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# Magnetic properties of $Gd_2CuO_4$ crystals

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Magnetic-susceptibility and magnetization measurements on single crystals of the $CuO_2$-planar compound $Gd_2CuO_4$ indicate copper moment ordering near 260 K, producing an internal field at the gadolinium site that induces substantial anisotropy in the magnetic response. Dilute substitutions for gadolinium and copper leave the essential physics unaffected. We suggest that copper ordering also occurs in $Eu_2CuO_4$ on the basis of substitutional studies but is not detected in other rare-earth-based compounds in this series. Rare-earth size appears to play an important role.

## I. INTRODUCTION

With the discovery of high-temperature superconductivity in $CuO_2$-layer compounds,[1] attention has focused on the potential importance of copper magnetism for superconductivity. Such interest is generated by observations of antiferromagnetic order of copper ions in nonsuperconducting versions of both $RBa_2Cu_3O_{7-\delta}$ (Refs. 2 and 3) and $La_2CuO_{4-\delta}$ (Ref. 4) materials. In the latter case, for temperatures less than the Néel temperature $T_N$, the application of a magnetic field perpendicular to the $CuO_2$ planes induces a metamagnetic transition to a weak ferromagnetic state that coexists with antiferromagnetism.[5-7] This transition, permitted by a slight distortion of the octahedrally coordinated oxygen atoms about copper,[6,8] is driven by an antisymmetric superexchange mechanism proposed by Dzyaloshinski[9] and Moriya.[10]

In addition to the superconducting materials, there is another interesting set of semiconductorlike compounds $R_2CuO_4$ that contain $CuO_2$ planes.[11-14] These materials form in a tetragonal crystal structure, when $R$ is one of the light rare-earth elements praseodymium through gadolinium, with $CuO_2$ planes in which oxygen atoms are square-planar coordinated about copper.[15] The magnetic properties of powder samples of $R_2CuO_4$ have been studied in some detail by Saez-Puche, Norton, and Glaunsinger.[16] They conclude that $Cu^{2+}$ ions are ordered antiferromagnetically below room temperature and that the general magnetic behavior is relatively straightforward once crystal-field effects have been accounted for. This is borne out, at least partially, in magnetic measurements on single crystals of $Eu_2CuO_4$.[17,18] Tovar *et al.*[18] find a pronounced anisotropy ($\sim$30%) in the susceptibility of $Eu_2CuO_4$ which at low temperatures is well described by considering crystal-field splitting of the excited states of $Eu^{3+}$. However, at temperatures above approximately 100 K, agreement between the measured and calculated susceptibilities is outside the estimated uncertainty in either result, suggesting that copper contributes non-negligibly to the susceptibility. Further, electron-spin resonance[17] of dilute $Gd^{3+}$ in $Eu_2CuO_4$ crystals gives a temperature-dependent $g$ shift indicative of antiferromagnetic interactions that may be associated with moments on the $CuO_2$ planes.

The results on single crystals[17,18] of $Eu_2CuO_4$ clearly suggest that magnetism in the $R_2CuO_4$ series could be richer than that deduced from powder-sample studies.[16] To investigate this possibility, we have performed magnetic-susceptibility, magnetization, and specific-heat experiments on single crystals of $Gd_2CuO_4$. The magnetic susceptibility of $Gd_{2-x}Eu_xCuO_4$ and $Eu_{2-x}Tb_xCuO_4$ crystals has also been determined to establish if copper magnetism found in $Gd_2CuO_4$ persists in $Eu_2CuO_4$.

## II. EXPERIMENTAL DETAILS

Thin, platelike crystals of $R_2CuO_4$ were grown from PbO- and CuO-based fluxes. (Additional details of the preparation procedure are given elsewhere.[19,20]) X-ray analysis[19] at room temperature showed that the crystals were tetragonal with space group $I4/mmm$ and that the crystallographic $c$ axis was parallel to the thin dimension. Refinement of the x-ray spectra gave lattice constants for $Gd_2CuO_4$ of $a=3.892(1)$ Å and $c=11.878(3)$ Å, with a site occupancy of 0.99(2) for gadolinium and 1.01(5) for oxygen, indicating that the crystals were stoichiometric. The possibility of lead incorporation into the structure was examined by electron microprobe analysis, which showed that the lead content, if any, was less than 1% of copper. Further, magnetic measurements on crystals grown in either PbO- or CuO-based fluxes were identical within experimental uncertainty. Unlike $La_2CuO_4$,[6,21] with quasi-tetragonal lattice parameters $a=3.81$ Å and $c=13.15$ Å, the magnetic properties of $Gd_2CuO_4$ were insensitive to anneals in various gas atmospheres, suggesting that the oxygen content is highly stable.

Susceptibility and magnetization measurements were

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performed with a Quantum Design superconducting quantum interference device magnetometer using applied fields from ~1 G to 50 kG. Calibration of the magnetometer against a National Bureau of Standards traceable platinum standard gave a susceptibility accurate to ±1% for magnetic fields greater than 1 kG. At very low fields, 1 to 10 G, error in the field value is estimated to be ±0.5 to ±1 G. All measurements were taken on warming from the lowest temperature unless otherwise specified.

## III. RESULTS AND DISCUSSION

### A. $Gd_2CuO_4$

The magnetic susceptibility measured in a 2-kG magnetic field applied perpendicular ($\chi_\perp$) and parallel ($\chi_\parallel$) to the $CuO_2$ planes of $Gd_2CuO_4$ is shown in Fig. 1(a). In this and subsequent figures, unless otherwise specified, the susceptibility has been defined as the ratio of the magnetization $M$ to the applied field $H(\chi \equiv M/H)$. Above room temperature, there is little if any field-direction-dependent anisotropy in $\chi$. However, below this temperature, $\chi_\parallel$ exceeds $\chi_\perp$ except at the lowest temperatures where a mean-field-like temperature dependence of $\chi_\parallel$ and $\chi_\perp$ is evident. Such behavior would suggest antiferromagnetic order near 9 K [Fig. 1(a) inset] with the gadolinium sublattice magnetization parallel to the $CuO_2$ planes.

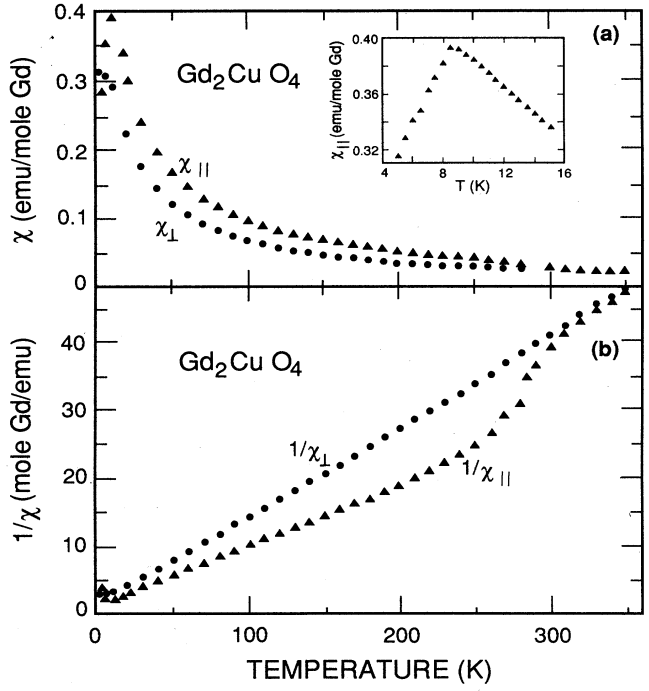


FIG. 1. (a) Magnetic susceptibility $\chi$ of a $Gd_2CuO_4$ single crystal as a function of temperature determined with a 2-kG field $H$ applied parallel ($\chi_\parallel$) and perpendicular ($\chi_\perp$) to the crystallographic $a$-$b$ plane. In these measurements $\chi$ is defined as the ratio $M/H$, where $M$ is the magnetic moment per mole of gadolinium. The inset shows an expanded view of the temperature dependence of $\chi_\parallel$. (b) Inverse molar susceptibility of $Gd_2CuO_4$ as a function of temperature for field directions in the plane and along the tetragonal $c$ axis. Note the development of substantial anisotropy beginning near 280 K. Values for the effective moment and paramagnetic Curie temperature are given in the text.

Figure 1(b) shows the same data plotted as $1/\chi_\perp$ and $1/\chi_\parallel$ versus temperature. In this case, the development of anisotropy is readily apparent. Above room temperature, these plots give an effective moment $\mu_{\rm eff}$ of $7.7\mu_B$/Gd and a paramagnetic Curie temperature $\Theta_p = 0 \pm 2$ K. However, for $H$ perpendicular to the $CuO_2$ planes and temperatures below ~240 K, $\mu_{\rm eff\perp} = 7.95\mu_B$/Gd and $\Theta_p = -12.6$ K; whereas, for $H$ parallel to the planes and temperatures less than ~200 K, $\mu_{\rm eff\parallel} = 9.68\mu_B$/Gd and $\Theta_p = -18.8$ K. These values are to be compared to $\mu_{\rm eff} = 8.20\mu_B$/Gd and $\Theta_p = -15$ K obtained[16] on powder samples measured in fields of 7.5 to 12.5 kG. For reference, Hunds' rules give $\mu_{\rm eff} = 7.94\mu_B$/Gd in the absence of interactions.

Because the susceptibility peak in $\chi_\parallel$ at 9 K suggests antiferromagnetic order of gadolinium moments, we have measured the specific heat $C$ of several crystals of $Gd_2CuO_4$. Results of these measurements are shown in Fig. 2 where a λ-like anomaly in $C/T$ vs $T$ is found, with the peak near 6.5 K, characteristic of a cooperative phase transition. A linear extrapolation of $C/T$ from the lowest measured temperature (1.4 K) to the origin allows for an estimate of the entropy associated with this transition. Such a construction gives an entropy of $0.99R\ln 8$ between $T = 0$ and 20 K, which is within experimental uncertainty identical to the entropy expected for ordering of the gadolinium $J = S = \frac{7}{2}$ spin. The phonon contribution to $C$ in this temperature range is negligible as determined from specific-heat measurements[22] on single crystals of $Eu_2CuO_4$ which give a Debye temperature of 380 K. (The electronic specific-heat coefficient of $Eu_2CuO_4$ is $0 \pm 0.2$ mJ/mole K$^2$.) Therefore, the specific-heat anomaly should be considered as arising from antiferromagnetic order of gadolinium moments at $T_N^{\rm Gd} = 6.5$ K. This value of $T_N^{\rm Gd}$ is well outside the estimated uncertainty in thermometry for either the specific heat or susceptibility measurements and suggests that the peak in $\chi_\parallel$ at 9 K should

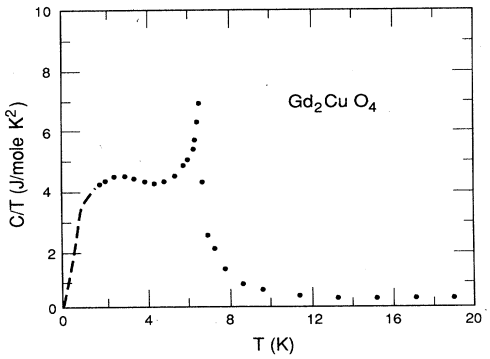


FIG. 2. Specific heat $C$ divided by temperature $T$ vs temperature for a collection of single crystals of $Gd_2CuO_4$. The λ-like anomaly peaked at 6.5 K denotes antiferromagnetic ordering of the gadolinium moments. The dashed line represents how the extrapolation of $C/T$ was made to $T = 0$.

not be regarded, in this case, as a direct measure of the Néel temperature of gadolinium.

Because the specific heat was measured in the earth's magnetic field only and the susceptibility was determined in a 2-kG field, we have investigated the field dependence of $M/H$ to see if an unusual field dependence of $\chi$ could explain the discrepancy between inferred values of $T_N^{Gd}$. The magnetic moment measured in an applied field of $\sim 1$ G as a function of temperature is shown in Fig. 3. These data reveal two sharp maxima, one near 260 K in the temperature range where $\chi_\parallel$ departs most strongly from Curie-Weiss behavior, and a second near 20 K. Careful inspection of these data also shows a smaller peak in $M_\parallel(T)$ near 6.5 K. Magnetic-moment measurements as a function of field indicate (Fig. 4) that the large peak near 20 K in 1 G moves to lower temperatures with increasing field and merges with the anomaly associated with Néel ordering of gadolinium for fields greater than 5 kG. These results demonstrate why a peak in $\chi_\parallel$ was found at 9 K when measurements were performed in a 2 kG field. Therefore, for small applied fields, the most prominent features in the data of Fig. 3 are not associated with antiferromagnetic order of gadolinium but must be related to the presence of other, e.g., Gd-Cu and Cu-Cu, interactions. As we shall argue, the susceptibility behavior, not associated with Néel ordering of gadolinium, at low temperatures can be interpreted in light of understanding magnetic interactions responsible for the high-temperature peak in $M_\parallel(T)$ (Fig. 3).

Consider, now, the effect of modest fields on the magnetic susceptibility around 260 K. Data obtained at fields of 10, 30, and 50 G are shown in Fig. 5 for a crystal of $Gd_{2-x}Ca_xCuO_4$ with $x \simeq 0.1$. (This particular crystal

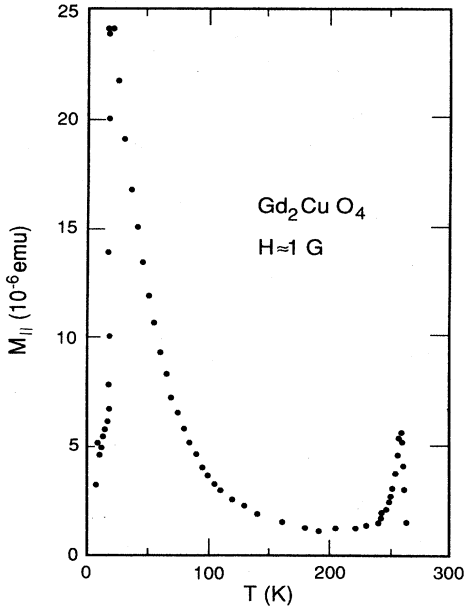


FIG. 3. Magnetic moment of a 7-mg single crystal of $Gd_2CuO_4$ measured in a field of approximately 1 G applied parallel to the $CuO_2$-plane direction. Note three anomalies at 260 K, 20 K, and 6.5 K. Above 270 K the moment becomes unmeasurably small.

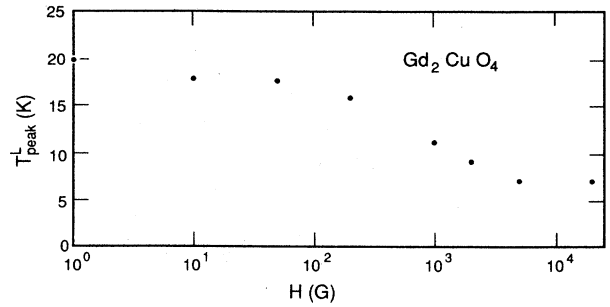


FIG. 4. Temperature at which a large peak appears in low-temperature magnetization measurements of single crystal $Gd_2CuO_4$ (see Fig. 3) as a function of magnetic field applied parallel to the tetragonal $a$-$b$ plane. For fields above 5 kG, the peak temperature saturates at 6.5 K, which is coincident with the lambda anomaly in $C/T$.

was chosen because its mass was nearly five times larger than typical $Gd_2CuO_4$ crystals and therefore provided a larger susceptibility signal. In extensive studies, we have found that calcium-containing crystals are quantitatively similar in magnetic properties to $Gd_2CuO_4$ crystals. Likewise, $Gd_2CuO_4$ crystals in which zinc or nickel has been partially substituted for copper show similar magnetic effects, only the temperature at which the peak in $\chi_\parallel$ occurs is depressed somewhat.) Inspection of Fig. 5 reveals a strong-field dependence of both the shape and magnitude of $\chi_\parallel$. Further, in the 10-G data there is hysteresis depending on whether the crystal was cooled in zero field before applying 10 G or whether it was cooled in field. Tests for hysteresis were not made at other field values. For comparison we also show data on this crystal obtained with an approximately 1-G field perpendicular to the $CuO_2$ planes. In this case there is only a very weak susceptibility anomaly near 260 K that appears because of slight misalignment of the crystal. These data together

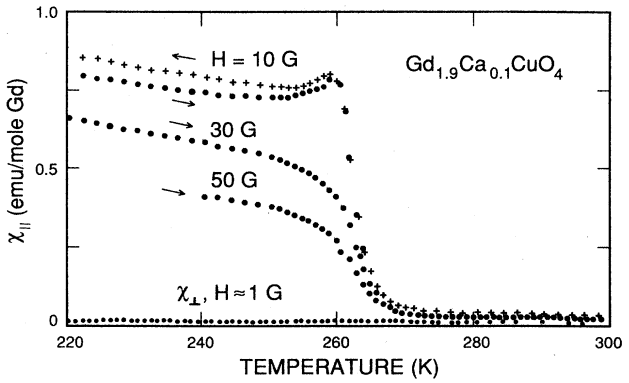


FIG. 5. Temperature dependence of the magnetic susceptibility of a single crystal of $Gd_{2-x}Ca_xCuO_4$, with $x \simeq 0.1$, for various small fields applied in the $CuO_2$-plane direction. Note the appearance of hysteresis in $\chi_\parallel$ below 260 K depending on whether the sample was zero-field cooled or cooled in a 10-G field. For comparison we also show the magnetic susceptibility of this sample measured in an approximately 1-G field perpendicular to the $CuO_2$ planes.

suggest the presence of weak ferromagnetism.

To investigate this possibility in more detail, we have determined magnetization versus field curves for a single crystal of $Gd_{2-x}Ca_2CuO_4$ ($x \simeq 0.1$ on the basis of starting composition in the flux) at temperatures around the transition temperature. Results of measurements performed with a specially designed vibrating-sample-type magnetometer, capable of excellent field resolution and accuracy ($\sim 1$ mG), are shown in Fig. 6. Above 298 K, $M_\parallel$ vs $H$ is linear, passes through the origin, and is reversible within experimental uncertainty. However, at 269 K, $M_\parallel(H)$ acquires a distinctly different character at very low fields where there is a very large $dM/dH$. Similar results are also found in $Gd_2CuO_4$ crystals. At higher fields and temperatures greater than 20 K [Fig. 7(a)], $M_\parallel$ again becomes proportional to the applied field. Analysis of the data in Fig. 7(a) where $M_\parallel$ is linear in the field gives $\mu_{\text{eff}\parallel} = 8.25 \pm 0.1 \mu_B$/Gd and $\Theta_p = -16 \pm 1$ K, values in good agreement with those reported by Saez-Puche, Norton, and Glaunsinger[16] on powder samples. This value of $\mu_{\text{eff}\parallel}$ also agrees well with that determined from measurements on a single crystal of $Gd_2CuO_4$ at a field of 20 kG.

An extrapolation of the high-field, linear portion of the curves in Fig. 7(a) shows them intersecting at a common point ($5 \pm 5$ emu/mole Gd, $-0.74 \pm 0.07$ kG), indicating the presence of an internal field $H_I = 0.74$ kG at the gadolinium site that is unchanged in the temperature range 20 to $\gtrsim 200$ K. However, for $T < 20$ K [Fig. 7(b)], $H_I$ begins to decrease and at 7 K the parallel magnetization is linear in field form 0 to 5 T (data not shown). Below $T_N^{Gd} = 6.5$ K, $dM/dH$ is constant to $\sim 1.4$ kG at which field the slope increases to a linear $M_\parallel$ vs $H$ curve that extrapolates through the origin. This unusual behavior indicates a relatively strong interplay among Gd-Gd, Gd-Cu,

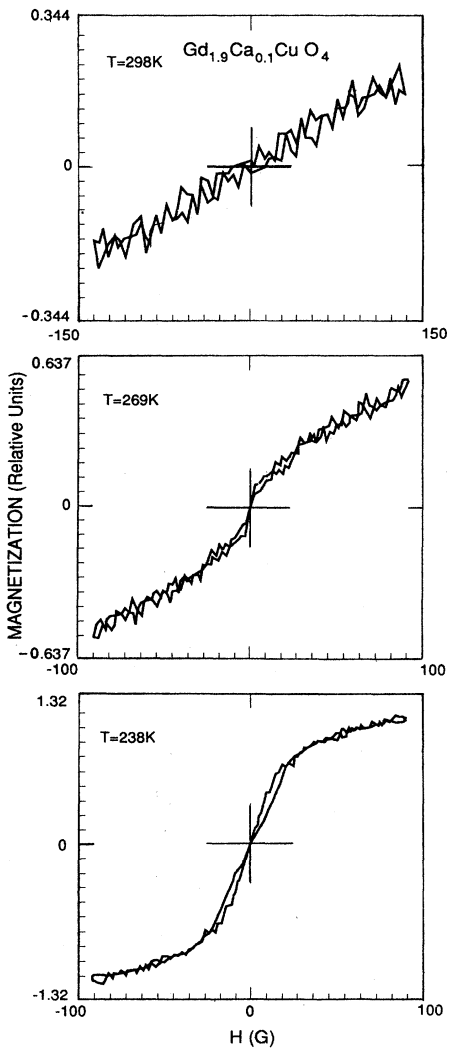


FIG. 6. Magnetic moment as a function of small fields applied parallel to the $CuO_2$ planes of $Gd_{2-x}Ca_xCuO_4$, with $x \simeq 0.1$, at various fixed temperatures. Data shown are for both increasing and decreasing fields. For temperatures at 269 K and below, a weak ferromagnetic character is clearly visible in these data (note scale changes).

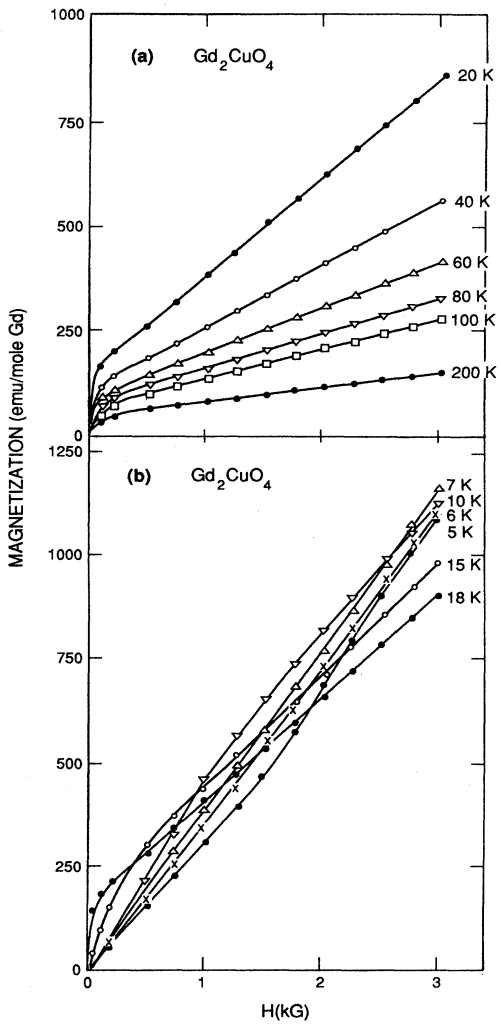


FIG. 7. Magnetization of single crystal $Gd_2CuO_4$ vs fields applied in the tetragonal $a$-$b$ plane for various fixed temperatures. An extrapolation of the linear, high-field portion of each curve in (a) intersects at a common point ($5 \pm 5$ emu/mole Gd, $-0.74 \pm 0.07$ kG). See text for discussion.

and Cu-Cu interactions.

In the absence of microscopic information, an interpretation of these results is not straightforward. However, we suggest two scenarios that could lead to the observed behaviors. A central assumption in both is that copper orders antiferromagnetically in $Gd_2CuO_4$ near 260 K, analogous to copper ordering[6] in $La_2CuO_4$ at $T_N^{Cu} \leq 328$ K. Both possibilities include additional common features that will be discussed subsequently. The primary difference between the two interpretations rests in the mechanism producing an internal field. For an internal field to be present, purely tetragonal symmetry of the copper moments must be broken. One possibility is that symmetry breaking is induced by magnetoelastic stress[23] placed on the lattice through the copper-ordering process. This mechanism is expected to lead to a very weak crystallographic distortion, consistent with the absence of a significant change in preliminary x-ray powder-diffraction patterns at temperatures well below 300 K. The internal field resulting from the lowered crystal symmetry polarizes the gadolinium moments in the $CuO_2$-plane direction, thereby enhancing the low-field susceptibility. At temperatures below 20 K, Gd-Gd interactions begin to dominate over the polarizing effect of the internal field, leading to a suppression of the weak ferromagnetic character. This interpretation does not require canting of copper moments away from antiferromagnetic alignment.

A second interpretation can be made that invokes an analogy to $GdCrO_3$.[24] In $GdCrO_3$, chromium ions order antiferromagnetically near 170 K. In addition to antiferromagnetism, a weak ferromagnetic component perpendicular to the chromium sublattice magnetization arises from canting of chromium moments away from strictly antiferromagnetic alignment. The origin of spin canting is attributed to an antisymmetric exchange interaction, as discussed by Dzyaloshinski[9] and Moriya.[10] The ordered chromium-spin system produces an internal field that is opposite in direction to the ferromagnetic component of the chromium moment. Following Cooke, Martin, and Wells[24] and referring to Fig. 7(a), we write for the measured moment $M$ of $Gd_2CuO_4$

$$M = M_{Cu} + C_{Gd}(H_I + H_a)/(T + \Theta_p) , \quad (1)$$

where $M_{Cu}$ is the canted copper moment, $C_{Gd}$ is the Curie constant of gadolinium, and $H_a$ is the applied field. When $H_a = -H_I$, $M = M_{Cu}$. The common intersection point for the curves in Fig. 7(a) then gives $M_{Cu} = 10 \pm 10$ emu/mole, Cu $= 1.8 \times 10^{-3} \pm 1.8 \times 10^{-3} \mu_B$/Cu. The sign of $M_{Cu}$ indicates that the ferromagnetic component of copper is in the direction of the applied field. [We note that the average value of $M_{Cu}$ is similar[5,6] to the field-induced weak ferromagnetic moment, $\sim 3 \times 10^{-3} \mu_B$/Cu, in $La_2CuO_4$ at low temperatures. However, the lower bound of $M_{Cu}$, $M_{Cu} = 0$, reduces Eq. (1) to the situation considered in the preceding paragraph.] Implicit in this interpretation of our data again is the assumption that the Cu-O coordination in $Gd_2CuO_4$ is no longer exactly square planar. In crystals of high symmetry, specifically inversion symmetry in the superexchange route, the antisymmetric coupling vanishes and the $D$-$M$ interaction is no longer effective.[10] In this interpretation the loss of crystal symmetry does not necessarily occur because of magnetoelastic coupling.

Certain characteristics of magnetism in $Gd_2CuO_4$ are independent of the mechanism responsible for an internal field. These include the very low-field anomaly (Fig. 3) in $M_\parallel$ at 260 K that we attribute to antiferromagnetic ordering of copper spins. The ordering transition then permits the existence of an internal field. The large anisotropy in $\chi$ and field dependence of $\chi_\parallel$ near the magnetic phase transition can be understood straightforwardly with either interpretation of the internal field. At 6.5 K, the gadolinium moments order antiferromagnetically with antiparallel moments in the $CuO_2$ planes, as inferred from mean-field-like behavior of $\chi_\parallel$ and $\chi_\perp$ at large fields. Magnetization versus field at 7 K is linear and passes through the origin [Fig. 7(b)], indicating the absence of an internal field and/or a ferromagnetic component to the copper magnetization. Low-field measurements (Fig. 3) suggest that this begins to happen near 20 K. The field dependence of $M_\parallel$ for temperatures less than 7 K, however, is not understood.

### B. $Gd_{2-x}Eu_xCuO_4$ and $Eu_{2-x}Tb_xCuO_4$

As mentioned in the Introduction, $Eu_2CuO_4$ is an anisotropic Van Vleck paramagnet.[18] This anisotropy and the temperature dependencies of $\chi_\parallel$ and $\chi_\perp$ are well described in terms of crystal-field splittings of thermally excited $J$ multiplets. However, above $\sim 100$ K, deviation from the calculated behavior suggests a magnetic contribution to the susceptibility from copper ions. In Sec. III A, the importance of copper magnetism in $Gd_2CuO_4$ was established, which leads to the speculation that similar effects may be important in $Eu_2CuO_4$. Supporting evidence is shown in Fig. 8 where we plot the position of the high-temperature peak in $M_\parallel$, measured in $\sim 1$ G, as a function of europium content in $Gd_{2-x}Eu_xCuO_4$. (We note that the low-temperature anomaly in $M_\parallel$ is not detected in samples with $x > 1$, presumably because of reduced Gd-Gd interactions produced by dilution with europium.) These data suggest that copper ordering of the sort found in $Gd_2CuO_4$ should be present in $Eu_2CuO_4$ near 245 K.

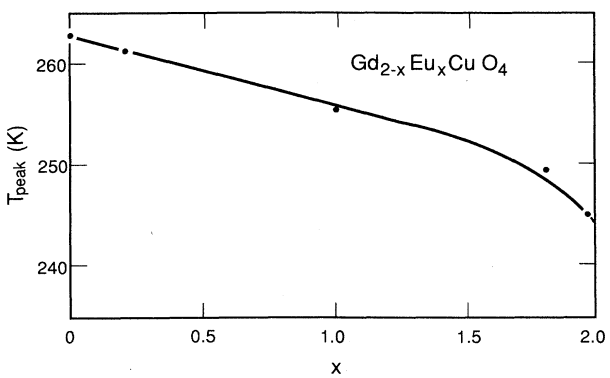


FIG. 8. Temperature at which a peak appears in magnetization measurements on a crystal of $Gd_{2-x}Eu_xCuO_4$ subjected to a field of $\sim 1$ G applied parallel to the plane direction as a function of europium content.

Because the ground state of $Eu^{3+}$ has $J=0$ and any internal field produced by copper ordering in $Eu_2CuO_4$ would couple only to thermally populated $J>0$ states of $Eu^{3+}$, a low-field anomaly is expected to be very weak, particularly if europium substitution reduces the magnitude of the internal field. We have searched for but not found an anomaly in either $\chi_\perp$ or $\chi_\parallel$ at low fields. However, measurements of $\chi_\parallel$ in an applied field of 10 G show an apparent slope change near 230 K, and data obtained at 40 kG have a very weak anomaly near 280 K of the type found in $\chi_\parallel$ of $Gd_2CuO_4$. Although these results are by no means definitive, they are highly suggestive of copper ordering in the vicinity of 245 K. The magnetic susceptibility[25] of other $R_2CuO_4$ crystals ($R$=Sm, Nd, and Pr) is also anisotropic; however, in none of these crystals is there detectable evidence for the type of copper ordering found in $Gd_2CuO_4$ and possibly $Eu_2CuO_4$, indicating that the anisotropy arises primarily from crystal-field effects. Likewise, no detectable copper ordering is found when 10% gadolinium is substituted into crystals of $Nd_{2-x}Gd_xCuO_4$ and $Sm_{2-x}Gd_xCuO_4$.

Besides diluting Gd-Gd interactions, europium substitution into $Gd_{2-x}Eu_xCuO_4$ also expands the lattice because of the larger ionic radius of europium relative to gadolinium. On the other hand, assuming Vegard's rule, substituting terbium for europium should produce an average unit-cell volume approaching that of $Gd_2CuO_4$ when $x\simeq 1$ in $Eu_{2-x}Tb_xCuO_4$. Results of magnetic-moment measurements parallel to the $CuO_2$ planes in a crystal of $Eu_{2-x}Tb_xCuO_4$, with $x$ nominally equal to 1, reveal a magnetic response very similar to that of pure $Gd_2CuO_4$. Therefore, the magnetic behavior of $Gd_2CuO_4$ is not unique to gadolinium but must be dominated by copper magnetism that depends sensitively on the average Cu-Cu and/or Cu-$R$ spacing. These observations also are consistent with the lack of magnetic anomalies in other $R_2CuO_4$ and gadolinium-doped $R_2CuO_4$ crystals since in these cases the lattice will always be expanded relative to $Gd_2CuO_4$. We suggest that the internal field is not possible in these cases because the larger $R$ ions stabilize the tetragonal crystal structure.[26]

## IV. SUMMARY

Below $\sim$270 K, an internal field of $\sim$0.74 kG and weak ferromagnetic behavior develops in the $CuO_2$-plane direction of $Gd_2CuO_4$ which is associated with antiferromagnetic order of copper spins. That such behavior can occur implies a lowering of the tetragonal crystal symmetry found at room temperature. The ferromagneticlike moment in $Gd_2CuO_4$ begins to disappear below $\sim$20 K and is not detectable at 7 K, presumably due to Gd-Gd interactions that result in antiferromagnetic order at 6.5 K of gadolinium moments parallel to the $CuO_2$ planes. Minor changes in these effects are produced upon dilute substitutions of calcium for gadolinium and nickel or zinc substitution for copper but the essential physics appears to be unaffected. With europium substitution for gadolinium, the position of the low-field high-temperature peak moves to lower temperatures. Although no definitive signature for copper-spin ordering could be found in crystals of $Eu_2CuO_4$, suggestive evidence implies magnetic ordering of copper in $Eu_2CuO_4$ near 250 K. No evidence for copper ordering is found in other $R_2CuO_4$ crystals; however, their magnetic susceptibilities are substantially anisotropic, presumably because of crystal-electric fields. Magnetic measurements on $Eu_{2-x}Tb_xCuO_4$ indicate that copper magnetism in the $R_2CuO_4$ system depends sensitively on rare-earth size.

The intriguing question remains as to why the $R_2CuO_4$ materials do not become superconducting even though they contain $CuO_2$ layers. A structural feature common to all the known high- ($T_c\geq 40$ K) temperature superconductors is an oxygen atom that is either octahedrally or pyramidally coordinated to the $CuO_2$ planes.[26] This is not the case in $R_2CuO_4$ compounds or related $CuO_2$-layered materials, such as $T_2CuO_2X_2$ where $T$=Sr or Ca and $X$=Cl or Br, which also are not superconductors.[26] This out-of-plane oxygen seems to be a necessary condition for permitting doping to a metallic conductivity with a concomitant suppression of long-range copper magnetism and the appearance of a superconducting ground state.[27] Therefore, crystal chemistry may play an important role in providing insight into the mechanism responsible for high-superconducting transition temperatures.

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[27]A possible argument is that the $d_{z^2}$ orbital, rather than the $d_{x^2}-d_{y^2}$ orbitals in cuprates with out-of-plane oxygens, are half-filled and localized. See also Ref. 26.