Magnetoelectric effects in antiferromagnetic Gd_2CuO_4

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Induction of a magnetic moment by an electric field has been discovered in antiferromagnetic Gd_2CuO_4 at a temperature below 6.5 K. The dependence of $M_x(E_z)$ is linear, while $M_x(E_y)$ exhibits significant hysteresis. Contributions to the static and dynamic magnetic susceptibility which are proportional to E, E^2, and EH have been observed. Linear displacement of the antiferromagnetic resonance by an electric field has been discovered. The antiferromagnetic resonance spectrum in an electric field and the variation of the magnetic susceptibility caused by rotation of the antiferromagnetism vector in an electric field have been calculated using a two-sublattice model of the antiferromagnetically ordered rare-earth sublattice. The experimental results are qualitatively consistent with this model. The presence of structural distortions or contributions of higher-order terms to the thermodynamic potential has been postulated to account for some of the results. © *1995 American Institute of Physics.*

1. INTRODUCTION

Antiferromagnetic Gd_2CuO_4 has an unusual magnetic structure. The spins of the copper ions undergo antiferromagnetic ordering at the temperature $T_N(\mathrm{Cu})=280$ K, so that in the basal planes of the tetragonal crystal lattice the directions of the magnetic moments alternate in a checkerboard pattern.[1] Antiferromagnetic ordering of the gadolinium ions occurs at $T_N(\mathrm{Gd})=6.5$ K. At this point the spins of the gadolinium ions form ferromagnetic layers, which are magnetized parallel to the basal planes,[2] and the copper and gadolinium subsystems now have different magnetic symmetries. The magnetic structure of the crystal becomes noninvariant with respect to the inversion centers, allowing the existence of a linear magnetoelectric effect. A magnetoelectric effect was detected in Gd_2CuO_4 in Ref. 3 from the appearance of electric polarization under the action of a magnetic field [the so-called $(ME)_H$ effect]. Applying symmetry analysis to a two-sublattice model of the gadolinium sublattice with neglect of the interaction with the copper sublattice, Wiegelmann *et al.*[3] obtained the following terms of the thermodynamic potential, which correspond to the magnetoelectric effect in the magnetic structure of Gd_2CuO_4:

$$\frac{1}{(4M_0)^2}\tilde{\Phi}_{ME}=\lambda M_z(P_x L_x+P_y L_y)+\Lambda P_z\mathbf{M}\cdot\mathbf{L}+\lambda_1(M_xP_xL_z+M_yP_yL_z)+\lambda_zP_zM_zL_z. \quad (1)$$

Here the x axis points in the [100] direction, and the z axis points in the [001] direction of the tetragonal crystal lattice; $2M_0$ is the maximal magnetization of one of the two gadolinium sublattices; $\mathbf{P}$ is the electric polarization, and $\mathbf{M}$ and $\mathbf{L}$ are the magnetization and the antiferromagnetism vector in units of $4M_0$. In a magnetic unit cell there are four gadolinium ions, two ions from each of the two sublattices in the model under consideration.

In the magnetic structure of Gd_2CuO_4 we have $L_z=0$, and the two magnetoelectric moduli α_{zx} and α_{xz} are nonzero. They are related to the magnetoelectric constants λ and Λ in the following manner:

$$\alpha_{zx}=4M_0\frac{dM_x}{dE_z}=\frac{dP_z}{dH_x}=4M_0L\Lambda\chi_{\|}k_{zz}, \quad (2)$$

$$\alpha_{xz}=4M_0\frac{dM_z}{dE_x}=\frac{dP_x}{dH_z}=4M_0L\lambda\chi_{\perp}k_{xx}. \quad (3)$$

Here $\mathbf{E}$ and $\mathbf{H}$ are the electric and magnetic field strengths; k_{zz} and k_{xx} are the corresponding dielectric susceptibilities, and $\chi_{\|}$ and $\chi_{\perp}$ are the magnetic susceptibilities in the directions parallel and perpendicular to $\mathbf{L}$, respectively.

The modulus α_{zx} is proportional to the product $\chi_{\|}L$ and should, therefore, vanish when $T=0$ and $T=T_N(\mathrm{Gd})$. The other magnetoelectric modulus should increase with decreasing temperature as $\chi_{\perp}L$.

This paper describes the results of observations of the linear magnetoelectric effect, i.e., induction of a magnetic moment by an electric field [the $(ME)_E$ effect], and the linear antiferromagnetic Stark effect, i.e., displacement of the antiferromagnetic resonance spectrum by an electric field, as well as the results of observations of the influence of the electric field on the magnetic susceptibility. A brief report on these experiments was published in Ref. 4.

We observed a quadratic antiferromagnetic Stark effect and a quadratic influence of the electric field on the magnetic susceptibility in antiferromagnetic Nd_2CuO_4 (Ref. 5), but a linear magnetoelectric effect was not detected in that case.

2. EXPERIMENTAL METHODS

The change in the magnetization $\delta\mathbf{M}$ under the action of an electric field $\mathbf{E}$ was measured using a SQUID

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magnetometer[6] at 1.2 K. A sample measuring $1\times1.5\times1$ mm^3 was glued between two flat electrodes by a conducting adhesive. The pickup coil detected the appearance of $\delta\mathbf{M}$ in the direction perpendicular to **E**.

A magnetic resonance spectrometer with a reentrant cavity and no modulation of the magnetic field was used to measure the microwave magnetic susceptibility χ^{ω} and to observe antiferromagnetic resonance in an electric field. The working frequency of the spectrometer was $f=35.7$ GHz, and the Q factor of the rectangular cavity, which measured $7.2\times3.4\times20$ mm^3 and was tuned to the TE_{014} mode, was about 1000. Within the cavity at a distance of 1 mm from a wide wall there was an insulated copper plate, which did not alter the Q factor of the cavity significantly. A voltage relative to the walls of the cavity was supplied to the plate. The sample was placed between the plate and the wide wall of the cavity at the antinode of the microwave magnetic field. When the voltage was turned on, an electric field **E**, which was perpendicular to the external magnetic field **H**, appeared in the sample. The microwave field **h** in the sample was perpendicular to both **H** and **E**. In these experiments the sample measured $1.5\times0.7\times0.9$ mm^3.

Resonant absorption in the sample results in a decrease in the microwave power U which passes through the cavity. The change in the real part of the susceptibility of the sample causes a displacement of the natural frequency of the cavity, which also causes a change in the response signal. When the magnetic field is swept, the antiferromagnetic resonance line can be recorded as $U(H)$, the microwave generator should be tuned to the resonant frequency of the cavity, and the displacement of the natural frequency of the cavity during the recording process must be small; otherwise, the line will be distorted significantly. Distortion of the line shape can be avoided either by selecting sufficiently small sample dimensions or by placing the sample in the cavity at a site where the microwave field does not have the peak value.

Small shifts of the antiferromagnetic resonance line and small changes in χ^{ω} under the action of an electric field were measured using a modulation technique with a variable electric field having a frequency $F=1.95$ kHz. When the field **E** acts on χ^{ω}, a variable component of the microwave power passing through the cavity appears and oscillates with the same frequency. The amplitude δU of this component was determined using a phase-sensitive amplifier.

If the resonant magnetic field depends on the applied electric field, δU will depend on H as the derivative dU/dH.

To ensure the sensitivity of the spectrometry to the small changes in the high-frequency susceptibility that occur in the electric field, a sufficiently large sample was selected. The plot of $U(H)$ then has the form of the distorted antiferromagnetic resonance line recorded under the conditions of saturation of the cavity response to large changes in the susceptibility.

The loss maximum on the temperature dependence of the imaginary part of the microwave susceptibility for our sample corresponds with good accuracy to the temperature $T_N(\mathrm{Gd})=6.5$ K, and the resonant field coincides with that observed for the same frequency in Refs. 2 and 7.

3. EXPERIMENTAL RESULTS

3.1. Static magnetic properties in an electric field

We studied the influence of an electric field on the static magnetization for two relative orientations of the electric field and the measured component of the magnetic moment.

The experiment showed that the field E_z causes linear variation of δM_x in the absence of a magnetic field (Fig. 1a). The figure also shows the variation of the magnetization as a function of the electric field in an external magnetic field $H_x=63$ Oe. Similar measurements were performed for other field values up to 200 Oe. The results of these experiments are described by the equation

$$\delta M_x(H)=\alpha E_z+H_x(\beta E_z+\gamma E_z^2).$$

Thus, we discover a linear effect of the electric field on the magnetic moment, as well as linear and quadratic effects on the magnetic susceptibility χ_{xx}. In a field $E_z=10$ kV/cm the change in the susceptibility due to the linear part of the dependence is equal to 3×10^{-8}, and the change due to the quadratic part equals 10^{-8} emu.

The electric field E_y also causes variation of the magnetization M_x, and the plot of $\delta M_x(E_y)$ in a zero magnetic field exhibits considerable hysteresis (Fig. 1b). This finding reveals magnetoelectric coupling between M_x and E_y, which is not described by the expression (1), and attests to the presence of a spontaneous magnetic moment. An electric field also influences the susceptibility in this orientation, as is seen from Fig. 1b.

3.2. High-frequency magnetic properties in an electric field E_y when $H_z=H_x$ and $H_y=0$

The antiferromagnetic resonance in Gd_2CuO_4 was thoroughly described and experimentally studied in Refs. 2 and 7. We studied the influence of an electric field on its lower branch, which has a 25.2 GHz gap at 1.8 K.

The magnetic field in the xz plane was directed at a 45° angle to the x axis, and the electric field was directed parallel to the y axis. Such a configuration makes it possible to utilize the interaction between M_z and E_y described by the first term in (1) and, at the same time, to observe antiferromagnetic resonance at the working frequency of the cavity. When **H** is oriented parallel to z, the resonant field at that frequency becomes excessively large. Figure 2 presents plots of the dependence of U, dU/dH, and δU on the magnetic field. It is seen that $\delta U(H)$ is proportional to the derivative dU/dH near the antiferromagnetic resonance line, attesting to displacement of the resonant field by the electric field.

A single-domain antiferromagnetic sample was obtained by mean of cooling in the fields **E** and **H** (Ref. 8). The direction of **L** parallel to the easy axis (the bisector of the coordinate angle in the xy plane) is determined in this case by the sign of the product $\mathbf{E}\cdot\mathbf{H}$ when the Néel temperature is passed . In a sample which has not undergone such magnetoelectric annealing, the linear magnetoelectric effect is compensated to a considerable extent by the opposite sign of the effect in the domains differing with respect to the sign of **L**. Figure 2 presents the data obtained for a sample cooled in the fields $E_y=3$ kV/cm and $H=54$ kOe from 7.5 to 1.2 K, as

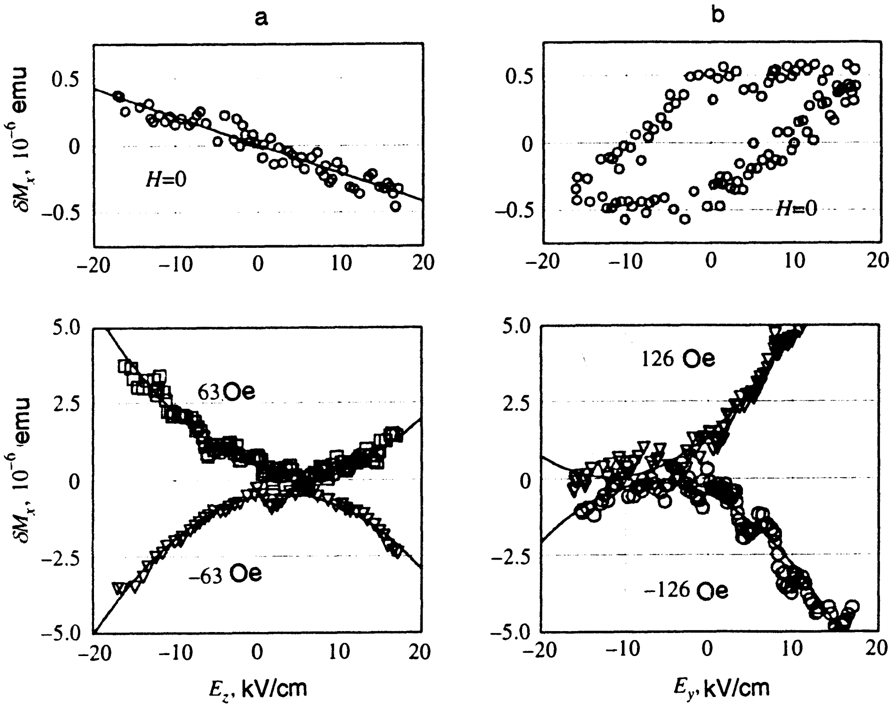

FIG. 1. a) Variation of the x component of the magnetization as a function of the electric field parallel to the z axis. b) Variation of the x component of the magnetization as a function of the electric field parallel to the y axis.

well as the results obtained after heating to 7.5 K and cooling with the same value of H, but with an inverted field **E**. The dependence of $\delta U(H)$ obtained after cooling in zero fields is also shown.

Magnetoelectric annealing with an inverted magnetic field also results in a change in the sign of δU over the entire range of variation of the magnetic field. Thus, it is seen that the signs of both fields used during the annealing influence the sign of the shift of the resonant value of the magnetic field.

We used the amplitude of δU to determine the magnitude of the shift of the resonant field δH, which amounts to 0.1 Oe in a 3 kV/cm electric field. In Fig. 3 it is seen from the data presented that the same electric field increases the absolute value of the antiferromagnetic resonance magnetic field in the region of positive magnetic fields and decreases it

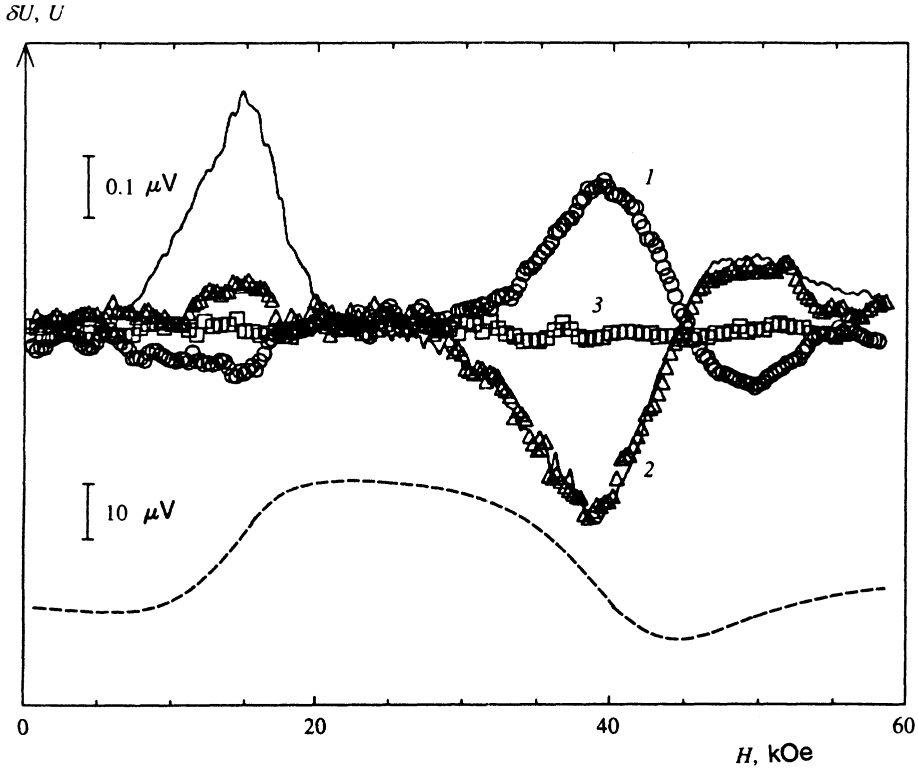

FIG. 2. Dependence of $\delta U(H)$: *1*) after annealing in the fields **E** and **H**; *2*) after annealing with an inverted field **E**; *3*) after annealing in zero fields. Solid line – $\alpha = 1.12 \times 10^{-4}$ dU/dH; dashed line – plot of $U(H)$; $E_y = 3$ kV/cm, $H_x = H_z$, tuning of the microwave generator at $H = 23$ kOe.

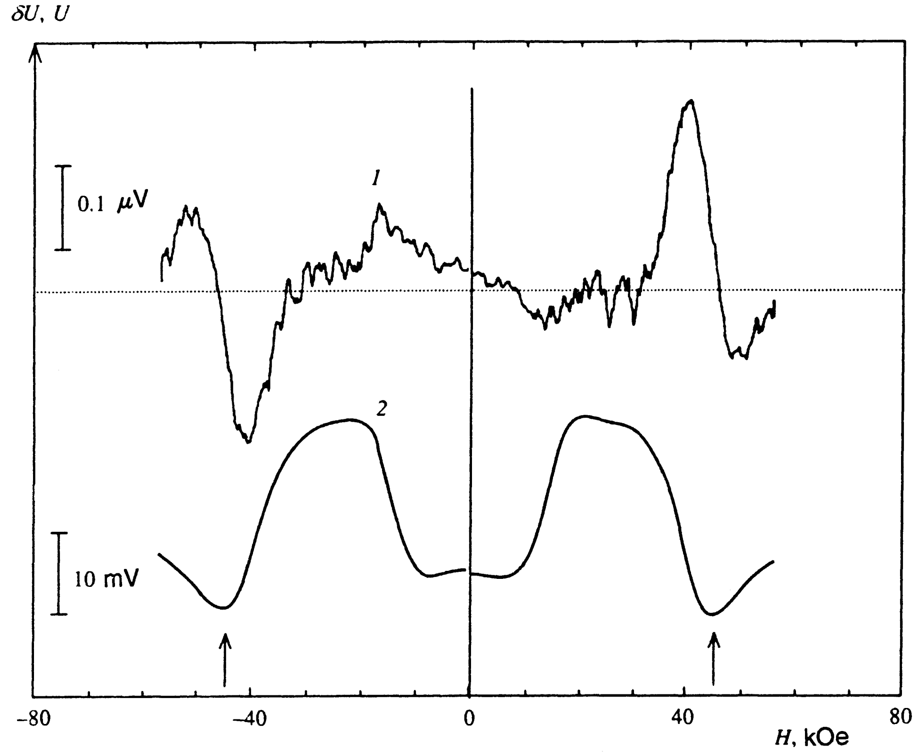

FIG. 3. Dependence of $\delta U(H)$ for $E=3$ kV/cm in an experiment with reversal of the polarity of the magnetic field (curve *1*) and dependence of the microwave signal U on the magnetic field (curve *2*). The resonant fields are indicated by arrows.

in the case of an inverted magnetic field. This influence of the electric field in our experiment can be interpreted as a manifestation of an effective magnetic field, whose vector is located in the xz plane. This effective field can be added to the external magnetic field or subtracted from it, as evidenced by the change in the sign of δU after reversal of the poles of the magnetic field (see Fig. 3). The sign of the effective field changes when the sign of **E** or the sign of **L** is reversed. The influence of the sign of the antiferromagnetism vector **L** can be traced by observing the change in the sign of δU after magnetoelectric annealing with reversal of the polarity of either **E** or **H**.

When the temperature is raised, the displacement of the antiferromagnetic resonance under the influence of the electric field decreases. The temperature dependence of δH is presented in Fig. 4.

Figures 2 and 3 reveal significant variation of the microwave signal U with H in the range of fields $|H|<20$ kOe. It is associated with the variation of the magnetic susceptibility χ_{xx} during spin flipping in the range $0<H_x<9$ kOe (Ref. 7). When the susceptibility varies, detuning of the cavity occurs, and the response signal varies. An appreciable value is also observed for δU in these fields (see Fig. 2), attesting to the influence of the electric field on the susceptibility χ^{ω} with respect to the weak field **h** perpendicular to **E** and **H**.

To determine the magnitude of the changes $\delta\chi'$ and $\delta\chi''$ in the real and imaginary parts of the susceptibility χ^{ω} separately, we measured δU at various detunings $\Delta=f-f_0$. Here f and f_0 are, respectively, the frequency of the microwave generator and the natural frequency of the cavity. Then these parameters can be determined using the relations derived for TE modes in a rectangular cavity:

$$\delta\chi'=\frac{\delta U(\Delta_{-1/2})-\delta U(\Delta_{+1/2})}{U}\frac{V}{16\pi Q v}, \tag{4}$$

$$\delta\chi''=-\frac{\delta U(0)}{U}\frac{V}{8\pi Q v}, \tag{5}$$

Here Q is the quality factor of the cavity; $\Delta_{\pm 1/2}=\pm f/2Q$ is the positive or negative value of the detuning corresponding to "half-maximum" of the resonance curve of the cavity; v and V are, respectively, the volumes of the sample and the cavity. The resonance curve of the cavity and the plot of $\delta U(\Delta)$ obtained in a 14 kOe magnetic field at 1.2 K are shown in Fig. 5. Similar curves were obtained for other values of the magnetic field, and they were used to construct the plots of $\delta\chi'_{aa}(H)$ and $\delta\chi''_{aa}(H)$ presented in Fig. 6 according to Eqs. (4) and (5). Here the direction of the a axis coincides with the bisector of the coordinate angle in the xz plane, and the microwave field **H** was aligned in this direction in this experiment.

The experiment shows that in fields weaker than 20 kOe the response δU to the electric field contains a real part, which changes sign when the poles of the magnetic field are reversed. Thus, a correction to the magnetic susceptibility that is odd with respect to **E**·**H** is discovered.

3.3. High-frequency magnetic properties in an electric field E_z when $H=H_x$

We did not discover any linear displacement of the antiferromagnetic resonance for this configuration of the static fields. A small quadratic shift of the antiferromagnetic resonance, which is detected by observing the component of the signal U at the frequency $2F$, can be observed. The magni-

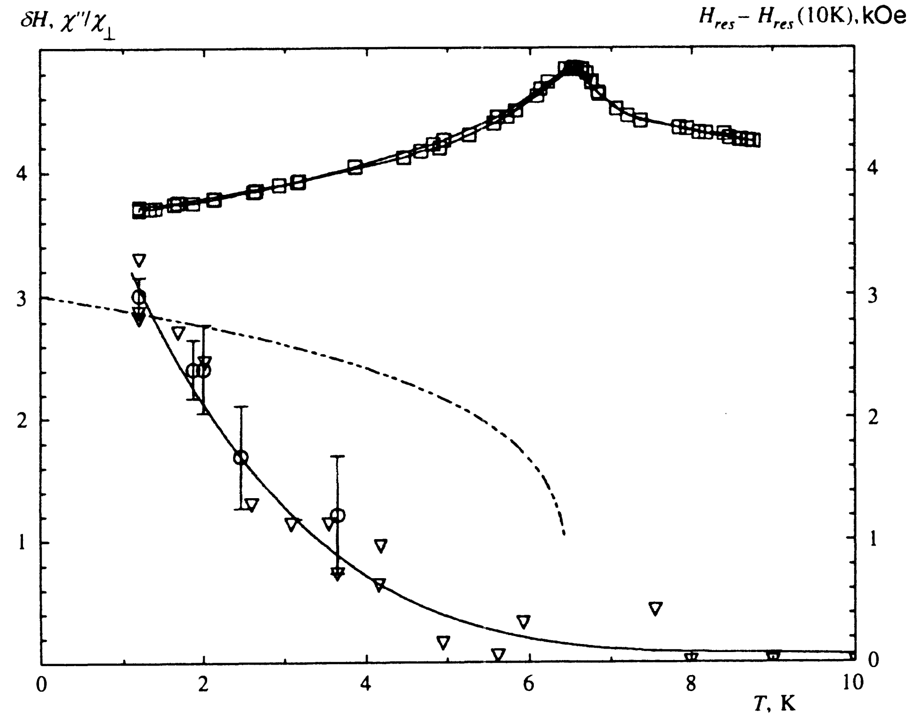

FIG. 4. Temperature dependence of δH (arbitrary units), ○), $H_{res}-H_{res}(10\ \mathrm{K})$ (▽), $[\chi''_{aa} - \chi''_{aa}\ (1.2\ \mathrm{K})]/\chi_\perp+3.7$ (□), and L(T) measured (dashed line) according to data from Ref. 2 in arbitrary units.

tude of the quadratic shift in an electric field equal to 3 kV/cm is approximately 100 times smaller than the linear shift at the same value of the electric field described in the previous section.

As in the case of the preceding configuration of the static fields, components of the magnetic susceptibility which are linearly dependent on the electric field, viz., $\delta\chi'_{yy}$ and $\delta\chi''_{yy}$, are observed. The signs of these components are determined by the sign of E during the magnetoelectric annealing performed with the polarization of the fields described. The dependence of δU on the magnetic field after magnetoelectric annealing with **E** in two opposite directions is shown in Fig. 7. Curve *3* was obtained when the sample was placed at a certain distance from the maximum point of the microwave magnetic field and corresponds to nonlinear displacement of the antiferromagnetic resonance.

Figure 8 presents plots of the dependence of the changes appearing in the real and imaginary parts of the high-

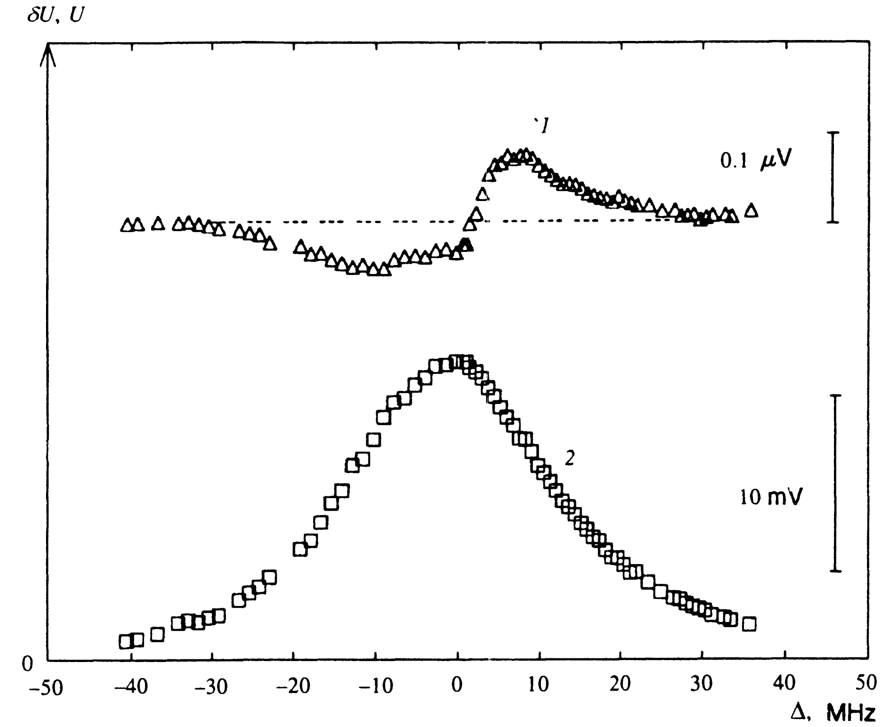

FIG. 5. Plots of $\delta U(\Delta)$ (*1*) and $U(\Delta)$ (2). Dashed line – zero-level line for δU.

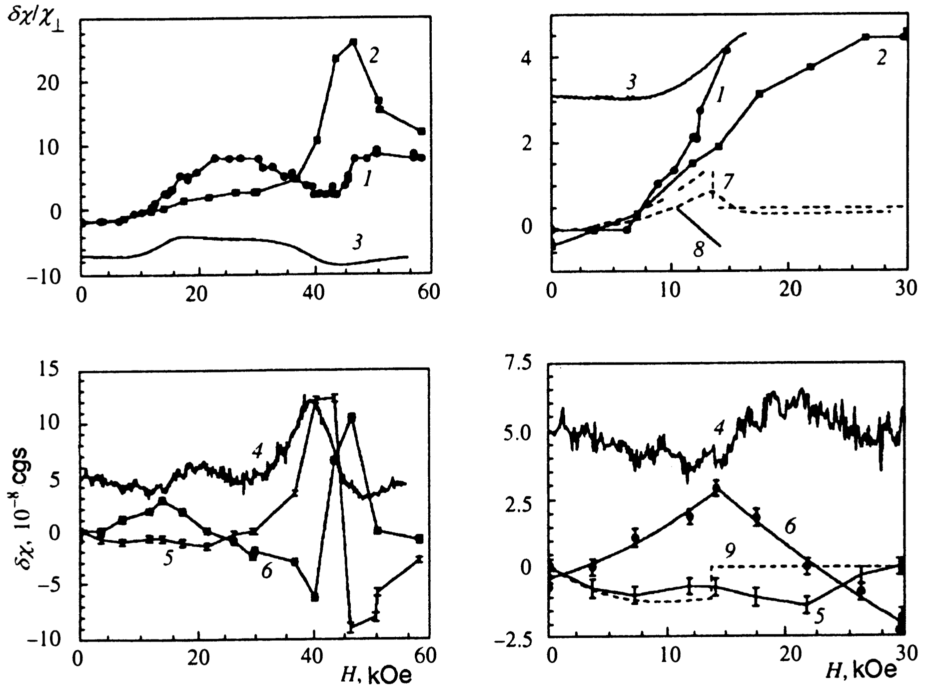

FIG. 6. Dependences of following parameters on the magnetic field: *1*) $[\chi'_{aa}-\chi'_{aa}(0)]/\chi_\perp$; *2*) $[\chi''_{aa}-\chi''_{aa}(0)]/\chi_\perp$; *3*) U in arb. units, arbitrary vertical shift; *4*) δU; *5*) $\delta\chi'_{aa}$ for $E_y=3$ kV/cm; *6*) $\delta\chi''_{aa}$ for $E_y=3$ kV/cm; *7*) $[\chi_{xx}-\chi_{xx}(0)]/\chi_\perp$ (calculation); *8*) $[\chi_{aa}-\chi_{aa}(0)]/\chi_\perp$ (calculation based on data from Ref. 7); *9*) $\delta\chi\,(H)$ [calculation based on (12)].

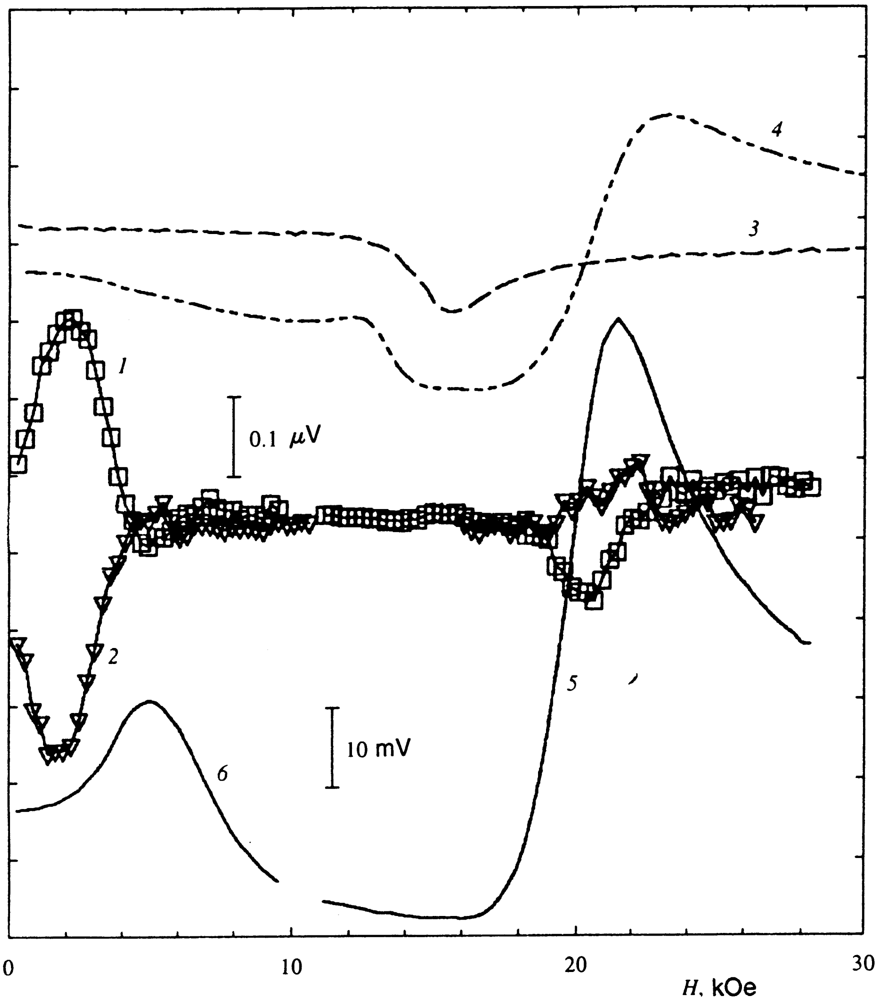

FIG. 7. Plots of $\delta U(H)$ for $\mathbf{H}\|[100]$ and $\mathbf{E}\|[001]$: after magnetoelectric annealing in the fields $E_z=3$ kV/cm and $H_x=28$ kOe (*1*) and after annealing with a reversed electric field (*2*). Curve *3* – record of the antiferromagnetic resonance line when the sample is not located at the antinode of the microwave magnetic field. Curve *4* – $Q(H)$ in arbitrary units. The values of δU for $H<10$ kOe were obtained with the generator tuned to the frequency of the cavity in a 5 kOe field [$U(H)$ – curve *6*], and the values for $H>10$ kOe were obtained in a 21 kOe field by tuning [$U(H)$ – curve *5*].

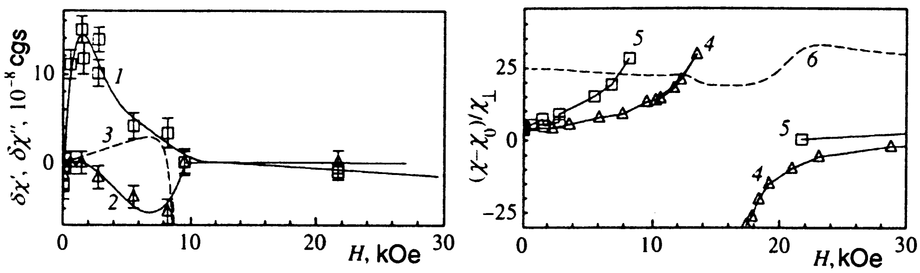

FIG. 8. Dependence of $\delta\chi'_{yy}$ (curve *1*) and $\delta\chi''_{yy}$ (curve *2*) on the magnetic field for **H**‖[100] and **E**‖[001]. Curve *3* – calculated dependence of $\delta\chi_{yy}$ on the magnetic field according to Eq. (15) after multiplication by 2; *4–6* –dependence of $[\chi'_{yy}-\chi'_{yy}(0)]\chi_\perp$, $[\chi''_{yy}-\chi''_{yy}(0)]\chi_\perp$, and Q on the magnetic field (arbitrary units).

frequency magnetic susceptibility in response to the electric field on the magnetic field, as well as the microwave signal.

In the case of this field configuration, in contrast to the results described in the preceding section, appreciable values of $\delta\chi'_{yy}$ and $\delta\chi''_{yy}$ appear in a zero magnetic field after magnetoelectric annealing under certain conditions. The results of measuring the magnitude of the response δU to an electric field after annealing with various combinations of field polarities are shown in Fig. 9. The presence of a magnetic field during the magnetoelectric annealing is essential, and its direction has an influence on the form of $\delta U(H)$. However, when the polarity of **H** used during the magnetoelectric annealing is reversed, the magnetoelectric signal δU recorded after the annealing changes, but this change is not confined to the change in sign observed in the case of reversal of the polarity of **E**. The function $\delta U(H)$ can be represented in the form of a sum of a function which is even with respect to H and an odd function, the odd component changing sign when the sign of H is reversed during the magnetoelectric annealing. Such a conclusion can be drawn by comparing the plots of $\delta U(H)$ shown in Fig. 9.

Figure 10 presents the temperature dependence of $\delta\chi'_{yy}$. It is seen that for the polarization of **E** and **H** under discussion there is a maximum on the temperature dependence, in contrast to the dependence of the shift of the antiferromagnetic resonance for the preceding polarization.

3.4. High-frequency magnetic properties in an electric field E_y with $H=H_x$

Here there is no linear displacement of the antiferromagnetic resonance. A dependence of χ^{ω}_{zz} on the electric field is observed after cooling from 7.5 K in an electric field. The presence of a magnetic field with various strengths up to 54 kOe during the annealing and its direction do not have any effect on the observed value of δU and its dependence on the magnetic field. Figure 11 presents plots of $\delta U(H)$ obtained after annealing with various values of E. The experiments with a reversed magnetic field show that δU is an even function of the magnetic field and reaches its highest value when the value of the magnetic field equals zero. Plots of the dependence of $\delta\chi'_{zz}$ and $\delta\chi''_{zz}$ on the magnetic field are also shown in Fig. 11. As the temperature increases, $\delta\chi'_{zz}$ decreases.

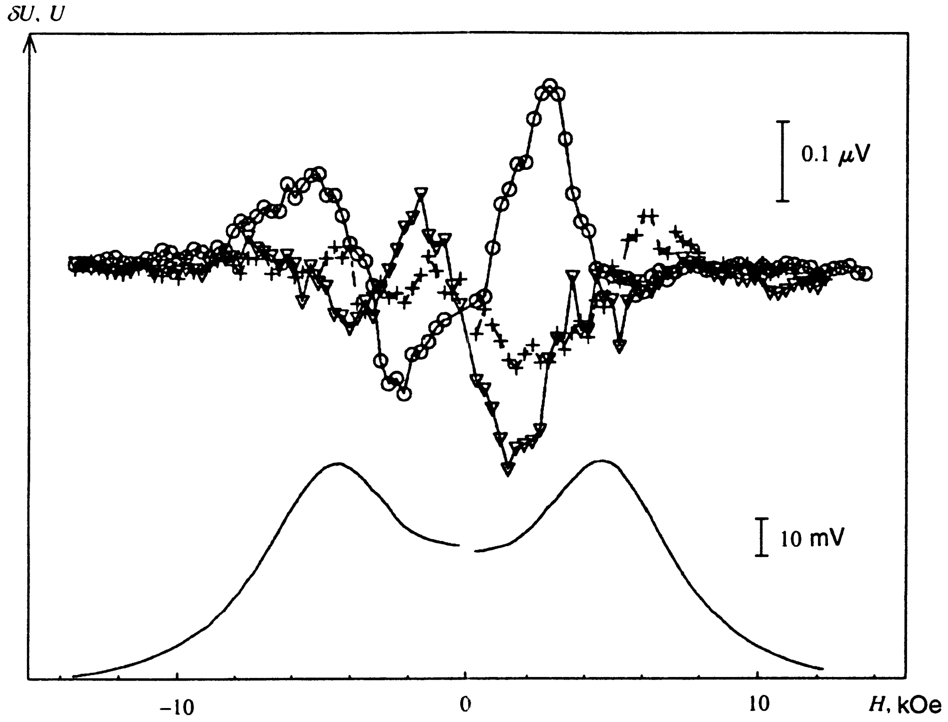

FIG. 9. Dependence of $\delta I(H)$ for **H**‖[100] and **E**‖[001] after magnetoelectric annealing with various polarities of the fields **E** and **H**: O—$E=3$ kV/cm, $H=12$ kOe; ∇—$E=3$ kV/cm, $H=12$ kOe; +—$E=-3$ kV/cm, $H=-12$ kOe; solid line—plot of $U(H)$.

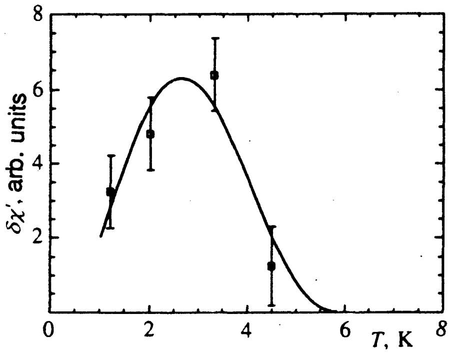

FIG. 10. Dependence of $\delta\chi'_{yy}$ on the temperature for $\mathbf{H}\|[100]$ and $\mathbf{E}\|[001]$.

4. THEORETICAL CALCULATIONS

4.1. The model

To describe the magnetic properties of antiferromagnetic Gd_2CuO_4 we shall use an expansion of the thermodynamic potential for a two-sublattice antiferromagnet with consideration of the plane–axis anisotropy and the tetragonal anisotropy in the xy plane. Such a description is simplified, since it ignores the presence of the copper magnetic sublattice and replaces the four gadolinium sublattices by two. However, this model can be used to trace the appearance of several magnetoelectric phenomena.

Thus, we shall utilize the expression for the magnetic part of the thermodynamic potential Φ obtained in Refs. 2 and 7. We supplement it with terms which describe the interaction of the electric and magnetic degrees of freedom from Ref. 3, as well as pure electrical terms. The magnetoelectric terms in (1) which are proportional to L_z are unimportant for determining the corrections to $\mathbf{M}$ and $\mathbf{L}$ that are linear with respect to $\mathbf{E}$, since we have $L_z=0$ when $E=0$. For the case of low temperatures and $\mathbf{L}\perp\mathbf{M}$ we obtain

$$\frac{1}{4M_0}\tilde{\Phi}=H_eM^2+\tfrac{1}{2}H_AL_x^2-H_tL_x^2L_y^2-\mathbf{M}\cdot\mathbf{H}+4M_0\lambda M_z\mathbf{P}\cdot\mathbf{L}+4M_0\Lambda P_z\mathbf{M}\cdot\mathbf{L}-\mathbf{E}\cdot\mathbf{P}+\frac{1}{2k_{ii}}E_i^2. \quad (6)$$

Here H_e is the exchange field, and H_A and H_t are the fields of the uniaxial and tetragonal anisotropy, respectively.

The behavior of the magnetic structure at low temperatures for $E=0$ and its description on the basis of the model just described were studied in Refs. 2 and 7. In the ground state the antiferromagnetism vector in a zero magnetic field is oriented in the [110] direction. When $\mathbf{H}$ is parallel to the x axis, $\mathbf{L}$ aligns itself to the [010] direction as the magnetic field increases from zero to $H_c=\sqrt{4H_tH_e}$, but $\mathbf{L}$ does not change its orientation when the field increases further, remaining perpendicular to the magnetic field. A second-order phase transition takes place in the field $H=H_c$. As a consequence of the great difference between $\chi_\|$ and $\chi_\perp$, as well as the nonuniformity of the rotation of the magnetization as the magnetic field varies, the susceptibility turns out to be dependent on H in the range of fields from zero to H_c, but at $H=H_c$ the susceptibility χ_{xx} undergoes an abrupt change, decreasing by a factor of 2. For $H>H_c$ the susceptibility ceases to vary and remains equal to $\chi_\perp$.

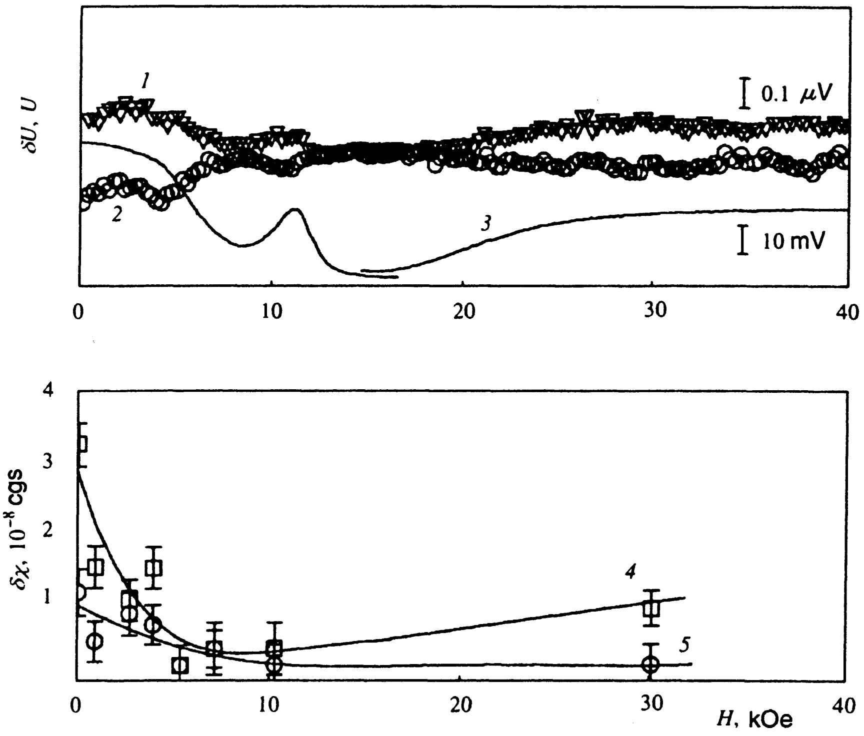

FIG. 11. Experiment under the conditions $\mathbf{H}\|[100]$ and $\mathbf{E}\|[010]$. Dependences on the magnetic field for δU after annealing in a field $E=3$ kV (*1*), δU after annealing in a field $E=-3$ kV (*2*), U (*3*), $\delta\chi'_{zz}$ (*4*), and $\delta\chi''_{zz}$ (*5*). The values of δU and U in fields weaker than 12 kOe were obtained with tuning of the generator in a zero field, and the values in stronger fields were obtained with tuning in a 40 kOe field.

4.2. Antiferromagnetic resonance spectrum in an electric field

Let us consider the range of magnetic fields in which $H_x>H_c$ and $H_y=0$. In our experiments antiferromagnetic resonance is observed in just such a region. Here rotation of the antiferromagnetic vector in a plane is already forbidden, and the magnetization of the crystal is determined with good accuracy by $\chi_\perp=4M_0/(2H_e)$. Here, as in all the ensuing calculations we assume H, H_c, H_t, $H_A \ll H_e$.

The Landau–Lifshitz equations for **E** parallel to the y axis and **H** lying in the xz plane have the form

$$\frac{1}{\gamma}\frac{dm_x}{dt}=-(H_z-\sigma)m_y+\left(H_A+\sigma\frac{H_z}{2H_e}\right)l_z,$$

$$\frac{1}{\gamma}\frac{dm_y}{dt}=-H_zm_z+(H_z-\sigma)m_x-\sigma\frac{H_x}{2H_e}l_y,$$

$$\frac{1}{\gamma}\frac{dm_z}{dt}=H_xm_y+\left(\sigma\frac{H_z}{2H_e}+2H_t\right)l_x,$$

$$\frac{1}{\gamma}\frac{dl_x}{dt}=\sigma l_y+2H_em_z+\sigma\frac{H_z}{2H_e}m_z,$$

$$\frac{1}{\gamma}\frac{dl_y}{dt}=-(H_z-\sigma)\frac{H_t}{H_e}l_x-\frac{H_xH_A}{2H_e}l_z,$$

$$\frac{1}{\gamma}\frac{dl_z}{dt}=\sigma\frac{H_x}{2H_e}m_z-2H_em_x. \tag{7}$$

Here **l** and **m** are small deviations of **L** and **M** from their equilibrium values, γ is the magnetomechanical ratio, and $\sigma=4M_0\lambda P_yL_y$. Also, σ is the value taken with sign reversed of the effective magnetic field appearing in the z direction under the action of E_y:

$$H_{\text{eff}}=-\frac{1}{4M_0}\frac{d\tilde{\Phi}_{ME}}{d\mathbf{M}},$$

The equations of motion are distinguished from the equations in a zero electric field by the terms containing σ. This difference involves, in particular the replacement of H_z by $H_z-\sigma$, the addition of an effective field to the projection H_z when the electric field is turned on. The resonant frequencies of the small oscillations are determined from the equation

$$\left(\frac{\omega}{\gamma}\right)^4-\left(\frac{\omega}{\gamma}\right)^2(H_z^2+2H_AH_e-4H_eH_t+H_x^2)+2H_AH_eH_x^2$$
$$+\sigma H_z\left[\left(\frac{\omega}{\gamma}\right)^2\left(2+\frac{2H_t}{H_z}\right)+4H_tH_e-2H_AH_e-H_z^2\right.$$
$$\left.+H_x^2-2H_tH_z\right]=0. \tag{8}$$

We are interested in the small shift of the resonant value of the magnetic field at a fixed frequency ω that arises in an electric field. For $H_z=H_x=H/\sqrt{2}$ this shift is given by the equality

$$\delta H=\sigma\left[\frac{1}{\sqrt{2}}+2\frac{H_t((\omega/\gamma)^2-H^2)}{H(2(\omega/\gamma)^2+4H_eH_t-2H_AH_e)}\right]. \tag{9}$$

Using the values $2H_e=110$ kOe, $H_A=9$ kOe, and $H_t=0.75$ kOe known from Ref. 2, we find that the second term in the last equation amounts to 0.14 of the first term and, therefore, weakly influences δH, i.e., the electric field mainly alters the z projection of the antiferromagnetic resonance magnetic field by the magnitude of the effective field σ.

For $H_z=0$ and $E=E_y$ it also follows from Eq. (8) that there is no shift of the antiferromagnetic resonance, which is linear with respect to σ.

A similar calculation reveals that there is likewise no linear shift of the antiferromagnetic resonance by an electric field for static fields with the following configuration: $\mathbf{E}\|[001]$, $\mathbf{H}\|[100]$. This finding can be attributed to the fact that the effective field in this case is perpendicular to the external magnetic field and the variation of the total magnetic field is quadratic in **E**.

4.3. Variation of χ_{xx} in a field E_y with $H_x=H_z$ and $H_y=0$

The magnetic susceptibility in fields $H_x<H_c$ is determined by two factors: the function $M(H)$ proper and the orientational contribution associated with the rotation of the magnetic moment relative to the magnetic field. The function $M(H)$ is specified by the angle between **L** and **H** owing to the significant difference between the parallel and perpendicular susceptibilities of the antiferromagnet. At low temperatures we have $\mathbf{L}\perp\mathbf{M}$, $L^2+M^2=1$, and it is convenient to use the variables M (the absolute value of the magnetization in units of $4M_0$) and θ (the angle between **L** and the y axis). Both contributions to the susceptibility depend on θ. In the absence of an electric field, the angle θ depends on the x component of the magnetic field in the following manner:[7]

$$\sin^2\theta=\frac{1}{2}\left(1-\frac{H_x^2}{H_c^2}\right). \tag{10}$$

We assume $L\approx 1$, which is true in magnetic fields which are small compared with $2H_e$. Then, when the magnetic field is oriented in the xz plane and the electric field is parallel to the y axis, the expression for the thermodynamic potential (6) takes the form

$$\frac{1}{4M_0}\tilde{\Phi}=H_eM_\perp^2-\frac{H_t}{4}\sin^2 2\theta-M_\perp H_x\cos\theta+M_\perp H_y\sin\theta$$
$$+4M_0\lambda P_yM_z\cos\theta+H_eM_z^2$$
$$-M_zH_z. \tag{11}$$

Here $M_\perp$ is the component of **M** lying in the xy plane.

In determining the changes in the magnetic susceptibility χ_{xx} under the action of the electric field creating the polarization P_y, we bear in mind that these changes are small. Minimizing of the potential $\tilde{\Phi}$ with respect to M_z, $M_\perp$, and θ, we find the small changes in $M_\perp$ and θ appearing under the influence of the electric field and use them to determine the change in the susceptibility. In this case, to determine the corrections to **M** and **L** which are linear with respect to the electric field, we can assume $P_i = k_{ik} E_k$, neglecting the magnetoelectric contribution to the electric polarization. For $H_x = H_z$, $H_x < H_c$ we obtain

$$\delta\chi_{xx} = -\chi_\perp \frac{4M_0\lambda P_y}{H_c} \frac{H}{H_c}\left(1+\left(\frac{H}{\sqrt{2}H_c}\right)^2\right)^{-3/2}. \qquad (12)$$

The physical meaning of this result is that owing to the magnetoelectric interaction corresponding to the term $16M_0\lambda P_y M_x L_y$ in (6), in the presence of a nonzero magnetic field parallel to the z axis, the electric field changes the orientation of $\mathbf{L}$ relative to the magnetic field, which, in turn, causes a change in the magnetic susceptibility.

4.4. Variation of χ_{yy} in a field E‖[001] for H‖[100]

The magnetoelectric contribution to the thermodynamic potential $16M_0^2\Lambda P_z \mathbf{L}\cdot\mathbf{M}$ is significant for this configuration. Its influence should vanish when the temperature is lowered, since $\mathbf{M}\perp\mathbf{L}$ at low temperatures. However, this term is governed by the exchange interaction, and its manifestations can be significant even under conditions such that $\chi_\parallel \ll \chi_\perp$. We assume that $\chi_\parallel$ is small, but nonzero. Then, in a first approximation with respect to the static fields, the magnetization is given by the expression

$$\mathbf{M} = \chi_\perp \mathbf{H} - (\chi_\perp - \chi_\parallel)(\mathbf{L}\cdot\mathbf{H})\mathbf{L} + \chi_\parallel \Lambda P_z \mathbf{L}. \qquad (13)$$

Plugging this expression into (6), we find

$$\frac{1}{4M_0}\tilde{\Phi} = -\tfrac{1}{4}H_t \sin^2 2\theta - \frac{\chi_\perp}{2}H_x^2 + \frac{\chi_\perp - \chi_\parallel}{2}(H^2\sin^2\theta + 2H_xH_y\sin\theta\cos\theta) + 4M_0\chi_\parallel \Lambda P_z(H_z\sin\theta + H_y\cos\theta). \qquad (14)$$

Minimizing this expression with respect to θ, we find the small variations in M_y appearing when an electric field and a weak measuring field H_y are turned on. Then the part of the susceptibility which depends on the electric field is determined:

$$\delta\chi_{yy} = \chi_\parallel \frac{4M_0\Lambda P_z H_x}{H_c^2} \frac{1}{1+(H_x/H_c)^2}\left[\frac{1+2(H_x/H_c)^2}{2\sin\theta} - \frac{1}{(H_c/H_x)^2 - 1}\right]. \qquad (15)$$

Here $\sin\theta$ is defined by the expression (10). In the limit $H_x \to H_c$ the value of $\delta\chi_{yy}$ determined in the linear approximation tends to infinity as a result of the disappearance of the rigidity with respect to reorientation of the magnetization in the y direction near the phase transition.

When $H_x > H_c$ holds, $\mathbf{L}$ is not reoriented under the influence of the electric field, and $\delta\chi_{yy} = 0$.

5. DISCUSSION

The observation of a magnetic moment δM_x induced by an electric field E_z makes it possible to estimate the magnetoelectric modulus: $\alpha_{zx} \sim 10^{-8}$ emu. This value is a severe underestimate, since in our static experiments the sample was not subjected to magnetoelectric annealing and was not single domain. As follows from the results in Ref. 3, a sample cooled in zero fields has a magnetoelectric effect at least a hundred times weaker than a sample subjected to magnetoelectric annealing. It follows from the data in Ref. 3 on the $(ME)_H$ effect observed after magnetoelectric annealing that $\alpha_{zx} = 3\times 10^{-5}$ emu at $T = 5$ K. Thus, these results are consistent with one another.

The magnetoelectric modulus α_{xz} can be determined from the results of experiments involving the observation of antiferromagnetic resonance in an electric field by calculating the value of $\sigma = 4M_0\lambda k_{xx}E_x$ from Eq. (9). The value determined from the shift of the resonant field for $E_y = 3$ kV/cm corresponds to $\alpha_{xz} = 1\times 10^{-4}$ emu. The value $\chi_\perp = 1.03\times 10^{-3}$ determined from the data in Ref. 2 was used here. The value of α_{xz} found above is consistent with the data in Ref. 3 on the electric polarization induced by a magnetic field, from which we obtain $\alpha_{xz} = 7\times 10^{-5}$ emu at $T = 5$ K.

Let us use the characteristics obtained for the magnetoelectric effect in Gd_2CuO_4 to evaluate the influence of an electric field on the susceptibility according to the calculations presented above in Sec. 4.

For $E = E_y$ and $H_x = H_z$, the shift of the antiferromagnetic resonance gives a value of 0.15 Oe for $4M_0\lambda P_y$ in a field $E_y = 3$ kV/cm. Then, using Eq. (12), we obtain the plot of $\delta\chi_{xx}(H)$ presented in Fig. 6 (curve 7). In our experiment the dynamic susceptibility is measured at a frequency on the order of the resonant frequency and can thus differ significantly from the static susceptibility. In this experiment the microwave magnetic field was directed in the xz plane at a 45° angle to the axes, i.e., χ_{xx}^ω and χ_{zz}^ω have equally significant influences on the result. Figure 6 compares the values and field dependences of the static susceptibility $\chi_{aa} = (\chi_{zz} + \chi_{xx})/2$ obtained on the basis of the experimental results from Ref. 2 and the dynamic susceptibilities for our sample. Equation (12) was derived including the change in the static susceptibility χ_{xx}. In view of these circumstances, the agreement in the order of magnitude and the character of the dependence on the magnetic field for the observed values of $\delta\chi_{aa}'$ and $\delta\chi_{aa}''$ and the calculated dependence $\delta\chi_{xx}(H)$ seems satisfactory to us.

Using the value of the modulus $\alpha_{zx} = 3\times 10^{-5}$ emu from Ref. 3, we calculate $\delta\chi_{yy}$ from Eq. (15) to compare it with the results of the experiments with E‖[001] and H‖[100]. It should be borne in mind that the measurements in Ref. 3 were performed at 5 K and that the value of the modulus at 1.2 K, which is needed for the calculations of $\delta\chi_{yy}$, can differ severalfold from that value under the conditions of our experiment. The results of the calculations of $\delta\chi_{yy}$ are shown in Fig. 8. It is seen that in this case, too, there is qualitative agreement in the values and the character of the field dependence for the changes in the dynamic susceptibilities and the results of the calculation of the change in the static susceptibility. The nonzero value of $\delta\chi_{yy}'$ observed for $H_x > H_c$ cannot be explained in the present model and probably attests to an interaction between the gadolinium and copper sublattices. This interaction apparently prevents complete flipping of the gadolinium sublattices perpendicularly to the magnetic field, since the fields used are small compared with the characteristic fields of the copper subsystem. This hypothesis was also advanced in Ref. 3 to account for the electric polarization of the sample in a magnetic field $H_x > H_c$.

Thus, the variations of the magnetic susceptibility which are odd with respect to EH (Figs. 2 and 6) can be explained on the basis of a simplified model of the effect with the thermodynamic potential (6): when $H \neq 0$, the electric field changes of the orientation of **L** and the susceptibility.

The linear shift of the antiferromagnetic resonance at $H_z = H_x$ and its absence when $\mathbf{H} \| [100]$ holds are also in good agreement with the calculation of the shift of the antiferromagnetic resonance in an electric field performed in subsection 4.1.

The shift of the antiferromagnetic resonance and the values of $\delta\chi'_{aa}$ and $\delta\chi''_{aa}$ increase monotonically as the temperature is lowered. This should be expected from the monotonic variation of L, which determines the temperature dependence of σ in Eq. (9), and the product $\chi_\perp L$ appearing in Eq. (12). However, it is seen from the results presented in Fig. 4 that the temperature dependence of the effect does not follow the temperature dependence of the magnetization of the sublattice, as could be expected on the basis of the simple model and in the molecular-field approximation. We note that $H_c(T)$ does not follow the form of $M_0^2(T)$ predicted by molecular-field theory. The form of $H_c(T)$ can be determined from the temperature dependence of the antiferromagnetic resonance field H_{res} when $H = H_x$ using the following equation from Ref. 7: $(\omega/\gamma)^2 = H_{\text{res}}^2 - H_c^2$.

The part of the susceptibility $\delta\chi'_{yy}$, which depends on E_z, has a maximum as the temperature is varied in accordance with the temperature dependence of the product $\chi_\| L$, which determines $\delta\chi_{yy}$ according to Eq. (15).

However, the induction of the magnetic moment δM_x by an electric field E_y, the presence of a weak ferromagnetic moment, and a magnetic susceptibility in a zero magnetic field that depends on the electric field cannot be explained in the simplified model.

Moreover, the weak ferromagnetism stipulated by the terms which are bilinear with respect to L and M is forbidden for tetragonal crystals, which include Gd_2CuO_4. However, a weak ferromagnetic moment was observed here at temperatures below T_N(Cu) and above T_N(Gd) (Ref. 9). To account for this fact it was assumed that there are weak distortions of the tetragonal lattice.[10] We observe a spontaneous ferromagnetic moment, which is no less than $\sim 10^{-9}$ of the magnetization of the sublattice, at a temperature considerably below T_N(Gd) (Fig. 1b). The magnetoelectric interaction corresponding to the term in the potential proportional to $E_y M_x$ which was observed in our experiments (see Fig. 1b) is also impossible in the original $I4mmm$ crystallographic group. We note here that symmetry allows or forbids the simultaneous existence of spontaneous electric polarization with a susceptibility proportional to E, which was observed in our experiments. Apparently, the spontaneous magnetic moment also generates spontaneous electric polarization through the magnetoelectric interaction. In this respect Gd_2CuO_4 behaves similarly to nickel–iodine boracite,[11] which is a weakly ferromagnetic magnetoelectric ferroelectric.

The components of the magnetic susceptibility which are linear in **E** that are observed in a zero magnetic field when $\mathbf{E} \| [010]$ and $\mathbf{E} \| [001]$ ($\delta\chi_{zz}$ and $\delta\chi_{yy}$, respectively) can be responsible for the presence of terms of the form $pE_i M_j^2 L_k^2$ in the expansion of the thermodynamic potential. Terms of the form $qE_i^2 M_j^2 L_k^2$ should also be introduced to describe the quadratic component of the magnetic susceptibility with respect to the electric field.

However, the observed effects can also be described without including terms of such high orders. We assume that the symmetry of the crystal resulting from distortion of the structure allows terms of the form $L_y M_x \pm L_x M_y$ and $E_y M_x L_y$ in the expansion of the thermodynamic potential. The former contribution allows weak ferromagnetism and, consequently, a spontaneous magnetic moment. Then an influence of the electric field on the orientation of **L** and the magnetic susceptibility χ_{yy} in a zero magnetic field arises, similar to the influence considered in subsections 4.3 and 4.4. The term of the latter form describes the observed interaction between M_x and E_y. When these additional contributions to $\tilde{\Phi}$ are present, the linear influence of E_y on χ_{zz} in a zero magnetic field can be explained in the following manner. The spontaneous magnetic moment in the plane is accompanied by spontaneous electric polarization, which, according to (1), produces a small nonzero value of L_z. Then the field E_y causes linear variation of the component of **L** perpendicular to the magnetic field, which has a significant influence on the susceptibility. When $L_z = 0$ holds, the latter variation would be quadratic.

In conclusion we present the terms of the thermodynamic potential Φ in variable E and H which it must contain to describe the magnetoelectric effects that we observed:

$$\Phi_{ME} = \kappa_i H_i + \alpha_{ik} E_i H_k + \gamma_{ik} E_i H_k^2 + \beta_{ikl} E_i H_k H_l^2 + \tau_{ik} E_i^2 H_k^2. \tag{16}$$

Our experiments revealed that the coefficients α_{zx}, α_{xy}, α_{xz}, γ_{zx}, γ_{xz}, β_{xzx}, β_{zxy}, τ_{zx}, τ_{xy}, τ_{xz}, and κ_x are nonzero.

6. CONCLUSIONS

Several magnetoelectric effects were observed in the experiments at a temperature below the ordering of the gadolinium spin subsystems. Some of the observations are described qualitatively by the two-sublattice model of an antiferromagnetically ordered rare-earth sublattice with a low-order magnetoelectric interaction (6). This model accounts for our observations of the induction of a magnetic moment M_x by an electric field E_z, displacement of the antiferromagnetic resonance frequency in an electric field, and the effect of an electric field on the magnetic susceptibility, which is odd with respect to the magnetic field and is associated with the rotation of the antiferromagnetism vector under the action of the electric field.

To explain the dependence of $M_x(E_y)$, which exhibits hysteresis, and the influence of an electric field on the magnetic susceptibility in a zero magnetic field, structural distortions which allow weak ferromagnetism or an influence of terms of higher orders with respect to M in the thermodynamic potential must be postulated.

The existence of magnetoelectric properties in fields above H_c points out the influence of the copper magnetic sublattice.

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