Magnetic ordering in Eu_2CuO_4

T. Chattopadhyay
Institut Laue-Langevin, Boîte Postale 156X, 38042 Grenoble Cedex, France

J. W. Lynn, N. Rosov, and T. E. Grigereit*
Reactor Radiation Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

S. N. Barilo and D. I. Zhigunov
Institute of Physics of Solids and Semiconductors, Belarussian Academy of Sciences, 220726 Minsk, Belarussia

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Neutron-diffraction experiments have been performed to study the magnetic ordering of Cu ions in a single crystal of Eu_2CuO_4. Magnetic reflections corresponding to the wave vector $\mathbf{k}=(\frac{1}{2},\frac{1}{2},0)$ develop below the Néel temperature $T_N=265(5)$ K, showing a long-range antiferromagnetic ordering of Cu moments in Eu_2CuO_4. The low-temperature saturated moment was determined to be $(0.4\pm0.1)\mu_B$, with the spin direction restricted to the a-b plane. Magnetic-field-dependent studies show no hysteretic behavior at intermediate temperatures, which strongly suggests that the antiferromagnetic spin structure is of the noncollinear double-$\mathbf{k}$ type previously observed in Sm_2CuO_4 and also in Nd_2CuO_4 at the intermediate temperature. We do not find any evidence of spin reorientation below the Néel temperature down to 1.4 K, the lowest temperature investigated.

I. INTRODUCTION

The magnetic properties of the high-temperature superconducting and related materials have been investigated in great detail following the suggestion that they might play an important role in the underlying superconducting mechanism.[1,2] The Cu ions in these materials carry an unpaired spin and therefore it is possible that the magnetic fluctuations are responsible for the Cooper pairing. Indeed, fluctuating two-dimensional antiferromagnetic spin correlations in CuO_2 planes have been reported to exist up to very high temperatures in these compounds and persist even in samples which are doped to become superconductors and in which the Néel temperature is reduced to zero.[3] The magnetic properties of the hole-doped superconductors $La_{2-x}Sr_xCuO_4$ and $RBa_2Cu_3O_x$ ($R=$ rare-earth element) have been investigated quite extensively. Superconductivity has also been discovered in the class of materials $R_{2-x}Ce_xCuO_4$ ($R=$Pr, Nd, Sm, or Eu) for which electrons, rather than holes, are the charge carriers.[4–7] The systematic investigation of the magnetic properties of the electron-doped superconductors could further elucidate the possible relationship between magnetism and superconductivity, and therefore has been undertaken by us.

The magnetic ordering of the parent undoped materials R_2CuO_4 has been investigated by neutron scattering for a number of rare-earth ions. The magnetic moments of the Cu ions in these materials order in the temperature range 245–285 K whereas the rare-earth moments, when they are nonzero, order at much lower temperatures (1–6 K). The magnetic moments of the Cu ions in Nd_2CuO_4, Pr_2CuO_4, Sm_2CuO_4, and Gd_2CuO_4 order in antiferromagnetic structures with wave vector $\mathbf{k}=(\frac{1}{2},\frac{1}{2},)$.[8–16] The nearest-neighbor Cu magnetic moments in the CuO_2 planes are coupled antiferromagnetically. In Nd_2CuO_4 two reorientations of the magnetic moments of the Cu sublattice have been observed at 75 and 30 K. Also, a substantial interaction exists between the Cu and Nd sublattices. No such spin reorientations have been observed in other compounds. In this work we report neutron-diffraction investigations on Eu_2CuO_4. We have observed long-range antiferromagnetic ordering of the Cu magnetic moments below the Néel temperature $T_N=265$ K. No indication of Cu spin reorientations has been observed in the temperature range (10–271 K) investigated. Our results are in agreement with the polarized neutron-diffraction investigations of Gukasov *et al.*[17] with the exception that their sample had a lower Néel temperature (250 K). This might indicate a difference of oxygen stoichiometry between the two samples. The Néel temperature of R_2CuO_4 is known to be quite sensitive to oxygen stoichiometry.

Eu_2CuO_4 crystallizes in the tetragonal space group $I4/mmm$ (T' phase), with lattice parameters $a=3.91$ Å and $c=11.93$ Å at 295 K. In contrast to other magnetic R^{3+} ions in R_2CuO_4 compounds, Eu^{3+} ions have a nonmagnetic ground state. Eu^{3+} has an electronic configuration $4f^6$, which gives rise to seven energy levels (multiplets) of which $^7F_0$ ($S=3,L=3,J=0$) is the ground state. However, the first excited level $^7F_1$ is magnetic and is only about 280 cm^{-1} above the ground state. Eu_2CuO_4 therefore should behave like a Van Vleck paramagnet as far as the Eu^{3+} ions are concerned. Among the R_2CuO_4 compounds, Pr^{3+} ions in Pr_2CuO_4 are also in a nonmagnetic singlet ground state, but this has a completely different origin, viz., crystal-field effects. Pr^{3+} ions in Pr_2CuO_4 also do not order magnetically at low temperatures. Only the Cu^{2+} ions are expected to exhibit antiferromagnetic order. The temperature varia-

tion of the magnetic susceptibilities of polycrystalline Eu_2CuO_4 and other R_2CuO_4 compounds were investigated by Puche *et al.*,[18] as early as 1983. By fitting the magnetic susceptibility to the Van Vleck-type paramagnetic susceptibility equation, Puche *et al.*[18] determined the multiplet splittings of Eu^{3+} ions in Eu_2CuO_4. The appearance of signatures of weak ferromagnetism in the microwave spectrum is considered[19] to indicate the onset of magnetic order at about 215 K.

II. EXPERIMENTAL PROCEDURES

Single crystals of Eu_2CuO_4 were grown by the flux method using CuO as the flux. A very thin plate-shaped single crystal of irregular shape of approximate size $16\times10\times0.3$ mm^3 was chosen for the present neutron-diffraction experiment. The use of a thin plate-shape single crystal was necessary because of the large absorption cross section of natural Eu. The single crystal was not pure Eu_2CuO_4 but contained 1.5 at. % Nd replacing Eu atoms. The small Nd content should not appreciably change the magnetic properties of Eu_2CuO_4 and hence the magnetic ordering investigated can be considered to be representative of pure Eu_2CuO_4. Initial neutron-diffraction investigations were performed on the BT-2 triple-axis spectrometer at the National Institute of Standards and Technology (NIST) Research Reactor. A pyrolytic graphite PG(002) monochromator was used with a PG filter to suppress higher-order wavelength contaminations. No analyzer crystal was used. The incident neutron energy was 14.8 meV and the angular collimations before and after the monochromator and after the sample were 60′−20′−80′ (full width at half-maximum), respectively. The single crystal was mounted with the $[1\bar{1}0]$ direction vertical such that the (hhl) scattering plane could be explored, and was placed in a closed-cycle helium refrigerator for the initial work in zero field down to 10 K. The field-dependent experiments were done on the BT-9 triple-axis spectrometer at NIST with incident neutron energy 14.7 meV, 40′−48′−49′ collimation, and the same crystal orientation. A vertical field superconducting magnet system was used to perform isothermal field scans to 7 T for temperature down to 1.4 K.

III. RESULTS AND DISCUSSIONS

Figure 1 shows a transverse scan (sample rotation) of the 004 nuclear Bragg peak at 10 K and a Gaussian fit of the data points. The full width at half-maximum is 0.56°, consistent with the instrumental resolution and the mosaic spread. The peak is somewhat asymmetric and contains perhaps a second small peak on the higher angle side. In fact a much better fit is obtained by assuming two Gaussian peaks. Below the Néel temperature a number of magnetic peaks were found at superstructure positions corresponding to the wave vector $\mathbf{k}=(\frac{1}{2},\frac{1}{2},0)$. Figure 2 shows transverse scans of the $\frac{1}{2}\frac{1}{2}0$ and $\frac{1}{2}\frac{1}{2}1$ magnetic Bragg peaks at 10 K. The relative intensities of these two magnetic Bragg peaks already suggest that the magnetic structure is of the Sm_2CuO_4 type. We measured eight nuclear and 11 magnetic Bragg peaks at 10 K,

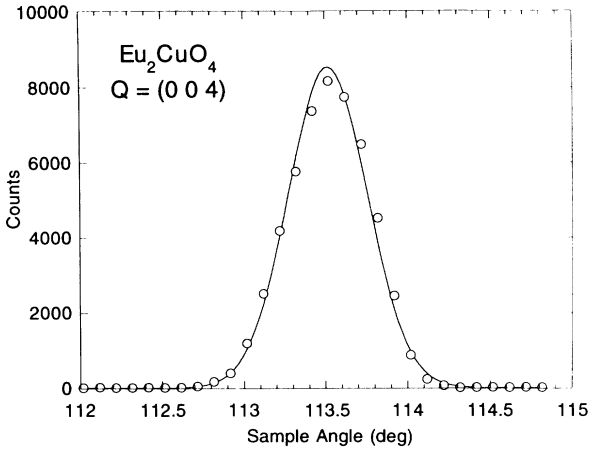

FIG. 1. Transverse scan (sample rotation) of the 004 nuclear Bragg peak. The solid line is a Gaussian fit. The full width at half-maximum is 0.56°.

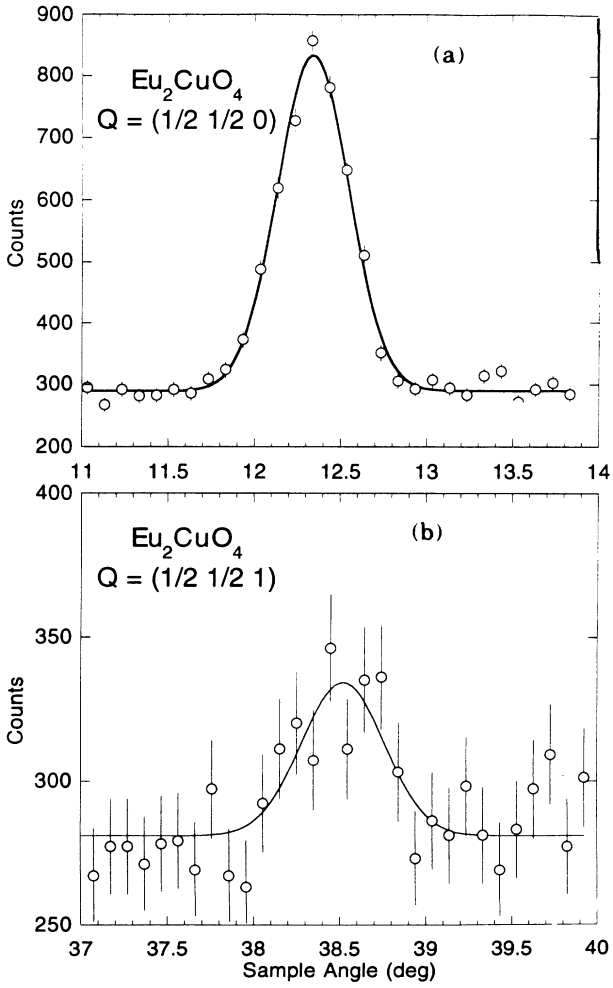

FIG. 2. Transverse scans of the (a) $\frac{1}{2}\frac{1}{2}0$ and (b) $\frac{1}{2}\frac{1}{2}1$ magnetic Bragg peaks observed at 10 K. The full widths at half-maximum are 0.48° and 0.58°, respectively.

which were corrected for absorption. The magnetic structure factors were put on an absolute scale by using the intensities of the nuclear Bragg peaks assuming the Nd_2CuO_4-type crystal structure of Eu_2CuO_4. The scattering lengths of Eu, Nd, Cu, and O were taken from Ref. 20. A least-squares refinement of the ordered magnetic moment of the Cu ions was performed using the structure factors of the magnetic reflections, and this gave a magnetic moment of $(0.4\pm0.1)\mu_B$. The magnetic form factor of Cu^{2+} ions was taken from Ref. 21. The value of the magnetic moment obtained agrees well with the value of Cu^{2+} magnetic moments obtained in other R_2CuO_4 compounds. Two possible models of the magnetic structure of Eu_2CuO_4 are shown schematically in Fig. 3. Figure 3(a) shows the collinear single-**k** magnetic structure and Fig. 3(b) shows the noncollinear double-**k** type formed by the coherent superposition of magnetic domains corresponding to the wave vectors $\mathbf{k}_1=(\frac{1}{2},\frac{1}{2},0)$ and $\mathbf{k}_2=(-\frac{1}{2},\frac{1}{2},0)$. The collinear structure has two possible domains, with the magnetic moments pointing along either the [110] or the $[1\bar{1}0]$ direction, the latter of which has to rotate to align itself perpendicular to the field, i.e., toward the [110] direction, since the exchange is greater than the anisotropy. When the field is removed the magnetic moments will remain in their rotated orientation as it is energetically equivalent to the original domain configuration. This would be a way to produce a single domain sample and hysteretic behavior should be observed. In the single-domain noncollinear structure the magnetic moments originally along [100] and [010] will also rotate toward [110] as the field is increased, approaching one domain of the collinear structure as the rotation angle $\alpha\rightarrow\pi/4$. However, this effect is reversible as the field is decreased, since the noncollinear structure must be energetically preferable at zero field in order for it to have formed in the first place. For observation of the $\frac{1}{2}\frac{1}{2}0$ magnetic reflection, the neutron momentum transfer **Q** lies parallel to [110] and so any magnetic domains or rotated configurations in this direction will be parallel to **Q**. These spins **S** will not contribute to the observed intensity since the magnetic scattering cross section is proportional to $\hat{\mathbf{Q}}\times(\hat{\mathbf{S}}\times\hat{\mathbf{Q}})$.[22] We therefore monitored the peak intensity of the $\frac{1}{2}\frac{1}{2}0$ magnetic reflection on varying the field along [110] at a variety of temperatures, one of which (at $T=150$ K) is shown in Fig. 4. The apparent reversibility between increasing and decreasing field implies that the magnetic structure of Eu_2CuO_4 is noncollinear, as has recently been found to be the case for Nd_2CuO_4 (Ref. 23) and Sm_2CuO_4 (Ref. 24).

We have measured the temperature variation of the integrated intensity of the $\frac{1}{2}\frac{1}{2}0$ magnetic reflection, which is shown in Fig. 5. Although the data points do not follow a smooth curve, any drastic spin reorientation effects as observed in Nd_2CuO_4 can be ruled out down to 1.4 K, the lowest temperature investigated. If a spin reorientation transition similar to those observed Nd_4CuO_4 at 75 and 30 K occurred, then the intensity of the $\frac{1}{2}\frac{1}{2}0$ magnetic reflection would abruptly drop to zero. We recall that the intensity of the magnetic peak is proportional to the square of the sublattice magnetization, which is the order parameter in this case. The interesting feature of the temperature vibration of the intensity of the magnetic peak is that it does not saturate at lower temperature. This has been observed in other Cu-O systems, and is thought to originate from the two-dimensional quantum fluctuations present in these highly anisotropic antiferromagnets.[25] We have fitted the intensity data to the equation

$$I=I_0\left[1-\frac{T}{T_N}\right]^{2\beta}, \tag{1}$$

and have varied I_0, T_N, and β. The results of this fit are given in the inset of Fig. 5. The Néel temperature is determined to be 271 ± 1 K and $\beta=0.33\pm0.02$. However, more detailed measurements of the peak intensities near T_N indicate the intensity vanishes above 265 K. Hence we have reported the Néel temperature as 265 ± 5 K. We

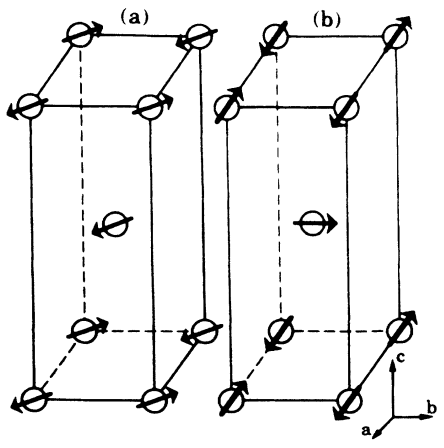

FIG. 3. Schematic representation of the two possible types of magnetic structure of Eu_2CuO_4: (a) collinear single-**k** type and (b) noncollinear double-**k** type. Only the copper atoms are shown.

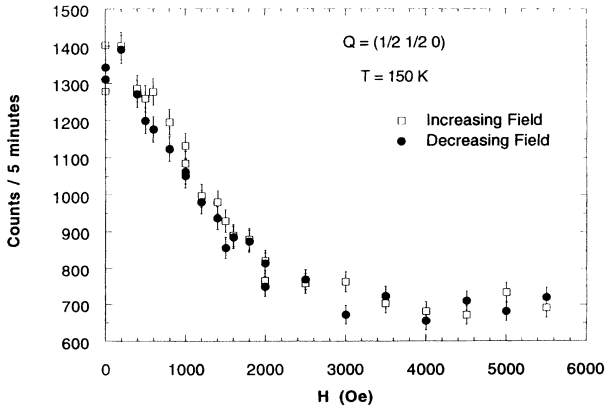

FIG. 4. The peak intensity at $t=150$ K of the $\frac{1}{2}\frac{1}{2}0$ magnetic reflection as a function of the applied magnetic field parallel to the $[1\bar{1}0]$ direction. The lack of hysteresis strongly suggests that the magnetic structure of Eu_2CuO_4 is noncollinear double-**k** type.

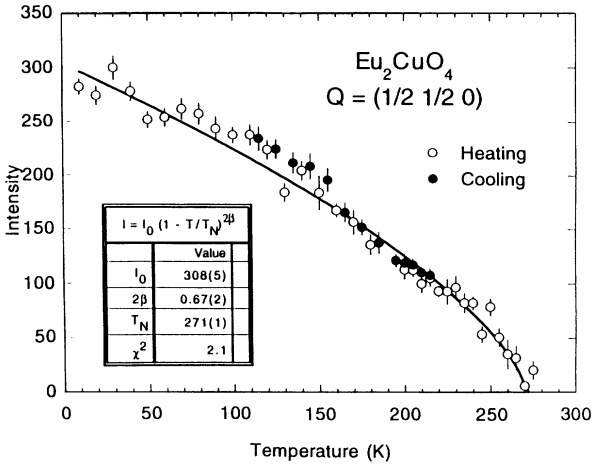

FIG. 5. Temperature variation of the integrated intensity of the $cf12\frac{1}{2}0$ magnetic reflection. The continuous curve is power-law fit. The results of the fit are shown in the inset.

notice, however, that the intensity does not quite follow a smooth curve and at about 150 K there exists a small anomaly in intensity. This anomaly is reproduced in the integrated intensity measured while heating and also while cooling the sample. The present intensity measurements do not establish the nature of this anomaly, but it is consistent with an anomaly observed in susceptibility at about the same temperature by Babinskii *et al.*[26] These authors have interpreted the anomaly to be due to the antiferromagnetic ordering of the copper ions at about $T=165$ K. They conclude that the contribution to the magnetic susceptibility at higher temperature is due to short-range magnetic ordering of the Cu ions. Our neutron-diffraction results establish this interpretation to be wrong. The width of the $\frac{1}{2}\frac{1}{2}0$ magnetic reflection does not change appreciably in the temperature range 10–271 K as indicated by the presence of diffuse magnetic scattering.

Our neutron-diffraction experiments establish that the Cu^{2+} ions in Eu_2CuO_4 orders at $T_N=265$ K to an antiferromagnetic structure which does not undergo any further phase transition down to 1.4 K . The reversible behavior of the $\frac{1}{2}\frac{1}{2}0$ peak intensity as a function of applied field along $[1\bar{1}0]$ strongly suggests that the magnetic structure of the Cu sublattice is noncollinear. It has been suggested that the magnetic structure of the whole family of R_2CuO_4 compounds, which are the parent materials for electron-doped superconductors, is likely the noncollinear double-**k** type.[23] If this is so, interesting theoretical consequences follow. It is known that[27] for a Heisenberg interaction and single-ion anisotropy only a single-**k** structure is stabilized. Higher-order exchange interactions like biquadratic exchange interactions must therefore be invoked in order to stabilize a double-**k** structure. Although it is certainly possible that the magnetic structures of the entire family of R_2CuO_4 compounds, which are the parent materials for electron-doped superconductors, is noncollinear double-**k** type, the actual magnetic structures of Pr_2CuO_4 and Gd_2CuO_4 remain to be checked by applying magnetic field or uniaxial stress along both [110] and [100] directions.

*Also at Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, MD 20742.

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