Magnetic ordering of Cu in Gd_2CuO_4

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Neutron-diffraction investigations have been performed to determine the magnetic ordering of Cu ions in a ^{158}Gd-enriched Gd_2CuO_4 single crystal. The Cu magnetic moments in Gd_2CuO_4 are found to order at about 285 K to an antiferromagnetic structure with the propagation vector $\mathbf{k}=(\frac{1}{2},\frac{1}{2},0)$. The antiferromagnetic structure is similar to that of La_2NiO_4. The magnetic moments of Cu ions are oriented parallel to [110].

The recent discovery of a family of superconductors $R_{2-x}A_x$CuO$_4$ (R =Pr, Nd, Sm, Eu; A =Ce, Th) has simulated numerous investigations of these compounds.[1–4] In contrast to other high-temperature cuprate superconductors, the charge carriers involved in the superconductivity of this series are electrons, rather than holes. These compounds have interesting magnetic properties including the coexistence of antiferromagnetism and superconductivity. The copper sublattice orders in the temperature range 250–280 K, whereas the rare-earth sublattice orders only at a very low temperature. Among the R_2CuO_4 family, Gd_2CuO_4 seems to be especially interesting for several reasons. Although Gd_2CuO_4 is as readily doped with CE or Th as the other members of the family, it does not, as they do, become superconducting. There have been several suggestions[5] for the absence of superconductivity in this compound, but no clear explanation has yet been given. The antiferromagnetic ordering of the CuO_2 layers is reported to be accompanied by the appearance of a weak ferromagnetic moment,[6–8] whose magnitude is inversely proportional to the temperature. Although an intrinsic weak ferromagnetic moment is forbidden[9] by the crystal symmetry $I4/mmm$ of Gd_2CuO_4, it may arise from a small local crystallographic distortion, as discussed later. We have already investigated[10] the magnetic structure of the Gd sublattice of Gd_2CuO_4 below 6.4 K, which consists of ferromagnetic (001) planes stacked antiferromagnetically along [100]. This compound provides an example of ferromagnetic (001) layers in high-temperature superconducting cuprates. Recently, Summarlin *et al.*[11] have also found ferromagnetic (001) Sm layers in Sm_2CuO_4. The magnetic ordering of Cu moments has already been investigated in Pr_2CuO_4, Nd_2CuO_4, and Sm_2CuO_4,[12–18] for which the Néel temperatures T_N are 255, 255 and 280 K, respectively. In Nd_2CuO_4 a series of magnetic phase transitions in which the Cu^{2+} spins reorient has been observed, while in Pr_2CuO_4 and Sm_2CuO_4 no changes occur in the Cu^{2+} spin structure. The determination of the magnetic structure of Gd_2CuO_4 is a more difficult problem because of the large absorption cross section of natural Gd. To determine the magnetic structure of the Cu^{2+} spins, we have therefore performed neutron-diffraction experiments on a large ^{158}Gd-enriched Gd_2CuO_4 single crystal.

Single crystals of Gd_2CuO_4 were grown by the flux method using CuO as the flux material. Neutron-diffraction experiments were performed on a large plate-shaped single crystal ($20\times10\times2$ mm^3) on the two-axis diffractometer P2AX of the Saphir reactor of the Labor für Neutronenstreuung, ETH Zürich. The crystal was mounted inside a Displex refrigerator on the diffractometer with the crystallographic [110] axis parallel to the ω axis of the diffractometer. A pyrolytic graphite (PG 002) monochromator was used to get an incident-neutron wavelength of 1.05 Å. A plutonium-aluminum alloy filter was used to supress the higher-order contamination.

Gd_2CuO_4 crystallizes in the tetragonal space group $I4/mmm$ (T' phase) and is isotypic with Nd_2CuO_4. The lattice parameters are $a=3.892$ Å and $c=11.878$ Å at room temperature. A search for magnetic reflections revealed weak magnetic intensity at $\mathbf{Q}=(\frac{1}{2},\frac{1}{2},1)$ below about 285 K. Figure 1 shows an ω scan of the $(\frac{1}{2},\frac{1}{2},1)$ magnetic peak at 47 K. The large background intensity is attributable mostly to the paramagnetic scattering of the relatively large disordered magnetic moments of the Gd sample. The intensity of this reflection decreases continuously with increasing temperature and becomes practically zero at $T_N=285\pm2$ K, apart from a small $\lambda/2$

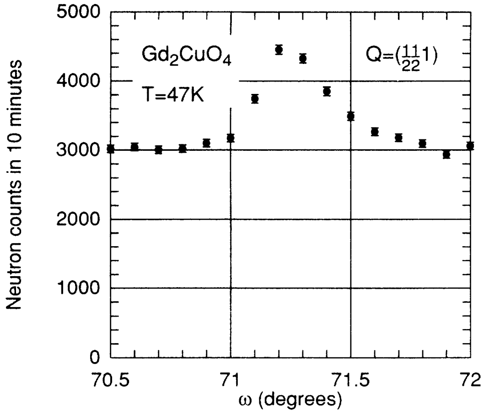

FIG. 1. Transverse scan of the magnetic Bragg peak observed in Gd_2CuO_4 at the superlattice position $(\frac{1}{2},\frac{1}{2},1)$ at 47 K. The full width at half maximum (FWHM) is $0.33°\pm0.02°$ and is resolution limited. The large background intensity is attributable mostly to the paramagnetic scattering of the relatively large disordered magnetic moments of Gd.

contribution. Figure 2 shows the temperature dependence of the sublattice magnetization obtained from the square root of the integrated intensity of the $\frac{1}{2},\frac{1}{2},1$ magnetic reflection. No temperature-dependent contribution was detected at $\mathbf{Q}=(\frac{1}{2},\frac{1}{2},0)$ although a small temperature-independent intensity at this superlattice point was found. This rather broad peak was too large to be entirely due to $\lambda/2$ contamination from the rather weak (110) nuclear reflection, and its origin has not been explained. The magnetic reflections observed are the same as those found in Pr_2CuO_4 and La_2NiO_4 and also that of the higher-temperature magnetic phase of Nd_2CuO_4. On the other hand, Sm_2CuO_4 and Nd_2CuO_4 (in the temperature range 30–75 K) have a strong magnetic reflection at $\mathbf{Q}=(\frac{1}{2},\frac{1}{2},0)$ and a very weak reflection at $\mathbf{Q}=(\frac{1}{2},\frac{1}{2},1)$. The present neutron-diffraction investigations indicate that the magnetic moments of the Cu^{2+} spins order at $T_N=285$ K with an antiferromagnetic structure with the propagation vector $\mathbf{k}=(\frac{1}{2},\frac{1}{2},0)$. The magnetic moments are parallel to [110], i.e., parallel to the propagation vector. Figure 3 shows the proposed magnetic structure of the Cu^{2+} sublattice of Gd_2CuO_4. It is to be noticed that this single-**k** collinear magnetic structure cannot be distinguished from an alternative double-**k** noncollinear structure discussed by Matsuda *et al.*[15] The noncollinear structure is derived from the collinear structure by coherent superposition of domains with propagation vectors $\mathbf{k}=(\frac{1}{2},\frac{1}{2},0)$ and $(\frac{1}{2},-\frac{1}{2},0)$.

The La_2NiO_4-type antiferromagnetic structure in Gd_2CuO_4 which develops at $T_N=285$ K remains stable down to 47 K, the lowest temperature investigated. Low-field magnetization measurements[19] indicate two further magnetic phase transitions of the Cu^{2+} sublattice at 15 and 7.8 K, respectively. Unfortunately, our present neutron-diffraction measurement using a Displex refrigerator could not be extended down to these low temperatures and the nature of the magnetic phase transitions at low temperatures remains undetermined. However, spin-orientation transitions such as those of Nd_2CuO_4 (La_2NiO_4 type to La_2CuO_4 type) are possible at these temperatures.

The main aim of the present investigation was to determine the magnetic ordering of the copper subsystem. However, R_2CuO_4 consists of both copper and rare-earth (R) magnetic sublattices which are interdependent through a Cu-R interaction. We therefore would like to discuss the effect of this Cu-R interaction in determining the magnetic properties of the R_2CuO_4 system. The magnetization measurements[5,6] show that the antiferromagnetic ordering of the CuO_2 layers in Gd_2CuO_4 below $T_N^{Cu}=285$ K is accompanied by the appearance of ferromagnetic components of moments of both Cu and Gd ions which increase with decreasing temperature. The contribution of the Gd ions to the ferromagnetic moment

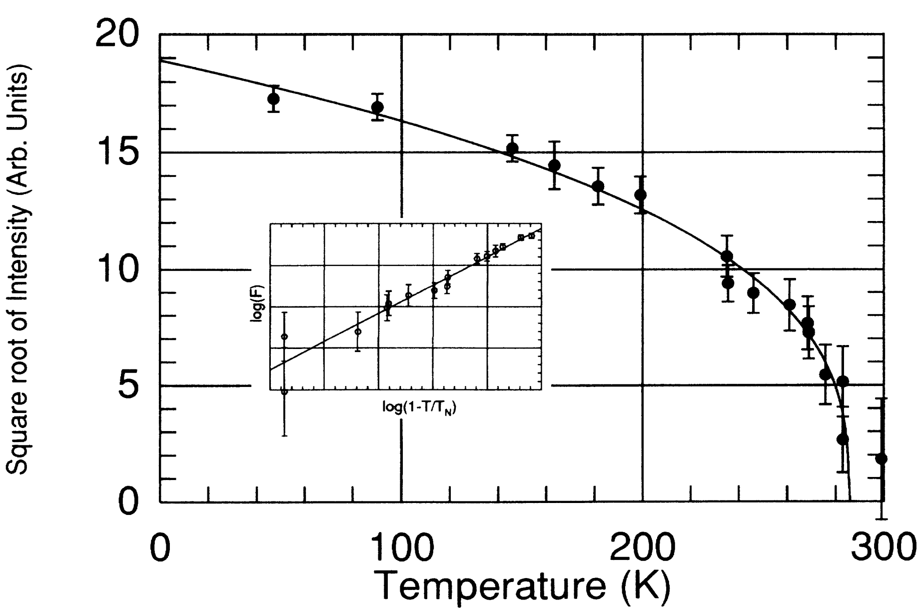

FIG. 2. Temperature variation of the sublattice magnetization of Gd_2CuO_4 obtained from the square root of the intensity of the $(\frac{1}{2},\frac{1}{2},1)$ magnetic reflection. The continuous decrease of the sublattice magnetization with increasing temperature shows that the phase transition at $T_N^{CU}=285\pm2$ K is of second order. The solid curve is a least-squares fit of the data to the equation $F=F_0(1-T/T_N)^{\beta}$, giving $F_0=19.0\ \pm0.03$ and $\beta=0.34\pm0.01$, with a goodness of fit of $\chi^2=0.492$. The inset shows a corresponding log-log plot.

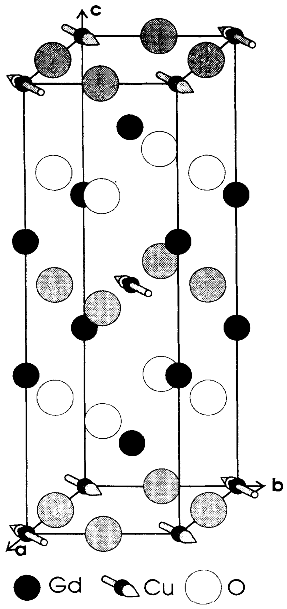

FIG. 3. Schematic representation of the magnetic structure of the copper sublattice of Gd_2CuO_4.

has been shown to be greater than that of Cu.[5] Electron-paramagnetic-resonance (EPR) measurements[5] on the Gd^{3+} ions show a line shift indicating the existence of an internal field acting in the *a-b* plane. The magnetization measurements[5,6] also show the polarization of the Gd ions by the Cu ions. To characterize the antiferromagnetic ordering of CuO_2 layers including small canting of moments, it is necessary to consider two vectors: the antiferromagnetic vector $\mathbf{l}=\mathbf{s}_1-\mathbf{s}_2$ and the ferromagnetic vector $\mathbf{m}=\mathbf{s}_1+\mathbf{s}_2$, where $\mathbf{s}_1$ and $\mathbf{s}_2$ are spins of the two neighboring sites of the CuO_2 layers. The origin of the weak ferromagnetism of Gd_2CuO_4 may be due to a small distortion of the local copper environment propagating with the same periodicity as the magnetic structure as is required to allow an antisymmetric Dzyaloshinsky-Moriya type of exchange interaction.[20,21] We consider two different possible types of Cu-R polarization in R_2CuO_4 compounds corresponding to the following two limiting cases.

(1) The Cu ions create a checkerboard field in the rare-earth planes with a translation period of $2a$. We can refer to this case as $\mathbf{l}$ polarization. This type of polarization must occur in Nd_2CuO_4 and Pr_2CuO_4 since no weak ferromagnetism has been detected. The value of the polarized magnetic moment M_R at the rare-earth site is proportional to the Cu sublattice magnetization M_{Cu} (or the antiferromagnetic vector $\mathbf{l}$) and the magnetic susceptibility χ_R of the rare-earth subsystem, leading to the equation $M_R=\alpha l\chi_R$, where α is the Cu-R interaction constant. This type of polarization cannot occur in Gd_2CuO_4 because this would lead to an M_R value of a few μ_B already at about 100 K because of the very large value of χ_R leading to large enhancement of the magnetic peak even at 100 K, which was not observed in the present neutron-diffraction experiments.

(2) The second possible type of polarization is that which would be caused by a ferromagnetic moment in the CuO_2 layers, creating a ferromagnetic field at the R site whose value and sign was the same at all R sites, thus inducing a ferromagnetic moment on the Gd subsystem. This type of Cu-R polarization can be referred as $\mathbf{m}$ polarization because in this case the observed Gd moment is not due to the canting of comparatively large rare-earth moments, but is proportional to the small value $\mathbf{m}$ of the ferromagnetism in the CuO_2 layers. Our results therefore suggest that the second type of Cu-R polarization is more likely in Gd_2CuO_4.

There is another point of interest which concerns the symmetry of the interaction between the Cu and R subsystems. Our previous neutron-diffraction investigation[10] showed that Gd layers in Gd_2CuO_4 order ferromagnetically below 6.5 K. In the present neutron-diffraction experiments, we have established that Cu^{2+} ions in CuO_2 layers of Gd_2CuO_4 order antiferromagnetically below $T_N^{Cu}=285$ K. Therefore, at low temperatures, the magnetic structures of the Cu and Gd sublattices have different symmetries. In this case the magnetic order of the Gd sublattice is independent of that of Cu, and hence there should be a specific-heat anomaly at the Gd ordering temperature. Indeed, such an anomaly[22] has been observed in Gd_2CuO_4 at about 6.4 K. A similar situation exists in Sm_2CuO_4, for which, again, ferromagnetic ordering of the Sm layers and antiferromagnetic ordering of the Cu layers occur,[11,18] and a similar specific-heat anomaly[22] has been observed at the ordering temperature of the Sm sublattice. A completely different situation exists for Nd_2CuO_4 and Pr_2CuO_4, for which the magnetic ordering of the rare-earth and copper sublattices is antiferromagnetic with compatible symmetries; it is therefore not strictly correct to speak of different ordering temperatures for the two sublattices. Both sublattices order at the same temperature, which is in the range 240–250 K. Indeed, no specific-heat anomaly, but only smeared transitions[22] have been observed in these two compounds.

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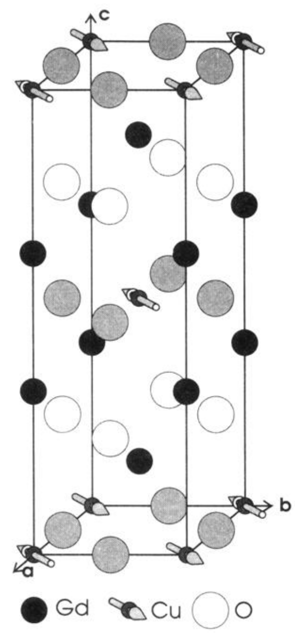

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