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Magnetoelectric effect in Gd_2CuO_4

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The magnetoelectric (ME) effect is observed in the tetragonal antiferromagnet Gd_2CuO_4 in magnetic fields up to 7 T. This is an observation of the ME effect in the class of tetragonal crystals with the general formula R_2CuO_4 (R =rare earth), which are parent compounds for high-T_c superconductivity. The ME effect is shown to exist only below the ordering temperature of the rare-earth magnetic subsystem at $T_N(Gd)= 6.5$ K in accordance with results based on a symmetry analysis. The field and temperature dependence of the effect confirm the magnetic structure revealed recently in this compound.

The magnetic properties of the $R_{2-x}Ce_xCuO_4$ (R=rare-earth ion) compounds, which belong to the family of recently discovered high-T_c superconductors with electron-type conductivity,[1] have been intensively investigated during the last few years, following the suggestion that the antiferromagnetism of the CuO_2 planes plays an important role in the superconductivity of these compounds.[2] In fact, the rare-earth subsystem is also of importance in the magnetism of these materials. Unlike in R-Ba-Cu-O compounds where the substitution of trivalent rare earths had little effect on their superconductivity, in electron-doped $R_{2-x}Ce_xCuO_4$ compounds the rare-earth subsystem affects strongly both magnetic and superconducting properties. According to Refs. 3–6, the superconductivity of $R_{2-x}Ce_xCuO_4$ is observed only for compounds containing light rare-earth ions (R =Nd, Sm, Eu, and Pr), and no superconductivity is observed in compounds with heavier rare-earth ions, starting from Gd. Also investigations of the upper critical field H_{c2} of $Sm_{1.85}Ce_{0.15}CuO_4$ give indications for an influence of the magnetic ordering of the rare-earth ions on the superconducting state.[7,8] It is therefore of main concern to elucidate the role of the rare-earth ions in forming the electronic properties of $R_{2-x}Ce_xCuO_4$ and of the parent compound R_2CuO_4.

Gd_2CuO_4 occupies a unique place in the family of electron doped high-T_c superconducting materials due to a number of unusual magnetic properties.[3–6] In addition, a ferromagnetic ordering of the rare-earth spins within the (a,b) layers, which are parallel to the CuO_2 layers, has been detected in Gd_2CuO_4 by means of neutron scattering.[9] Considering the possible correlation between nonsuperconducting and magnetic properties of Gd_2CuO_4 we looked for an independent method of studying the magnetic properties of the Gd spin system in Gd_2CuO_4. Therefore, we have undertaken a systematic search for the magnetoelectric effect[10] in this material, the existence of which is directly related to the symmetry properties of the magnetic structure in Gd_2CuO_4. In this paper we present experimental results of the magnetic field induced electric polarization in Gd_2CuO_4, which, to our knowledge, magnetoelectric effect has not been observed before in any compound with the general formula R_2CuO_4.

The magnetic structure of Gd_2CuO_4 includes two magnetic subsystems (copper and rare earth) with essentially different magnetic properties. The Cu spins become antiferromagnetically (AF) ordered just below room temperature, the corresponding magnetic structure being of two-dimensional (2D) type. The intrinsic ordering of the rare-earth magnetic subsystem is of 3D character. The specific spin arrangement in each magnetic subsystem is known from neutron experiments.[9–11] The antiferromagnetic ordering of the copper spins in Gd_2CuO_4 leads to a doubling of the crystal unit cell, preserving the space inversion symmetry of the system. In contrast, the rare-earth spin arrangement of ferromagnetic planes being antiferromagnetically coupled breaks the space in-

version but does not affect the translation symmetry. As a consequence, the two magnetic subsystems below the Néel temperature $T_N(\mathrm{Gd})$ manifest themselves rather independently both in static and resonance experiments.

Knowing the actual magnetic structure of Gd_2CuO_4 below $T_N(\mathrm{Gd})$, the magnetic symmetry of this compound belongs to the orthorhombic magnetic class $mm'm$ which allows a linear magnetoelectric (ME) effect with two independent nonzero components of the ME tensor

$$\alpha_{ac} \neq \alpha_{ca} , \qquad \text{where} \qquad \alpha_{ij} = \frac{\partial P_i}{\partial H_j} , \tag{1}$$

$\mathbf{P}$ being the electric polarization in an applied magnetic field $\mathbf{H}$. The indices denote the orthorhombic axes $\mathbf{a} \parallel [1,1,0]$, $\mathbf{b} \parallel [1,-1,0]$, $\mathbf{c} \parallel [0,0,1]$, imposed by the antiferromagnetic spin arrangement of the crystal. Above $T_N(\mathrm{Gd})$ the magnetic symmetry of the crystal is incompatible with a ME effect because of the presence of space inversion in the magnetic symmetry group. Another member of this family in which we have also found a ME effect of the same symmetry is Sm_2CuO_4, but this will not be discussed here.

As we have said before, it is the rare-earth subsystem which is responsible for the ME effect in this compound and neither Cu-Cu nor Cu-R spin–spin interactions affects substantially the character of the effect. Because of this one can only consider the rare-earth magnetic sublattice and ignore the copper sublattice when constructing the phenomenological description of the ME effect in Gd_2CuO_4. The small and, perhaps, undetectable influence of the copper subsystem on the ME effect will be briefly discussed later.

Following a phenomenological approach the state of the rare-earth magnetic subsystem is specified by the two vectors $\mathbf{L} = \mathbf{S}_1 - \mathbf{S}_2$ and $\mathbf{M} = \mathbf{S}_1 + \mathbf{S}_2$, where $\mathbf{S}_1$ and $\mathbf{S}_2$ denote the sublattice magnetizations of the rare-earth. The entire phenomenological free energy W can be represented as a sum of three contributions:

$$W(\mathbf{S},\mathbf{P}) = W_m(\mathbf{S}) + W_{\mathrm{me}}(\mathbf{S},\mathbf{P}) + W_e(\mathbf{P}) , \tag{2}$$

where $W_m(\mathbf{S})$ is a purely magnetic contribution to the total free energy; $W_{\mathrm{me}}(\mathbf{S},\mathbf{P})$ is a ME contribution, and $W_e(\mathbf{P})$ is a purely electric one.

The first term on the right-hand side of Eq. (2) determines the ground state of the magnetic system and whether or not a ME effect is to appear. In the absence of a magnetic field the AF ground state of $W_m(\mathbf{S})$ is specified by $\mathbf{L} \parallel \mathbf{a} \parallel [110]$ in correspondence with Ref. 9.

An external magnetic field distorts this magnetic structure. At $H > H_{\mathrm{sf}}$ (H_{sf} is the critical field of the spin–flip phase transition) $\mathbf{L}$ becomes zero and the AF spin arrangement of the rare earth breaks down completely. Obviously, H_{sf} becomes zero as $T \to T_N(\mathrm{Gd})$.[9] Irrespective of the magnetic field direction, the magnetic symmetry group at $H > H_{\mathrm{sf}}$ contains the space inversion $1'$ and thus rules out the existence of an electric polarization. At $H < H_{\mathrm{sf}}$ the existence of the ME effect results from $W_{\mathrm{me}}(\mathbf{S},\mathbf{P})$ in Eq. (2). Taking into account the specific symmetry of the system one can easily obtain the following expression for $W_{\mathrm{me}}(\mathbf{S},\mathbf{P})$:

$$\begin{aligned} W_{\mathrm{me}}(\mathbf{S},\mathbf{P}) = {} & \Lambda P_z \mathbf{ML} + \lambda_z P_z M_z L_z \\ & + \lambda_1 (L_z M_x P_x + L_z M_y P_y) \\ & + \lambda (M_z L_x P_x + M_z L_y P_y) . \end{aligned} \tag{3}$$

The first contribution to $W_{\mathrm{me}}(\mathbf{S},\mathbf{P})$ is of exchange nature and the corresponding contribution to the ME effect is associated with the violation of the equality of the sublattice magnetization magnitudes. The remaining terms on the right-hand side of (3) are of relativistic origin, i.e., they result from the relativistic part of the spin–spin and spin–lattice coupling.

The expressions for $W_m(\mathbf{S})$ and $W_e(\mathbf{P})$ have the standard form for tetragonal crystals and we shall not write them here explicitly.

To calculate the electric polarization $\mathbf{P}$ as a function of the applied magnetic field $\mathbf{H}$, and conversely, the magnetic polarization $\mathbf{M}$ as a function of the applied electric field $\mathbf{E}$ we have to minimize $W(\mathbf{S},\mathbf{P})$ with respect to the sublattice magnetizations and electric polarization under a fixed external field.

In the case of a small external magnetic field, for which Eq. (1) can be applied, it can easily be seen that only the first and the last term on the right-hand side of Eq. (3) contribute to the linear ME effect. Using the minimization procedure described above, the following expression for the nonzero components of the ME tensor α can be obtained,

$$\alpha_{ca} = \frac{\partial P_c}{\partial H_a} = 2S\Lambda\chi_{\parallel}\kappa_{zz}, \quad \alpha_{ac} = \frac{\partial P_a}{\partial H_c} = S\lambda\chi_{\perp}\kappa_{xx} , \tag{4}$$

where $\chi_{\parallel}$ and $\chi_{\perp}$ denote the magnetic susceptibilities along and perpendicular to the vector $\mathbf{L}$, respectively; κ_{zz}, κ_{xx} denote the corresponding components of the electric susceptibility tensor. Obviously, the longitudinal susceptibility $\chi_{\parallel}$ decreases sharply as the temperature tends to zero. The two nonzero components α_{ca} and α_{ac} of the tensor of the linear ME effect have an exchange and a relativistic origin, respectively.

To obtain the electric polarization $\mathbf{P}$ as a function of an arbitrarily strong magnetic field we use a combination of molecular field approximation and pure symmetry arguments. The only thing we shall mention here is that for arbitrarily strong in–plane magnetic fields none but the z projection of the induced electric polarization can appear because of the conservation of the symmetry operation $2_z \times 1'$ of the magnetic point group (provided that all the sublattice magnetizations are perpendicular to the c direction). When $\mathbf{H} \parallel \mathbf{c}$ none but the a projection of the induced electric polarization will appear as is the case for the linear ME effect described in Eq. (4).

The single crystal of the dimension $5 \times 1.5 \times 1\ \mathrm{mm}^3$ used in these experiments has been grown by the flux method using CuO as flux material.[12] Electrodes were deposited with silver paint and contacted. The crystal was fixed to a sample holder of a conventional helium flow cryostat and placed in a resistive Bitter magnet.

The measurements were performed in static magnetic fields up to 20 T using a dc measuring technique, where the current between electrodes was measured and inte-

grated, leaving the sample at zero electric field. The integrated value was scaled and displayed as an electric charge. Two different magnetic field orientations were tested: parallel to the c axis ($\mathbf{H} \parallel z$) and perpendicular to the c axis ($\mathbf{H} \parallel x$). The polarization in both cases was measured perpendicular to the magnetic field, corresponding to the off–diagonal magnetoelectric tensor components α_{ac} and α_{ca}.

In Fig. 1(a) the field dependence of P_x is shown in magnetic fields $\mathbf{H} \parallel z$ at $T = 5$ K [this component of magnetic susceptibility coincides with $\chi_\perp$ from Eq. (4)]. The necessary condition for observing the effect was a precedent ME annealing using crossed magnetic and electric fields in accordance with the magnetic symmetry of the system. The curves in Fig. 1(b) were measured without precedent annealing. For this orientation, where $\mathbf{H}$ is perpendicular to $\mathbf{L}$, only the last term from Eq. (3) can produce a nonzero electric polarization $\mathbf{P} \parallel \mathbf{a}$, provided that the magnetic field is lower than H_{sf} and, consequently, $\mathbf{L} \neq \mathbf{0}$. In the low field region the corresponding linear ME effect is described by the component α_{ac} from Eq. (4). The dashed line in Fig. 1(a) is a result of the calculation of $P_x(H_z)$ on the basis of the mean-field expression $M_z L_x \sim H\sqrt{1 - H^2/H_{sf}^2}$, assuming $\mathbf{S}_1^2 = \mathbf{S}_2^2 = \text{const}$.

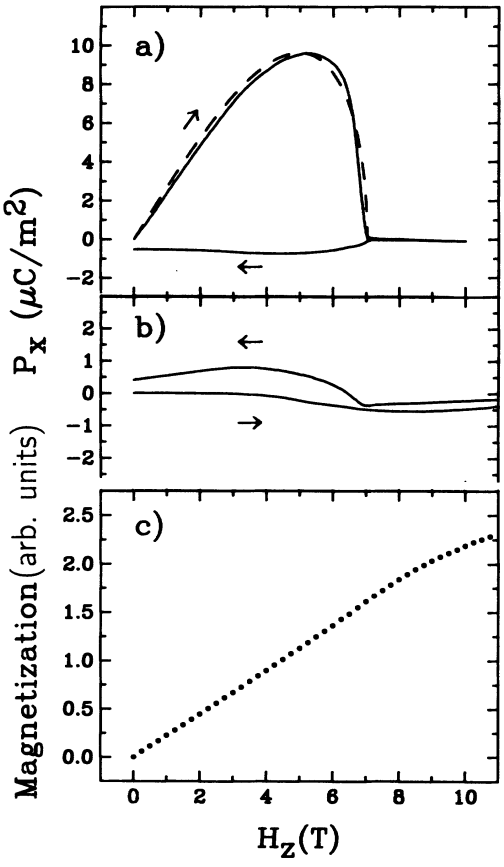

FIG. 1. The electric polarization P_x of Gd_2CuO_4 vs magnetic field $\mathbf{H} \parallel z$ at T=5 K after different ME annealing procedures: (a) E_x=500 V/cm and H_z=5 T, (b) no annealing. The dashed line in (a) is the result of a phenomenological calculation. (c) Magnetization of Gd_2CuO_4 vs magnetic field $\mathbf{H} \parallel z$ at $T = 5$ K.

As it is seen from Fig. 1 the ME signal disappears reaching the spin–flip field and also disappears rising the temperature above T_N(Gd), as expected from symmetry consideration. The ME signal does not reappear while reentering into the Gd-antiferromagnetic phase, that suggests a restoration of the antiferromagnetic domain structure suppressed previously by the annealing procedure. In Fig. 1(c) we show for comparison a measurement of the magnetization of the same sample for $\mathbf{H} \parallel z$ at the same temperature. Here due to thermal fluctuations the spin–flip field is no longer clearly observable.[9] The much better resolution of the spin–flip transition in the ME measurements allows a detailed measurement of the $H_{sf}(T)$–phase diagram.

The experimental results for $\mathbf{H} \parallel x$ are shown in Fig. 2. Again the necessary condition for observing the effect was a precedent ME annealing. Figure 2(b) shows curves with no preceding ME annealing, in contrast to Fig. 2(a) where the curves were obtained after an annealing with crossed magnetic and electric fields. For this orientation of the magnetic field a continuous spin reorientation takes place in Gd_2CuO_4 as the rare-earth spins rotate in the basal plane by an angle of 45° until the vector $\mathbf{L}$ reaches the direction y.[9] The end of the rotation corresponds to a magnetic field of 0.5 T at 5 K. In this case, according to Eq. (3), the ME effect with $P_c(H_x)$ exists until the end of the spin rotation, and is associated with the violation of the equality of the sublattice magnetization magnitudes (a pure exchange ME effect). The rather sharp anomaly at 0.5 T in Fig. 2(a) corresponds to the end of the continuous spin reorientation. The inset in Fig. 2(a) shows this region enlarged. The signal reappears while reenter-

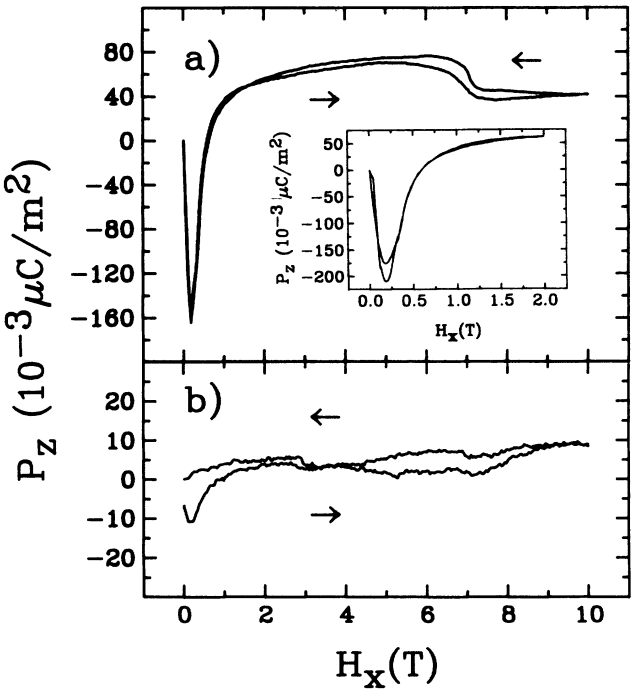

FIG. 2. The electric polarization P_z of Gd_2CuO_4 vs magnetic field $\mathbf{H} \parallel x$ at T=5 K after different ME annealing procedures: (a) E_z=1000 V/cm and H_x=0.25 T, (b) no annealing. The inset in (a) shows the low field data.

ing into the AF phase in contrast to the case for $\mathbf{H} \parallel z$ but does disappear rising the temperature above $T_N(\mathrm{Gd})$. An annealing procedure with oppositely oriented electric fields does lead to a change of sign of the ME signal.

The fact that a small ME effect for $\mathbf{H} \parallel x$ is still noticeable up to the spin flip field of H_{sf} might be attributed to the influence of the copper magnetic subsystem. Indeed, our symmetry analysis shows that the inclusion of the copper subsystem into the consideration does not change the symmetry of the linear ME effect tensor in Eq. (1) but does change the form of the magnetic contribution $W_m(\mathbf{S})$ to the total free energy. As a result, the orientation of the vector $\mathbf{L}$ does not coincide strictly with the y axis even at $H > 0.5$ T. For magnetic fields above the spin–flip phase transition the ME effect completely disappears, as it must, irrespective of a possible influence of the copper magnetic subsystem according to Eq. (3).

In summary, the observed ME effect in Gd_2CuO_4 exists only in coincidence with the antiferromagnetic spin arrangement within the rare-earth magnetic subsystem. When the intrinsic ordering of the rare-earth sublattices is broken by heating above $T_N(\mathrm{Gd})$ or applying a magnetic field above H_{sf}, the induced electric polarization of the system disappears irrespective of the external magnetic field direction. All the experimental results obtained are in full agreement with theoretical predictions made in the framework of a symmetry analysis and based on the magnetic structure of Gd_2CuO_4 proposed in Refs. 9 and 11. In this respect the existence of rare-earth ferromagnetic layers is the crucial feature for the occurrence of the ME effect in Gd_2CuO_4.

The presented experimental results resolve the magnetic properties of the rare-earth subsystem much better than reported results for magnetization measurements of Gd_2CuO_4.[9] Due to the fact that the ME effect of Gd_2CuO_4 is directly linked to the rare-earth subsystem, this technique offers a unique possibility to study the properties of this magnetic subsystem independently from the Cu magnetic subsystem. This information can be of importance in the investigation of the question whether the absence of superconductivity in Gd_2CuO_4, when doped with Ce, is related to the presence of ferromagnetic Gd layers. Studying the ME effect in other compounds of the family R_2CuO_4 (e.g., Sm) will yield further valuable information to understand the interaction between superconductivity and antiferromagnetic ordering of rare-earth ions in $R_{2-x}Ce_xCuO_4$.

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