Magnetoelectric effects in Gd_2CuO_4

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It has been observed that an electric field induces a magnetic moment in the antiferromagnet Gd_2CuO_4 at temperatures below 6.5 K. The plot of $M_x(E_z)$ is linear, while there is a substantial hysteresis in $M_x(E_y)$. Contributions to the static and dynamic magnetic susceptibility proportional to E, E^2, and EH have been observed. The electric field causes a linear shift of the antiferromagnetic resonance.

I. INTRODUCTION

The antiferromagnet Gd_2CuO_4 has an unusual magnetic structure. The spins of the copper ions become ordered in an antiferromagnetic manner at a temperature $T_N(\mathrm{Cu})=280$ K, with the directions of the magnetic moments in the basal planes of the tetragonal crystal lattice alternating in a checkerboard manner. At $T_N(\mathrm{Gd})=6.5$ K the gadolinium ions undergo an antiferromagnetic ordering. Ferromagnetic layers form. An alternation of the directions of the magnetic moments of these layers occurs as we move along the [001] direction. The copper and gadolinium magnetic subsystems thus differ in symmetry. Below $T_N(\mathrm{Gd})$, the magnetic structure becomes invariant under inversion centers of the crystal lattice, and a linear magnetoelectric effect can occur.[1] Wiegelmann *et al.*[1] observed the onset of an electric polarization of Gd_2CuO_4 when a magnetic field was applied parallel to the [100] axis (the x axis) or the [001] axis (the z axis). A symmetry analysis carried out in Ref. 1 yielded the following terms in the thermodynamic potential which are responsible for the magnetoelectric effect:

$$\Phi_{ME}=\lambda M_z(P_xL_x+P_yL_y)+\Lambda P_z\mathbf{M}\cdot\mathbf{L}. \qquad (1)$$

Here **P**, **M**, and **L** are respectively the dielectric polarization, the magnetization, and the antiferromagnetism vector.

In this letter we report observation of a linear magnetoelectric effect in Gd_2CuO_4 on the basis of the onset of a magnetic moment induced by an electric field. We then describe measurements of the shift of the antiferromagnetic resonance caused by the electric field, and we describe the observation of magnetoelectric effects of higher orders.

II. EXPERIMENTAL RESULTS

A. Static magnetic properties in an electric field

The magnetization change $\delta\mathbf{M}$ caused by the electric field **E** was measured with a SQUID magnetometer[2] at 1.2 K. The test sample, with dimensions of $1\times1.5\times1$ mm, was

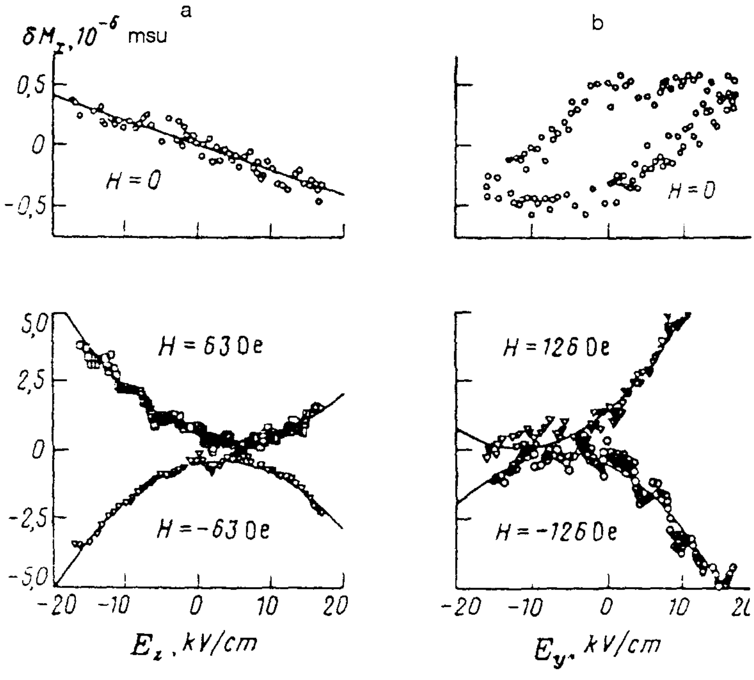

FIG. 1. a—Change in the x component of the magnetization as a function of the electric field along z. b—change in the x component of the magnetization as a function of the electric field along y (a counterclockwise circumvention of the hysteresis loop).

cemented between plane electrodes with conducting cement. The pickup coil detected the appearance of $\delta\mathbf{M}$ in the direction perpendicular to **E** and parallel to the external magnetic field **H**. The applied field E was varied from 0 to ± 20 kV/cm, and H from 0 to ± 200 Oe.

The experimental results show that the field E_z causes a linear change δM_x in a zero magnetic field (Fig. 1a). Also shown in this figure is the change in the magnetization as a function of the electric field in an external field H_x. The experimental results in a magnetic field and without such a field are described by the formula $\delta\mathbf{M}\ (\mathbf{E}, \mathbf{H}) = \alpha\mathbf{E} + \mathbf{H}(\beta\mathbf{E} + \gamma\mathbf{E}^2)$. We have thus observed a linear effect of the electric field on the magnetic moment and linear and quadratic effects on the magnetic susceptibility χ. In a field $E_z = 10$ kV/cm the change in the susceptibility due to the linear part of the dependence is 3×10^{-8}, and that due to the quadratic part is 1×10^{-8} msu.

An electric field E_y also leads to a change in the magnetization M_x; the plot of $\delta M_x(E_y)$ in a zero field has a substantial hysteresis (Fig. 1b). This result reveals a magnetoelectric coupling between M_x and E_y which is not described by (1). It is evidence of a spontaneous magnetic moment. The effect of an electric field on the susceptibility in this orientation is shown in the upper part of Fig. 1b.

B. High-frequency properties in an electric field

To measure the microwave magnetic susceptibility χ_ω and to observe the antiferromagnetic resonance (AFMR) at a frequency of 36 GHz in the electric field, we placed an isolated copper plate in the spectrometer cavity. A voltage was applied to this plate with respect to the cavity walls. An electric field **E** arose in the sample; this field was oriented perpendicular to the external magnetic field **H**. The microwave magnetic field **h** at the sample was perpendicular to both **H** and **E**. Resonant absorption in the sample leads to a decrease in the microwave power (U) transmitted through the cavity. The AFMR line at the given frequency is plotted as $U(H)$. The small shift of the AFMR line and the small changes in χ_ω upon the application of the electric field were measured by a modulation method. The field **E** was varied at $F = 1.95$ kHz. When the field **E** acts on χ_ω, the microwave power transmitted through the cavity acquires a variable component oscillating at this frequency. The amplitude of this component, δU, was determined with the help of a phase-sensitivity amplifier.

An AFMR in Gd_2CuO_4 was studied in detail in Ref. 3. We studied the effect of an electric field on its lower branch. If the magnetic field of the AFMR depends on the applied electric field, the amplitude of the response to the electric field, δU, should depend on **H** as the derivative dU/dH.

The magnetic field was directed in the xz plane at an angle of 45° from the x axis. The electric field was along the y axis. This orientation made it possible to use the interaction of components M_z and E_y described by the first term in (1) and also to observe the AFMR at the working frequency of the cavity, 36 GHz (in the orientation $\mathbf{H} \parallel z$, the AFMR field at this frequency is too strong). Figure 2 shows U, dU/dH, and δU versus the magnetic field. We see that the curve of $\delta U(H)$ is proportional to the derivative dU/dH near the AFMR line. This result is evidence that the field of the AFMR is shifted by the electric field.

To produce a single-domain antiferromagnetic sample we used cooling in fields[4] **E** and **H**. The direction of the vector **L** along the easy axis was determined by the sign of $\mathbf{E} \cdot \mathbf{H}$ during the crossing of the Néel temperature. In a sample not subjected to this annealing, the linear magnetoelectric effect is offset to a significant extent because of the opposite sign of the effect in the domains differing in the sign of **L**. Figure 2 shows data obtained on a sample cooled in fields $E_y = 3$ kV/cm and $H = 54$ kOe from a temperatrure of 7.5 K to 1.2 K, along with results obtained after heating to 7.5 K and cooling at the same value of H, but with the inverted field **E**.

From the value of δU we determine the shift of the AFMR field. It turns out to be 0.02 Oe at an electric field of 3 kV/cm. The effect of the electric field in our experiment is equivalent to the effect of an effective magnetic field whose direction is determined by the directions of the vectors **E** and **L**. This effective field can be added to or subtracted from the external magnetic field, as is indicated by the change in the sign of δU after the magnetic field is reversed.

In our experiments this shift of the AFMR field for a sample cooled in a vanishing field turned out to be lower by a factor of 20 than that for cooling in the specified fields. In this case this shift was masked by the noise.

In fields $H < 20$ kOe we observe a change in U due to a dependence of the magnetic

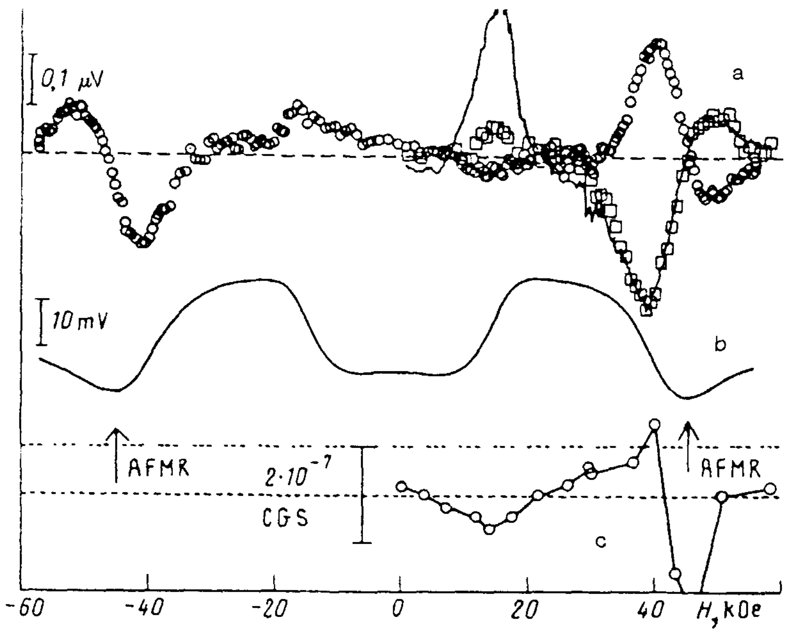

FIG. 2. a: Plot of $\delta U(H)$ for $E=3$ eV/cm. Circles—After annealing in fields **E** and **H**; squares—after annealing with an inverted field **E**. The solid line shows a quantity proportional to dU/dH. b: Plot of the microwave signal U versus the magnetic field. c: Change in the real part of the microwave susceptibility due to an electric field of 3 kV/cm versus the magnetic field. The horizontal dotted lines are zero levels: the upper one for δU and dU/dH, the central one for U, and the lower one for $\delta\chi'_\omega$.

susceptibility χ_ω on the magnetic field.[3] As a result of the change in χ_ω, the cavity becomes detuned, and the transmitted signal changes. In these fields, δU is quite large (Fig. 2), indicating that the electric field is affecting the susceptibility χ_ω measured with respect to a weak field **h**.

The experiments show that at $H<20$ kOe a substantial fraction of the quantity δU changes sign when the magnetic field is reversed. We thus are seeing an increment in the magnetic susceptibility which is odd in $\mathbf{E}\cdot\mathbf{H}$. Figure 2 also shows a plot of $\delta\chi'(H)$.

III. DISCUSSION

The observation of a magnetic dipole moment δM_x induced by an electric field E_z means that we can estimate the magnetoelectric modulus $\alpha_{zx}=dM_x/dE_z\sim 10^{-8}$ msu. This quantity is too low by more than an order of magnitude, since in our static experiments the sample was not subjected to a magnetoelectric reflection, and it was not in a single domain. Under the assumption that the shift of the AFMR is by an amount on the order of $H_{\rm eff}=-d\Phi_{MB}/dM_z$, we find the estimate $\alpha_{xz}=dM_z/dE_x\sim\chi\Lambda L\sim 10^{-5}$ msu.

These changes in the magnetic susceptibility, odd in $\mathbf{E}\cdot\mathbf{H}$, can be explained by the potential terms in Eq. (1). At $\mathbf{H}\neq 0$, the electric field leads to a change in the orientation of the vector **L** according to (1). This change should lead in turn to a change in the susceptibility, because of the known difference between the susceptibilities of an antiferromagnet in the directions parallel to and perpendicular to the vector **L**.

A weak ferromagnetism due to terms bilinear in **L** and **M** is forbidden for tetragonal crystals such as Gd_2CuO_4. However, a weak ferromagnetic moment has been observed here[5] at temperatures below T_N(Cu) and above T_N(Gd). This result has been explained by arguing that there are slight distortions of the tetragonal lattice.[6] We observe a spontaneous ferromagnetic moment $\sim 10^{-9}$ of the sublattice magnetization at a temperature well below T_N(Gd). A magnetoelectric interaction corresponding to the term of the potential $E_x M_y$ observed in our experiments (Fig. 1b) is also impossible within the framework of the original $I4mmm$ crystallographic group. We note that the symmetry allows or forbids a spontaneous electric polarization at the same time as the susceptibility proportional to **E**, which is observed in our experiments. The spontaneous magnetic moment thus probably also generates a spontaneous electric polarization through the magnetoelectric interaction. In this case, Gd_2CuO_4 is, like nickel iodide–boracite, a weakly ferromagnetic, magnetoelectric ferroelectric.[7]

In conclusion, here are the terms of the thermodynamic potential in terms of the variables **E** and **H** which this potential should contain in order to describe the magnetoelectric effects observed by us:

$$\Phi_{ME} = \kappa_i H_i + \alpha_{ik} E_i H_k + \gamma_{ik} E_i H_k^2 + \beta_{ikl} E_i H_k H_l^2 + \tau_{ik} E_i^2 H_k^2 . \tag{2}$$

In our experiments we observed nonzero coefficients

$$\kappa_x, \alpha_{zx}, \alpha_{xy}, \alpha_{xz}, \gamma_{zx}, \gamma_{xz}, \beta_{xzx}, \beta_{zxy}, \tau_{zx}, \tau_{xy}, \tau_{xz} .$$

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