering in the second group, which does not show the unusual magnetic features. As the extra splittings of the crystal-field fine structure for the Gd$^{3+}$ ESR lines were found in Eu$_2$CuO$_4$, a member of the group which shows the complex magnetic properties, it was felt that a more careful examination of the Gd$^{3+}$ fine structure spectrum for a compound that had none of the unusual magnetic features was warranted. Pr$_2$CuO$_4$ was chosen and in this article we present an accurate fitting of the crystal-field parameters for a spin Hamiltonian with $C_{4v}$ site symmetry.

To the accuracy given, we find no deviations from that Hamiltonian nor any anomalous behavior of the spectra which might be identified with the transition to the AF state.

EXPERIMENT

The samples used were single crystals of nominal composition Pr$_{1.98}$Gd$_{0.02}$ErCuO$_4$ grown from a PbO-based flux. Pb incorporation into the crystals was not detectable by x-ray fluorescence. The crystal structure is tetragonal ($I4/mmm$) with ideal lattice parameters $a = 3.961$ Å and $c = 12.214$ Å. Typical size of the crystals...
was 2 × 3 × 0.3 mm$^3$ with the c axis oriented parallel to the smaller dimension. The ESR experiments were performed at 9 and 35 GHz in the temperature range 2–300 K, using conventional spectrometers.

Figure 1 shows a low-temperature, well resolved fine structure spectrum (for Pr$_2$CuO$_4$:Gd) which allowed an accurate determination of the crystal-field Hamiltonian appropriate for the $C_{4v}$ point symmetry occupied by the rare-earth ions in these cuprate compounds:

$$H = g_\parallel \mu_B H S_z + g_\perp \mu_B (H x S_x + H y S_y)$$
$$+ b_2^{(m)} O_2^{(m)} + b_4^{(m)} O_4^{(m)} + b_6^{(m)} O_6^{(m)},$$

where $g_\parallel$ and $g_\perp$ are the gyromagnetic factors for the external magnetic field $H$ parallel and perpendicular to the c axis, respectively. $O_n^{(m)}$ are the Stevens operators and $b_n^{(m)}$ the corresponding crystal-field parameters. The $g$ values and crystal-field parameters obtained from the fitting of the experimental data at both frequencies are given in Table I. These parameters can reproduce the field for resonance of the spectrum within one-third of the linewidth (≈20 G) for any arbitrary magnetic field orientation and microwave frequency. The sign of the crystal-field parameters was determined from the temperature dependence of the relative intensity of the ESR lines at 35 GHz.

The observed difference between $g_\perp$ and the free Gd$^{3+}$ ion $g$ value (1.991) is smaller than in the case$^8$ of Eu$_2$CuO$_4$ (see Table I), indicating smaller couplings along the c axis for the Pr-based compound. However, there is a significant $g$-value anisotropy. Also, the crystal-field parameters given in Table I are smaller than those corresponding to Eu$_2$CuO$_4$. This reduction is consistent with the larger lattice parameter of Pr$_2$CuO$_4$. Figures 2–5 show the angular dependence of the ESR spectrum for Pr$_2$CuO$_4$:Gd for each microwave frequency for different crystal orientations.

Figure 6 shows the temperature dependence of the linewidth for two Gd$^{3+}$ ESR transitions. An initial temperature independent linewidth ($T < 40$ K) is in general expected for Gd$^{3+}$ ions (S state) in insulators. The sharp increase of the linewidth above 40 K is probably due to relaxation via thermally populated excited crystal-field Pr levels. Indeed, recent inelastic neutron scattering experiments in Pr$_2$CuO$_4$ determined the presence of a $\Gamma_3$ first excited level at about 13.7 meV above the $\Gamma_3$ ground state. This excited level could provide the relaxation channel for the Gd$^{3+}$ impurities, via an exchange or electric dipolar coupling mechanism.$^{10}$

As mentioned above, we have also prepared a single crystal of Pr$_{1.09}$Er$_{0.01}$CuO$_4$ and observed a single strong ESR resonance as expected for a ground-state Er$^{3+}$ dou-

| Table 1. Crystal-field parameters and $g$ values for Gd$^{3+}$ in Pr$_2$CuO$_4$, measured at $T=2$ K. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| $b_2^{(0)}$ (10$^{-4}$ cm$^{-1}$) | $b_2^{(0)}$ (10$^{-4}$ cm$^{-1}$) | $b_4^{(0)}$ (10$^{-4}$ cm$^{-1}$) | $g_\parallel$ | $g_\perp$ |
| -399(2)         | -33.1(7)        | 205(3)          | 1.985(8)        | 2.040(8)        |

FIG. 1. 35 GHz ESR spectrum of Gd$^{3+}$ in Pr$_2$CuO$_4$ at $T=4.2$ K.

FIG. 2. Angular dependence of the 9 GHz ESR spectrum of Gd$^{3+}$ in Pr$_2$CuO$_4$ for the dc magnetic field on the (001) plane. The dashed lines are guides to the eye.
broad. Along the c axis, at 4.2 K, we have measured a linewidth of ΔH = 60 Oe, which is considerably broadened by ~ 20 K. The resonance field as a function of angle is shown in Fig. 7, from which we deduce the g values, g_i = 17.94(5) and g_j ≤ 0.2. No splitting of this line was observed for angles of magnetic field from 0° to 85° away from the c axis. (Angles further from the c axis were not measured because the field for resonance is then shifted beyond the range of our magnet.)

**CONCLUSIONS**

The crystal-field parameters obtained by fitting the spin-Hamiltonian of Eq. (1) are consistent with the ob-

**FIG. 3.** Angular dependence of the 35 GHz ESR spectrum of Gd^{3+} in Pr$_2$CuO$_4$ for the dc magnetic field on the (001) plane. The dashed lines are guides to the eye.

**FIG. 5.** Angular dependence of the 35 GHz ESR spectrum of Gd^{3+} in Pr$_2$CuO$_4$ for the dc magnetic field in the plane from the c axis to the [100]. The dashed lines are guides to the eye.

**FIG. 4.** Angular dependence of the 9 GHz ESR spectrum of Gd^{3+} in Pr$_2$CuO$_4$ for the dc magnetic field in the plane from the [100] to the c axis. The dashed lines are guides to the eye.

**FIG. 6.** ESR linewidth of the Gd$^{3+}$ ($-\frac{3}{2} \leftrightarrow -\frac{1}{2}$) and ($-\frac{5}{2} \leftrightarrow -\frac{3}{2}$) transitions in Pr$_2$CuO$_4$ as a function of temperature.
observed ESR spectra being due to a Gd$^{3+}$ ion in a site of $C_4$ symmetry. In contrast to the ESR spectra of Gd$^{3+}$ in $Eu_2CuO_4$\(^2\) and $La_2CuO_4$\(^2\), which clearly showed an additional splitting of each fine structure level below the Néel temperature (this splitting was interpreted as a result of the internal field due to the Cu moments at the rare-earth site), no additional splittings were observed in $Pr_2CuO_4$ at any temperature or magnetic field orientation. Our experiments for $Pr_2CuO_4$ place a limit of $< 45$ Oe for the magnetic dipole field of the Cu moments at the rare-earth sites, in contrast to $\sim 500$ Oe found for $Eu_2CuO_4$ and $La_2CuO_4$. If one assumes that our samples have the same AF transition as observed by neutron scattering, we can conclude that the $Pr_2CuO_4$ is representative of that subgroup of the $R_2CuO_4$ which does not manifest an indication of the 3D-AF transition via any of the diverse magnetic signatures observed for the subgroup that do.\(^2\) We may speculate that the difference depends upon subtle lattice distortions which have not yet been detected. The reason for the absence of any splitting that could be attributed to the magnetic dipole field for the Cu moments also remains a puzzle.

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