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OBSERVATION OF COMPLEX MAGNETIC BEHAVIOR IN THE PEROVSKITE RARE EARTH COPPER OXIDE SYSTEMS, R_2CuO_4

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EPR, microwave absorption, and dc magnetization measurements were made on single crystals of the form R_2CuO_4 , which are the host compounds for the newly discovered series of electron cuprate superconductors. These measurements reveal two characteristic transition temperatures associated with a novel complex magnetic behavior, including weak ferromagnetism, two sharp peaks in the low field DC magnetization, an unusual anisotropy in the EPR resonance field for $R = Gd$, and two additional anisotropic microwave absorption modes. The higher characteristic transition temperature, at $\sim 270K$, is attributed to AF ordering of the Cu moments, and the lower, at $\leq 20K$, to a spontaneous canted spin reorientation. An understanding of this magnetic behavior is important in order to ascertain its relationship to possible mechanisms of high temperature superconductivity.

A new series of electron cuprate superconductors have recently been reported of the form $R_{2-x}Ce_xCuO_4$ ($R=Pr, Nd, Sm$, or Eu),^{1,2} and also doped with Th^{2+} instead of Ce . These materials are particularly interesting because (a) they exhibit electron (as opposed to hole) conductivity, and (b) they have the Nd_2CuO_4 structure,⁴ where the Cu-O atoms are simply arranged in a square planar array ($a = b$) with no apical (out of plane) coordinated oxygen.¹

We have measured the electron paramagnetic resonance (EPR), microwave absorption, and dc magnetization (M_{dc}), properties for a series of the undoped host R_2CuO_4 single crystals. These materials exhibit a rich and complex magnetic behavior which requires interpretation to determine the nature of the diverse exchange couplings between the Cu moments and the rare earth ligands. In particular, our data reveal two characteristic transition temperatures. The high characteristic temperature, HCT $\sim 270K$, is taken to be associated with antiferromagnetic ordering of the Cu^{++} moments as in La_2CuO_4 .⁵ The low characteristic temperature, LCT $\leq 20K$, is a new feature in these R_2CuO_4 materials,⁶ and may represent a spin reorientation of the canted weak ferromagnetism. Since the superconducting transition for the Ce and Th doped R_2CuO_4 are in the same temperature range in which the LCT occurs, it is particularly important to clarify the magnetic nature of these systems both above and below the LCT. A complete understanding of the magnetic parameters of these systems should then provide key insights as to whether magnetism per se plays an essential role in copper oxide superconductivity.

The microwave measurements were made using conventional EPR techniques with spectrometers operating at 9.2 or 35 GHz. M_{dc} measurements were made on either a SQUID or a vibrating sample magnetometer.

Our measurements reveal six different aspects, or signatures (S1-S6), of the distinctive magnetic properties of these systems. Not all six signatures appear in every compound, although each signature is found in enough

compounds to be regarded as potentially present in the entire class. The occurrence of S1-S6 for the samples studied is summarized in Table I, and discussed below.

S1) Specific Heat Peak: For some R there is a peak in the specific heat (at the temperatures shown in Table I) which is attributed to the antiferromagnetic ordering of their moments.⁶

S2) Sharp peaks in the dc magnetization: In Fig.(1) measurements of the dc magnetization as a function of temperature for a $EuTbCuO_4$ sample in a field of ~ 1 Oe applied parallel to the CuO (i.e., a-b) plane are presented. The two sharp peaks are similar to those found in Gd_2CuO_4 .⁶ Similar peaks are found for all the other samples indicated in Table I, however, their relative amplitude is dependent upon the rare earths used. Both of the peaks are broadened, and move to lower temperature, when the magnetic field is increased. There is evidence for a mild difference between field cooled and zero field cooled data. We note that there is a large anisotropy in these systems, and if the field is applied parallel to the c-axis there is no indication of either peak.⁶

The HCT peak always has an onset at $270 \pm 5K$, with the peak at $250 \pm 10K$, which we assume to be a consequence of the AF ordering of the Cu moments in analogy to La_2CuO_4 which undergoes an AF transition around this temperature.⁵ On the other hand, the LCT peak appears to reflect an unknown property of these systems, and we have no explanation for its origin at this time. As seen from Table I, in contrast to the HCT peak, the value of the temperature at which the LCT peak occurs is a function of the rare earths used and their relative concentration.

S3) Weak Ferromagnetism: Below $270 \pm 5K$ there is evidence for weak ferromagnetism, WF, which saturates when the magnetic field component in the Cu-O plane exceeds a value specific to the particular rare earths used. In Fig.(2) we present data at 77K for the dc magnetization as a function of magnetic field applied parallel to the a-b plane for several crystals. The key features of this class of data are: (i) At sufficiently high fields the magnetization is linear with a magnetic moment per atom corresponding to the rare earth free ion.

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TABLE I

System	Signature	S_2 (SGL)		S_3 (WF)	S_4 (EPR)	S_5 (MFA)	S_6 (LFA)	
	S_1 (Cp)	LCT	HCT				HCT	LCT
Pr_2CuO_4	$N^{(a)}$	N	N	N	*	N	N	N
$PrGdCuO_4$	-	N	N	N	N	N	N	N
Nd_2CuO_4	Y(~1.5K)	N	N	N	*	N	N	N
$Nd_{1.8}Gd_{0.2}CuO_4$	-	N	N	N	N	N	N	N
Sm_2CuO_4	Y(5.95K)	N	N	N	*	N	N	N
$SmGdCuO_4$	-	Y(268K)	Y(11K)	Y	Y	Y	Y	-
Eu_2CuO_4	-	N	N	N	*	Y ^(c)	-	-
$Eu_{1.97}Gd_{0.03}CuO_4$	-	Y	N(< 2K)	N	Y	Y	Y	N
$Eu_{1.8}Gd_{0.2}CuO_4$	-	Y(265K)	N(< 2K)	Y	Y	Y	Y	N
$EuGdCuO_4$	-	Y(266K)	Y(9K)	Y	Y	Y	Y	Y(10K)
$Eu_{0.2}Gd_{1.8}CuO_4$	-	Y(270K)	Y(18K)	Y	Y	Y	Y	Y(19K)
$EuTbCuO_4$	$N^{(b)}$	Y(275K)	Y(10K)	Y	*	Y	Y	Y(10K)
$EuDyCuO_4$	-	Y(275K)	Y(18K)	Y	-	-	-	-
Gd_2CuO_4	Y(6.5K)	Y(268K)	Y(19K)	Y	Y	Y	Y	Y(18K)
$GdTbCuO_4$	-	Y	Y(18K)	Y	Y	Y	Y	Y(18K)

S_1 - S_6 are measured signatures discussed in the text. LCT and HCT are the lower and higher characteristic temperatures, respectively. An entry of Y (or N) in the table means that the signature was (or was not) observed for the sample indicated. An asterisk (*) means that the EPR of the R moment was not observed. A dash (-) means the sample was not tested for that signature.

(a) possible nuclear Schottky anomaly

(b) down to 1K

(c) Observed onset is ~210K compared to ~280K for all other "Y" S_5 entries.

(ii) By extrapolating to zero magnetization, we find an internal field at the R site, $H_i(0)$, which is independent of the rare earths used, and is approximately 800 Oe. $H_i(0)$ is also independent of temperature down to that of the LCT peak, with a complex behavior at lower temperature.⁶

(iii) As can be seen in Fig.(2), the amount of field needed to saturate the WF varies, from ~100 Oe ($EuTbCuO_4$, Gd_2CuO_4 , $GdTbCuO_4$) to ~1000 Oe ($Eu_{1.8}Gd_{0.2}CuO_4$, or $SmGdCuO_4$).

(iv) When similar data are taken with the applied field making an angle θ to the a-b plane, the linear region is not established until higher values of field, qualitatively proportional to $1/\cos \theta$, and the corresponding field intercept goes as $H_i(0) \cos \theta$.

(v) Some finite hysteresis cannot be ruled out, but if there is a coercivity, it is less than 1 Oe, and the remanence is less than 2% of the extrapolated intercept at $H = 0$.

S4) Anisotropy in the Shift in the Resonant Field for the EPR of Gd: The only R for which an EPR signal is observed is Gd. For the sample series $(Eu_{1-x}Gd_x)_2CuO_4$ we always observe an EPR signal which can be attributed to the Gd moment. For $x=0.015$, the spectra correspond to the fine structure splittings expected for a Gd^{3+} free ion in a tetragonal host.⁷ However, for $x = 0.5, 0.9$, and 1, a single line is observed whose field for resonance, H_r , has an unusual dependence on the angle θ that the applied field makes with respect to the a-b plane.

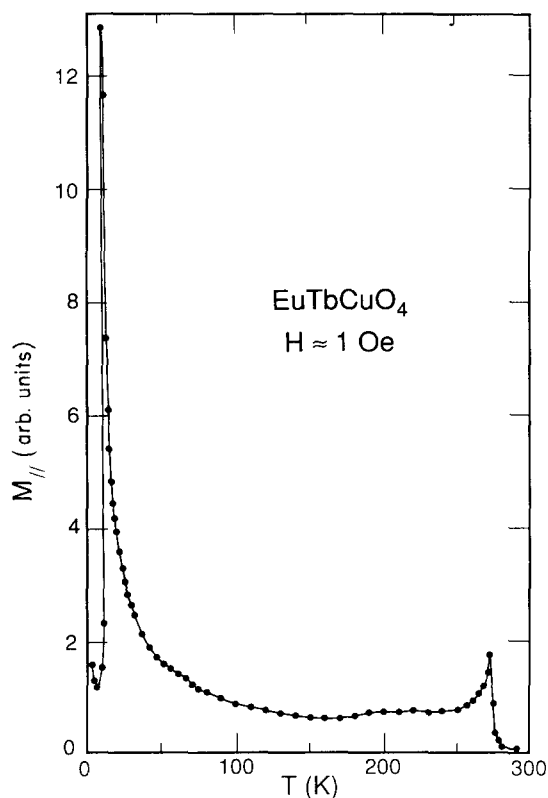


Figure 1. The dc magnetization versus temperature for EuTbCuO_4 measured in a field of 1 Oe applied parallel to the a-b plane. The higher and lower temperature peaks are termed HCT and LCT, respectively. These peaks depend on the field angle to the plane as discussed in the text. The solid line is a guide to the eye.

In Fig.(3) values of $H_r - H_0$ (H_0 is the field for resonance for $g = 2$) as a function of θ are presented for Gd_2CuO_4 at frequencies of 9.2 and 35GHz and temperatures of 80K and 300K. Note that at 300K H_r (as corrected for sample demagnetization) is essentially independent of θ , while at 80K there is the extreme anisotropic dependence shown. At any temperature the shift in H_r is independent of frequency, and therefore corresponds to an internal field, not a g-shift. In the insert of Fig.(3), the temperature dependence of H_r is presented for $\theta = 0$ and 90° . At any angle we find that the anisotropic shift in H_r has an onset at an HCT $\sim 270\text{K}$, becomes fully developed by $\sim 200\text{K}$, and then undergoes a dramatic reversal, at the LCT (in this case at $\sim 20\text{K}$) which correlates with the changes described under S2 and S3. For SmGdCuO_4 the Gd EPR exhibits a similar behavior to that described above. In contrast, for (Pr or Nd) GdCuO_4 , H_r is essentially independent of angle at any temperature which correlates with the absence of the other signatures for these two materials.

S5) Mid-field Absorption (MFA): In the insert to Fig.(4) we present the spectrometer output in the dx''/dH mode for EuTbCuO_4 . Similar signals are found for the samples indicated in Table I. (We note that for EuTbCuO_4 an EPR signal is not observed.) The field angle, θ , has been chosen near the c-axis which spreads out these two signals so they can be more clearly displayed. The signal which occurs at lower field will be discussed below as S6, the low field absorption. The other is called the mid-field absorption or S5. The S5 signal does not have a simple EPR lineshape, and there is some evidence from modulation frequency

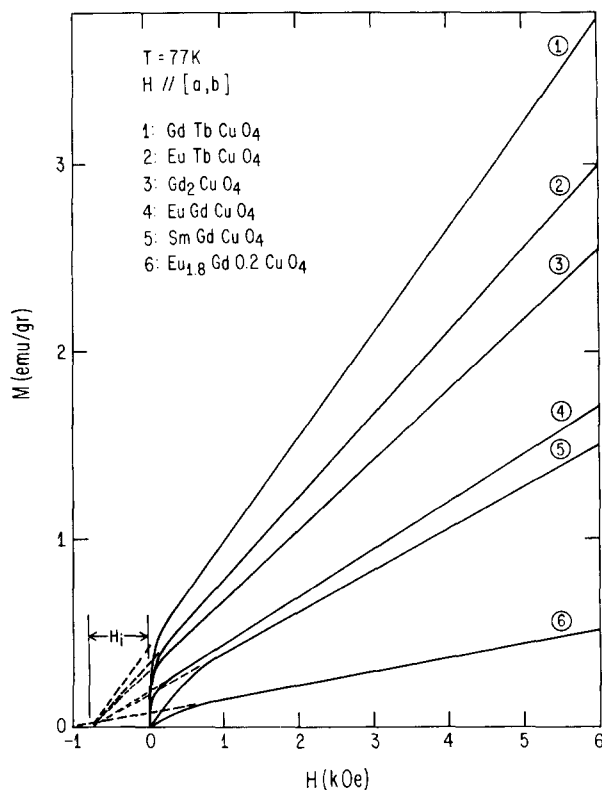


Figure 2. The dc magnetization, M , versus magnetic field applied parallel to the a-b plane for several compounds at 77K. The linear dependence at higher fields corresponds to the paramagnetism of the R ions. When extrapolated back to zero M , all the lines intersect near a reverse field, $H_i(0) = 800$ Oe. H_i depends on the angle of the applied field, θ , to the a-b plane as $H_i(\theta) = H_i(0)\cos\theta$. These properties are attributed to WF as discussed in the text.

studies which suggest that that it may have a composite substructure. In the insert we identify the low field maximal value, H_p , of the S5 signal, and in the body of Fig.(4) we present H_p as a function of θ for several samples. This angular dependence is found for any temperature between HCT and LCT. The solid lines are a fit to the data of the form $H_p(\theta) = K/\cos\theta$, where K depends on both the microwave frequency and the rare earths used, being a factor of 2-3 larger for the higher frequency.

In Fig.(5) the temperature dependence of H_p at 35 GHz for $\theta = 0^\circ$ and $\sim 85^\circ$ is presented. The data of Fig.(5) also show a HCT and LCT. The HCT of the S5 signal is first observed a few degrees Kelvin above the onset of the HCT of S4. In the insert H_p versus temperature is presented on an expanded scale in the vicinity of the LCT. There appear to be two branches of signal, the high temperature branch disappearing as we approach the LCT from above, and the low temperature branch appearing a few degrees Kelvin lower. While the general features of S5 are also found at 9.2GHz, we have only been able to observe the low temperature branch at 35GHz.

The S5 signal is very large by EPR standards. The integrated intensity corresponds to an effective number of Bohr magnetons per formula unit of between 3 and 30, depending upon the system studied. For the $(\text{Eu}_{1-x}\text{Gd}_x)_2\text{CuO}_4$ system there is a correlation of the intensity with increasing Gd concentration.

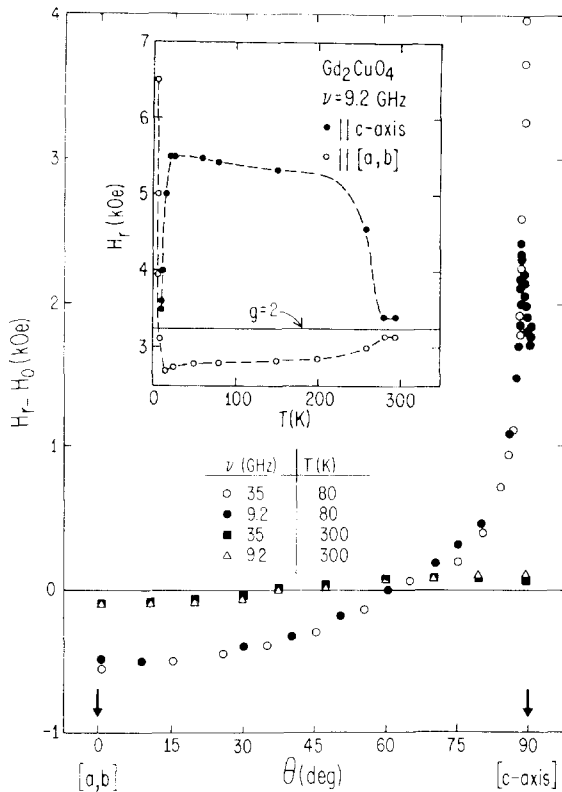


Figure 3. The field shift of the EPR of the Gd ion in Gd_2CuO_4 , relative to that for $g = 2$, versus the angle, θ , of the applied field relative to the a-b plane for the temperatures and frequencies indicated. Above 270K, H_T is basically independent of angle, whereas below and down to ~ 20 K there is the anisotropic behavior shown. Insert: H_T versus temperature for $\theta = 0^\circ$ and 90° . Note the rapid changes in H_T that occur at ~ 270 K (HCT) and ~ 20 K (LCT).

S6) Low Field Absorption (LFA): As noted above, there is a signal at a lower field displayed in the insert of Fig.(4). When we observe this signal as a function of temperature for fixed magnetic fields between 1-100 Oe applied parallel to the a-b plane, we find two peaks at temperatures corresponding to HCT and LCT. When the field is increased these peaks are broadened, suppressed, and shifted to lower temperature. In a study of the LCT peak of S6 as a function of dc field magnitude and angle, it is found that the temperature shift is only dependent upon the component of field in the a-b plane. At any temperature the LFA signal broadens with increasing field angle as $\sim 1/\cos\theta$.

In summary, in addition to the peak in the specific heat attributed to AF ordering of the R moments, there are two characteristic temperatures for those compounds which exhibit the diverse signatures discussed. The high characteristic temperature, HCT, of ~ 270 K is basically independent of the rare earths used, and is taken to be indicative of an AF ordering of the Cu spins. Above the HCT all measurements are isotropic. Below the HCT the signatures S2 - S6 are all highly anisotropic, with the dependences on angle of applied field as presented in Figs.(3) and (4) and as discussed in the text .

All the signatures reveal a second characteristic temperature, the LCT, whose value depends on the R used (Table I). We speculate that the LCT reflects a transition or rearrangement of the ordering of the Cu moments, similar to the spin reorientation temperatures found in the

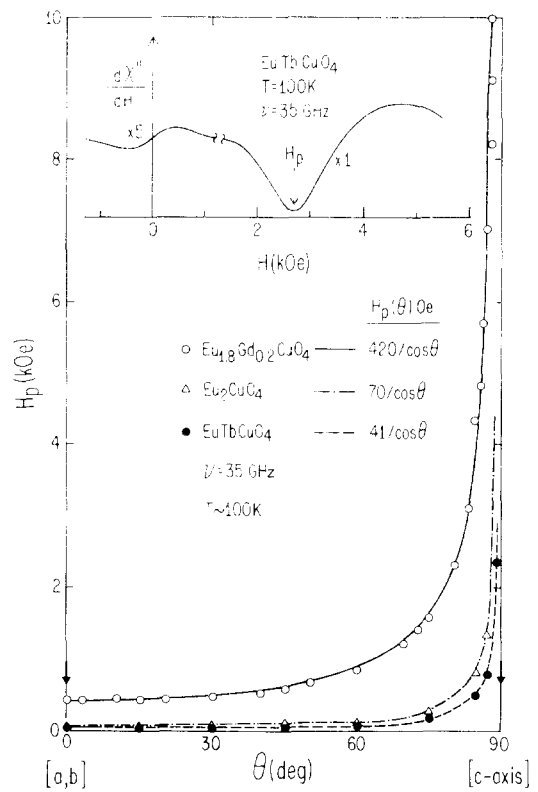


Figure 4. Insert: The 35 GHz EPR spectrometer output (dx''/dH) as a function of magnetic field for $EuTbCuO_4$ at 100K. There are two signals, the low field absorption, S6, and the mid-field absorption, S5. Main figure: The magnetic field position of the mid-field absorption peak, H_p , (as defined in the insert), as a function of the magnetic field angle, θ , for the samples indicated. The solid curves are a fit to the form $H_p(\theta) = K/\cos\theta$.

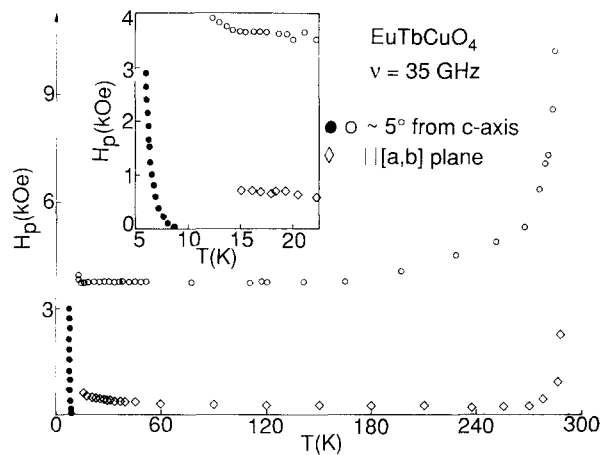


Figure 5. The value of H_p at 35GHz for $EuTbCuO_4$ (as identified in the Fig.(4) insert) as a function of temperature for the two field angles, θ , indicated. The onset at high temperature correlates with the HCT of S2,S3,S4, and S6. Insert: An expanded scale of the figure which shows the development of the second branch. Note that the temperature of transition between branches correlates with the LCT found in S2, S3, S4, and S6.

orthoferrites.⁸ We suggest that future neutron scattering experiments should focus on this temperature range.

We attribute the WF (S3) to a canting of the Cu moments due to the DM interaction,⁸ which implies that there must be small distortions from the basic tetragonal symmetry.

We are not aware of any prior system which exhibits the unusual anisotropy of the Gd EPR. The $H_i(\theta)$ of S3 alone cannot explain the shift, H_r-H_o , of the Gd EPR. The $1/\cos\theta$ dependences found for S3 and S5 are suggestive for the analysis of the angular dependence of H_r-H_o , however, we find that we cannot fit the entire curve of Fig.(3) with such a simple expression. Therefore, the shift is likely due to multiple mechanisms, with contributions to the total effective magnetic field at a Gd site from the dipolar and exchange fields of both the Cu and other Gd ions. A possible explanation for the sharp reduction of H_r within one degree of 90° for 9GHz is that the component of field in the plane becomes too small to "fully set" the WF discussed as S3.

The two mid-field absorption (S5) branches are totally new to us. The large effective moment per formula unit suggests that we may be observing the resonance of clusters or domains, which in turn feel an internal field due to the anisotropic exchange interactions.

We have initiated an investigation of the new superconducting $R_{2-x}(Ce \text{ or Th})_xCuO_{4-y}$ compounds¹⁻³ to determine their behavior with respect to the diverse magnetic signatures reported herein.⁹

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