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Reference


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Magnetoelectric studies of antiferromagnetic crystals in strong magnetic fields

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Abstract

Experimental studies of the magnetoelectric effect in the antiferromagnetic crystals Cr$_2$O$_3$, Gd$_2$CuO$_4$, and Sm$_2$CuO$_4$ have been performed in strong magnetic fields up to 20 T. The magnetoelectric effect is fully determined by the symmetry of the magnetically ordered material and yields hence valuable information about magnetic ground states. When the magnetic symmetry is changed at a magnetic field induced phase transition the magnetoelectric effect exhibits anomalies at the phase transition owing to the fact that the magnetoelectric signal is related to the antiferromagnetic order parameter $\mathcal{L}$. Even at temperatures close to the Neel temperature $T_N$ the obtained experimental data resolve the magnetic properties very well, giving the possibility to study magnetic phase transitions in the critical temperature range.

1. Introduction

The magnetoelectric (ME) effect, which is characterized by the appearance of an electric polarization on applying a magnetic field or of a magnetization on applying an electric field, is generally recognized to yield information about the magnetic point group. For many magnetic materials in which the effect has been found, following the discovery of the ME effect in Cr$_2$O$_3$ [1], the experimental results have helped to clarify magnetic structures [2]. However, nowadays the information about the magnetic point group of antiferromagnetic materials is usually obtained from neutron scattering experiments due to its additional ability to resolve intrinsic properties of the magnetic ordering. On the other hand, neutron experiments do not, up to now, have access to high magnetic fields. Therefore, the information about an antiferromagnetic system is supplemented by experimental high field data from, e.g. magnetization or antiferromagnetic resonance (AFMR) experiments. Relatively little interest has been given to the possibility of studying the ME effect in high magnetic fields where it yields information not only about the antiferromagnetic ground state but also about magnetic phase transitions [3]. In this paper we present experimental results for the ME effect of the antiferromagnets Cr$_2$O$_3$, Gd$_2$CuO$_4$, and Sm$_2$CuO$_4$ in high magnetic fields up to 20 T showing that this technique offers a powerful tool to study antiferromagnetic systems.

If only the linear ME effect is considered the constitutive equations become

$$P_i = \kappa_{ij} E_j + x_{ij} H_j,$$

$$M_i = \chi_{ij} H_j + x_{ij} E_j.$$
where the magnetization $M$ is proportional to the electric field $E$ and the electric polarization $P$ is proportional to the magnetic field $H$. The tensors $\kappa$ and $\chi$ represent the electric and magnetic susceptibilities while $\alpha$ represents the ME susceptibility. The ME tensor $\alpha$, defined in the ordinary way

$$
\alpha_{ij} = - \frac{\delta^2 F}{\delta E_i \delta H_j} = \frac{\delta P_i}{\delta H_j} = \frac{\delta M_j}{\delta E_i}, \quad i, j = x, y, z,
$$

(3)

is a second-rank axial tensor and contains nine components. The number of nonzero components and therefore the form of $\alpha$ is restricted by the requirement of being invariant under the symmetry operations of the magnetic point group of the given material. Not all magnetically ordered materials exhibit a ME effect. Due to symmetry considerations the effect can only be observed in materials where the space and time inversion symmetries are broken. This condition restricts the ME effect to 58 magnetic classes [4]. When the intrinsic ordering of the material is changed or broken by applying magnetic fields or by heating above the Néel temperature, the form of $\alpha$ does in general change according to the induced symmetry. Due to this change of $\alpha$ at the point of a phase transition, a sudden change of the magnetic-field-induced electric polarization is expected. In zero magnetic field the magnetic ordering and its critical behaviour at the transition has already been investigated for several materials by means of the electric-field-induced ME effect [3].

Antiferromagnetic materials can be divided into two classes, the low-anisotropic (Heisenberg) and the high-anisotropic (Ising) antiferromagnet. By applying the magnetic field parallel to the sublattice magnetization of a low-anisotropy antiferromagnet a spin-flop transition occurs at a critical field $H_{sf}$. It refers to a sudden rotation of the sublattice magnetization to an orientation perpendicular to the magnetic field. In the spin-flop phase the magnetic symmetry will be changed, consequently $\alpha$ also. By further increasing the magnetic field, the sublattice magnetizations align along the magnetic field up to the spin-flip field $H_c$ where they are fully aligned, the antiferromagnetic ordering is broken and the material is now found to be in a paramagnetic phase. Since all materials which we have investigated belong to the class of low-anisotropy antiferromagnets, results of ME studies of spin-flop and spin-flip transitions are presented.

2. Experimental set-up

In order to detect a static electric polarization of a ME material the first measurements were performed by recording the voltage between the electrodes of the sample on applying a magnetic field [5]. This technique has the disadvantage of being limited by the finite conductivity of the sample and being sensitive to magnetostriction effects changing the distance between the electrodes and therefore the measured voltage. We have measured the polarization of the sample by a DC-technique, where the current between the electrodes is measured and integrated. By this technique the sample is always left at zero electric field. The integrated value is scaled and displayed as charge. In this way charges of 0.01 pC were detectable. Electrodes were deposited by silver paint on the appropriate faces and the contacted samples were fixed to the sample holder by varnish. The measurements were performed in a resistive Bitter magnet providing static magnetic fields up to 20 T. The temperature was varied between 1.9 and 10 K in a conventional helium cryostat and measured by a calibrated RuO thermometer. Between 4.2 K and room temperature a helium flow cryostat was used and the temperature was measured by a calibrated platinum-resistance thermometer.

To measure the ME effect it is usually necessary to cool the sample through the $T_N$ with a simultaneously applied and properly oriented magnetic and electric fields in order to obtain a single antiferromagnetic domain state.

3. Results

3.1. $\text{Cr}_2\text{O}_3$

With respect to the magnetoelectric (ME) effect $\text{Cr}_2\text{O}_3$ is a well-known compound. It has been the first compound for which the ME effect was theoretically predicted in its antiferromagnetic phase [6] and it was the first compound where the effect was experimentally shown to exist [1].

$\text{Cr}_2\text{O}_3$ is a Heisenberg antiferromagnet with a Néel temperature of $T_N = 308$ K. In zero magnetic field the $\text{Cr}^{3+}$ spins align themselves parallel to the rhombohedral $c$-axis, forming an “easy-axis” antiferromagnet. The corresponding magnetic symmetry is $3 m'$ which is compatible with a linear ME effect with two independent nonzero components of the ME tensor:

$$
\alpha_{ij} = \begin{pmatrix}
0 & 0 \\
0 & \alpha_{yy} \\
\alpha_{xx} & 0
\end{pmatrix}
$$

(4)

with $\alpha_{xx} = \alpha_{yy}$. A small external magnetic field parallel to the $c$-axis lowers the symmetry to $3m'$ without affecting the form of the ME tensor.

When the external magnetic field is further increased parallel to the $c$-axis a spin-flop transition takes place at
a critical field \( H_{sf} \) ranging from 6.1 T at 4.2 K up to 12.5 T near the Néel temperature which has been studied by means of antiferromagnetic resonance [7] and ultrasonic attenuation [8]. Above this critical field \((H > H_{sf} \approx 10 \, \mathrm{T})\) the spins are found to be oriented perpendicular to the \( c \)-axis in the basal plane.

For the antiferromagnetic ordering of the spins in the basal plane two spin configurations are possible. Either the spins lie in a mirror plane leading to a magnetic class of \( 2/m' \) or parallel to a twofold axis leading to a magnetic class of \( 2'/m \). The two possible magnetic ground states in the spin-flop phase lead to different forms of the linear ME tensor:

\[
\begin{bmatrix}
x_{yy} & 0 & x_{yz} \\
x_{yz} & 0 & x_{zx} \\
x_{zx} & 0 & x_{xx}
\end{bmatrix}, \quad m': \begin{bmatrix} 0 & x_{yx} & 0 \\ x_{yx} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.
\] (5)

For an arbitrary orientation of the spins in the basal plane all nine ME tensor elements would be nonzero. So far only few experimental studies are known to have been performed in high magnetic fields but disagree on the magnetic symmetry of the spin-flop phase [9–13]. This might be due to the fact that a small projection of the magnetic field onto the basal plane determines the orientation of the spins.

In Fig. 1 the field dependence of the electric polarization \( P \) is shown in magnetic fields \( H \parallel z \). Figs. 1(a) and (b) show \( P_x(H_z) \) and \( P_y(H_z) \), respectively. For \( H < H_{sf} \) a linear ME effect is not expected from Eq. (4) and the small electric polarization detected below the critical field can be attributed to a rotation of the antiferromagnetic ordering from the \( c \)-axis in a misaligned magnetic field.

The spin-flop transition can clearly be observed by a sharp drop of the polarization at \( H = H_{sf} \). In the spin-flop phase the polarization \( P_x(H_z) \) and \( P_y(H_z) \) become a linear function of the magnetic field.

In Fig. 1(c) the electric polarization \( P_z(H_z) \) is shown. In agreement with Eq. (4) a linear ME effect is observed in the antiferromagnetic phase up to the critical field value \( H_{sf} \) where the polarization drops to zero. By increasing the magnetic field further the polarization becomes again a linear function of the magnetic field.

Constructing the phenomenological expression for the nonequilibrium free energy in the Landau theory of phase transitions by describing the magnetic subsystem in terms of the antiferromagnetic vector \( L \) and the magnetization vector \( M \), it can be shown that the electric polarization \( P_z \) in the antiferromagnetic phase of \( \text{Cr}_2\text{O}_3 \) becomes

\[
P_z \propto M_z L_z,
\] (6)

and the ME signal is directly proportional to a projection of the antiferromagnetic order parameter \( L \). At \( H_{sf} \), where a fast rotation of the antiferromagnetic vector from the \( c \)-axis into the basal plane occurs, the projection of \( L \) onto the \( z \)-direction vanishes.

In this study the ME effect has been investigated for the first time in static magnetic field up to 20 T and the resulting phase diagram of the spin-flop transition in the temperature range from 4.2 K to \( T_N = 308 \, \mathrm{K} \) is shown in Fig. 2, agreeing very well with reported AFMR data [7].

### 3.2. Gd\(_2\)CuO\(_4\)

The compound Gd\(_2\)CuO\(_4\) belongs to the family of high-\( T_c \) superconductors with electron-type conductivity [14] with the general formula \( \text{R}_2\text{CuO}_4 \) (\( \text{R} \) = rare earth). Unlike other members of the family, Gd\(_2\)CuO\(_4\) does not become superconducting under doping and a magnetic ordering of the Gd-spins has been observed at low temperatures. It is the possible correlation between
"nonsuperconducting" and magnetic properties that attracted attention to the magnetic subsystem of this compound. Gd$_2$CuO$_4$ was the first member of the family to exhibit a ME effect and the experimental results helped to clarify the magnetic ground state in this compound [15].

The magnetic structure of Gd$_2$CuO$_4$ includes two magnetic subsystems (copper and rare earth). The Cu spins become antiferromagnetically ordered just below room temperature ($T_{N}(Cu) = 285$ K), whereas the intrinsic ordering of the rare earth magnetic subsystem occurs at $T_{N}(Gd) = 6.5$ K. The specific spin arrangement in each magnetic subsystem, known from neutron scattering experiments [16, 17], is presented in Fig. 3. The antiferromagnetic ordering of the copper spins in Gd$_2$CuO$_4$ preserves the space inversion symmetry of the system. In contrast, the rare earth spin arrangement, which forms ferromagnetic planes parallel to the Cu–O planes with neighbouring rare-earth planes being antiferromagnetically coupled, breaks the space inversion symmetry. As a consequence, the two magnetic subsystems below $T_{N}(Gd)$ manifest themselves rather independently both in static and resonance experiments. Below $T_{N}(Gd)$ the magnetic symmetry of this compound belongs to the magnetic class $m'm'm$ which allows a linear magnetoelectric (ME) effect with the ME tensor

$$\chi_{ij} = \begin{pmatrix} 0 & 0 & \chi_{ac} \\ 0 & 0 & 0 \\ \chi_{ca} & 0 & 0 \end{pmatrix} ,$$

where $a$, $b$ and $c$ denote the orthorhombic axes. Above $T_{N}(Gd)$ the magnetic symmetry of the crystal is incompatible with a ME effect because of the presence of space inversion in the magnetic symmetry group. Also does the ME effect vanish once the spin-flip field is reached and the compound belongs to the magnetic class $m'm'm$ which rules out the existence of a ME effect.

In Fig. 4 the field dependence of $P_x$ is shown in magnetic fields perpendicular to the ferromagnetic rare-earth planes. In accordance with Eq. (7) the ME signal becomes for small magnetic fields a linear function of the magnetic field but the signal disappears reaching the spin-flip field $H_s$. It also disappears at temperatures higher than $T_{N}(Gd)$. Constructing the phenomenological expression for the non-equilibrium free energy, the electric polarization $P$ becomes for Gd$_2$CuO$_4$

$$P_x \propto M_x L_x$$

and the ME signal is proportional to a projection of the antiferromagnetic order parameter $L$. The curves have been measured at three different temperatures. For the highest temperature of 6.56 K which represents $T = 0.98 T_N$ ($T_N$ was found to be at 6.61 K) the spin-flip transition is still clearly resolved.

In Fig. 5 we show for comparison the measurement of the magnetization of the same sample for $H \parallel z$ at 1.5 and 5 K. Whereas the spin-flip transition is clearly observable at 1.5 K, at 5 K the transition is no longer observable due
found a ME effect giving us the possibility to investigate the magnetic ground state in detail. Sm$_2$CuO$_4$ possesses a crystal structure close to that of Gd$_2$CuO$_4$. The magnetic structure includes two magnetic subsystems (copper and rare earth). The Cu spins become antiferromagnetically ordered at $T_N$(Cu) = 285 K and the intrinsic ordering of the rare earth magnetic subsystem occurs at $T_N$(Sm) = 5.9 K. The spin arrangement in each magnetic subsystem is known from neutron experiments [19, 20]. The antiferromagnetic ordering of the copper spins in Sm$_2$CuO$_4$ again preserves the space inversion symmetry of the system. The rare earth spins order in ferromagnetic planes, the spins being oriented perpendicular to the Cu-O planes in contrast to Gd$_2$CuO$_4$. Neighbouring rare earth planes are antiferromagnetically coupled. Again does the ordering of the rare earth system break the space inversion symmetry and below $T_N$(Sm) the magnetic symmetry of this compound is thought to belong to the magnetic class $m'm'm'$ which allows a linear magnetoelectric (ME) effect with the ME tensor

$$\mathbf{x}_{ij} = \begin{pmatrix} x_{aa} & 0 & 0 \\ 0 & x_{bb} & 0 \\ 0 & 0 & x_{cc} \end{pmatrix}.$$  

Above $T_N$(Sm) the magnetic symmetry of the crystal is incompatible with a ME effect because of the presence of space inversion in the magnetic symmetry group. Also does the ME effect vanish once a critical field is reached.

In Fig. 6 the field dependence of $P_x$ is shown in magnetic fields perpendicular to the ferromagnetic rare-earth planes and therefore parallel to the spins. In accordance with Eq. (9) the ME signal becomes for small magnetic fields a linear function of the magnetic field but the ME effect to thermal broadening [16]. The much better resolution of the spin-flip transition in the ME measurements allows a detailed measurement of the $H_c(T)$-phase diagram.

3.3. Sm$_2$CuO$_4$

The compound Sm$_2$CuO$_4$ does also, like Gd$_2$CuO$_4$, belong to the family of high-$T_c$ superconductors with electron-type conductivity. Unlike Gd$_2$CuO$_4$, Sm$_2$CuO$_4$ does become superconducting under doping. In this case it is the possible influence of the magnetic ordering of the rare earth subsystems onto the superconducting state which has attracted attention to the magnetic subsystem of this compound and an investigation of the upper critical field $H_{c2}$ of Sm$_{1.85}$Ce$_{0.15}$CuO$_4$ gives indications for such an influence [18, 19]. In Sm$_2$CuO$_4$ we have also

![Fig. 4. The electric polarization $P_x$ of Gd$_2$CuO$_4$ versus magnetic field $H \parallel z$ at three different temperatures (the curves have been shifted correspondingly).](image)

![Fig. 5. Magnetization of Gd$_2$CuO$_4$ versus magnetic field $H \parallel z$ at the indicated temperatures.](image)

![Fig. 6. The electric polarization $P_x$ of Sm$_2$CuO$_4$ versus magnetic field $H \parallel z$ at 5.40 K.](image)
disappears reaching a critical field while a residual electric polarization remains. This polarization is left unchanged for decreasing magnetic fields. This net ferroelectric moment at zero magnetic field is only compatible with the lower magnetic symmetry of $m'm'$. The curves have been measured at 5.40 K which represents $T = 0.94T_N$ ($T_N$ was found to be 5.77 K) and a transition is clearly observable.

4. Conclusion

The experimental results presented for the ME effect for the antiferromagnets Cr$_2$O$_3$, Gd$_2$CuO$_4$ and Sm$_2$CuO$_4$ have shown that the magnetic-field-induced ME effect contains detailed information about the magnetic ground state and the behaviour of a magnetic system in strong magnetic fields. Due to the fact, that the ME effect in antiferromagnets is related to the antiferromagnetic order parameter makes this technique a valuable tool to study magnetic systems. In high magnetic fields these information about magnetic phase transitions are difficult to obtain with other techniques.

References