Effect of a magnetic field on the ferroelectric domain structure of $TbGd(MoO_4)_3$

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(Submitted 27 January 1992; resubmitted 25 February 1992)
Pis'ma Zh. Eksp. Teor. Fiz. **55**, No. 6, 353–357 (25 March 1992)

A pulsed magnetic field can change the electric polarization along the [001] direction of a single crystal of the metastable, orthorhombic, ferroelectric, ferroelastic β' phase of the mixed terbium–gadolinium molybdate, $TbGd(MoO_4)_3$. This change has been measured. The length of the field pulses was 0.01 s. Their strength was varied up to 100 kOe. The measurements were carried out at 78 K for various orientations of the field in the (001) plane. In certain orientations, the magnetic field alters the ferroelectric domain structure of the sample.

The $TbGd(MoO_4)_3$ single crystal was grown by the techique described in Ref. 1. This material has the symmetry space group Pba2, the symmetry point group mm2, and ferroelectric and ferroelastic properties. Although we did not have access to data on the temperature of the transition to the paraelectric phase (space group $P\bar{4}2m$,

 0021-3640/92/060356-06$03.00

point group $\bar{4}2m$) of $TbGd(MoO_4)_3$, we do know the ferroelectric Curie temperatures for $Gd_2(MoO_4)_3$ and $Tb_2(MoO_4)_3$. These temperatures are 159 °C and 160 °C, respectively.[2] The test sample was a (001)-cut plane-parallel plate 1 mm thick in the form of an equilateral octagon. The distance between opposite sides was 9 mm. In the original state, the sample contained a large number of structural domains of two types, with different orientations of the [100] and [010] axes. The spontaneous-polarization vectors in the domains were antiparallel and ran along the [001] axis.[2] In cases of this sort, x-ray measurements reveal no more than two perpendicular directions along which the [100] and [010] axes of the different structural domains may lie. We denote these directions by X and Y (Fig. 1).

The crystal structure of rare-earth molybdates is sensitive to stress in the basal plane. The [100] and [010] axes differ in length; specifically, the [010] axis is slightly longer than the [100] axis. Compression along the [010] axis changes the crystal structure. The ferroelectric domains in which the [100] axis is oriented along the compression direction become preferred from the energy standpoint. They grow, at the expense of the less-favored domains, in which the [010] axis is oriented along the compression direction.[2]

Before the measurements, the sample was put in a single domain by compression along the X direction. This process was monitored visually in polarized light. This single-domain state persisted after the compression was ended. The volume fraction of the part of the sample which was not in the single-domain state was less than 1%.

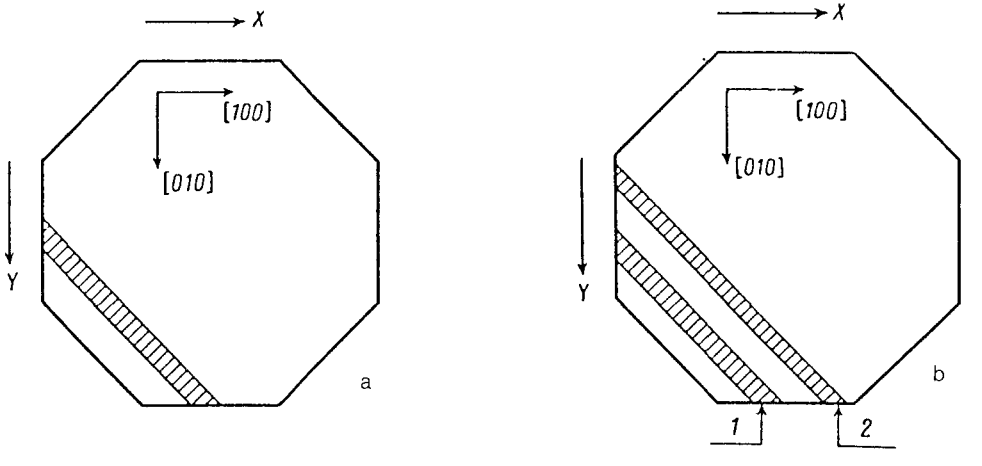

FIG. 1. Schematic diagram of the structural domains with a reversed electric polarization which arise in a single-domain $TbGd(MoO_4)_3$ when a magnetic field is applied. a: Domain structure after the first magnetic field pulse. The unhatched part of the octagon shows the initial, single-domain state of the sample. The arrows show the crystallographic directions of the original single-domain state. The hatched region represents the reverse domain. The [100] and [010] axes are rotated through 90° in the hatched region. The [001] axis and the electric polarization vector are reversed. b: Domain structure after the second magnetic field pulse. 1—Reverse domain which arises after the first pulse; 2—reverse domain which arises after the second pulse.

Consequently, the X direction coincided with the [100] crystallographic axis before the measurements were begun.

We measured the electric polarization P along the [001] direction in a pulsed magnetic field. This field was oriented in various directions: along X, along Y, and along the bisector of the angle between the two. The measurement procedure is described in Ref. 3.

Figure 2a shows the time evolution of the magnetic field. Figure 2b shows the corresponding time evolution of the electric polarization at a temperature of 78 K for

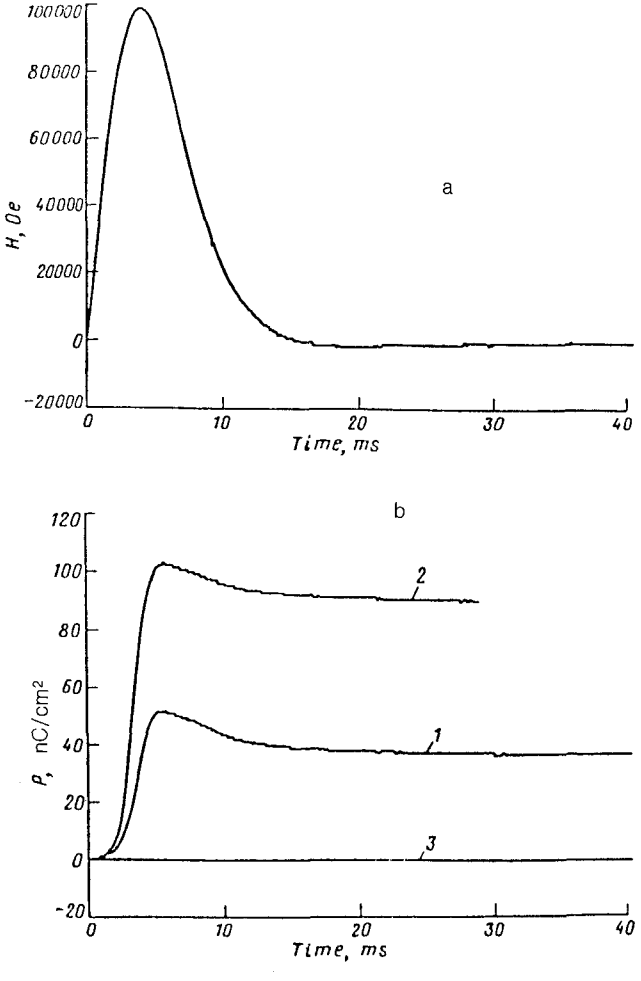

FIG. 2. a: Time evolution of the magnetic field. b: Time evolution of the electric polarization induced by the magnetic field in the single-crystal $TbGd(MoO_4)_3$ sample, along the [001] direction, at 78 K. 1—The field is parallel to the X direction, and this is the first field pulse; 2—the field is parallel to the X direction, second pulse; 3—the field is parallel to the bisector of the angle between X and Y. c: Time evolution of the polarization. The field is parallel to Y. The labels show the order in which the curves were recorded.

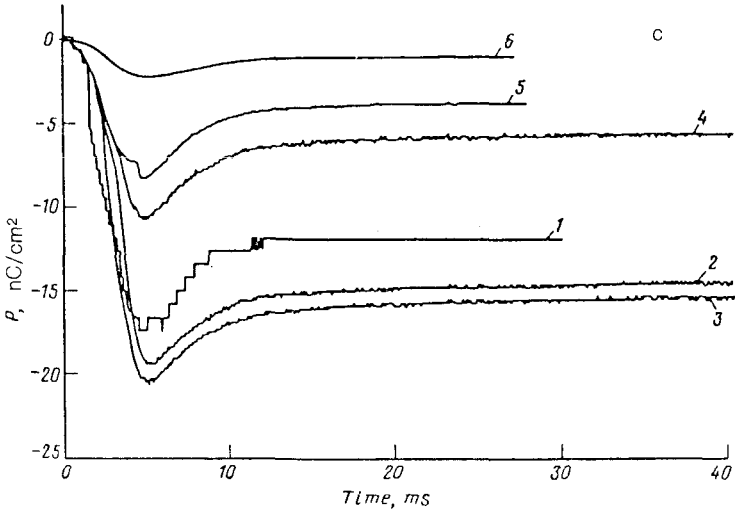

FIG. 2. (*Continued*)

various field orientations. Curves 1 and 2 were measured in a field parallel to X. Curve 1 was measured in the single-domain sample, i.e, in a field parallel to [100]. We see that the polarization lags noticeably behind the field in time. In a field of 100 kOe, the change in the polarization is greater than 50×10^{-9} C/cm^2. As the field is reduced to zero, the polarization does not vanish. The remanent polarization is 40×10^{-9} C/cm^2. This behavior corresponds to the appearance of a reverse domain in the sample. The area of the latter domain amounts to about 10% of the total area of the sample if we assume that the spontaneous polarization of the sample at 78 K is not greatly different from that of $Tb_2(MoO_4)_3$ at 298 K ($P_S = 180\times10^{-9}$ C/cm^2; Ref. 4).

After curve 1 was measured, the sample was removed from the apparatus and examined visually in polarized light. Because of the field, the sample was no longer in a single-domain state. Its domain structure is shown schematically in Fig. 1a. The unhatched part of the octagon here shows the initial, single-domain state. The hatched part shows the reverse domain, i.e., that part of the sample in which the magnetic field caused an irreversible change in structure, accompanied by a reversal of the electric polarization. The boundaries of the domain lie in the $(1\bar{1}0)$ plane. The area of this domain is less than 10% of the area of the sample. This figure agrees well with that found from the polarization measurements.

After the sample was inspected, it was put back in the detector, and the field was applied again. The change in the electric polarization which occurred in this case is shown by curve 2 in Fig. 2b. This curve is qualitatively similar to curve 1. The corresponding domain structure is shown schematically in Fig. 1b. We see that the reverse domain which arose after the first field pulse is still here, and now there is a second, similar domain.

The field was then directed along the bisector of the angle between X and Y. The

corresponding $P(t)$ dependence is shown by curve 3 in Fig. 2b. The change in the polarization was well below 10^{-10} C/cm^2. The measurements on the single-domain sample in this orentation yielded the same result, within the experimental errors. After curve 3 was measured, the sample was reexamined in polarized light. No changes in the domain structure were observed.

The field was then directed along Y. The results of these measurements are shown in Fig. 2c. The numbers of the curves are the order in which they were recorded. The change in the polarization is negative; the maximum absolute value of the change is 20×10^{-9} C/cm^2. The repeated application of the pulsed field caused this value to decrease to 1×10^{-9} C/cm^2 (curve 6 in Fig. 2c). Examination in polarized light revealed that the sample was in a single-domain state after this treatment.

The steps on the curves in Fig. 2 are an instrumental effect, stemming from our use of digital oscilloscopes, with only 8-bit analog-to-digital converters.

These experiments thus showed that at 78 K a magnetic field alters the electric polarization and the domain structure of $TbGd(MoO_4)_3$.

One possible explanation of this effect can be found from two well-known experimental facts.

The first, which we have already mentioned, is that compression along the [010] axis (or extension along the [100] axis) makes the ferroelectric domains with different orientations of these axes nonequivalent from the energy standpoint. The domains which are favored from the energy standpoint grow at the expense of the less-favored domains.

The second fact is that all the rare-earth metals and compounds comprising them, which have been studied to date, have huge magnetostrictive deformations, on the order of 10^{-4}–10^{-3}, even in the paramagnetic state.[5–9] Large values of the magnetostriction stem from a nonzero orbital angular momentum of 3^+ ions. Gadolinium is an exceptional case. The 3^+ gadolinium ion has a zero orbital angular momentum, and the magnetostriction of metallic gadolinium and its compounds is lower by two orders of magnitude than that for other rare earths. The ions of the rare-earth elements usually retain their individuality in various compounds.[5]

It was shown in Refs. 10 and 11 that the magnetic properties of the molybdates of terbium and gadolinium are determined by the 3^+ ions of terbium and gadolinium.

There is thus every reason to suggest that the rare-earth molybdates are not exceptional cases and that large magnetostrictive deformations arise in them. If so, we see why the effect of a magnetic field, which leads to the appearance and growth of new structural domains, is analogous to the effect of mechanical deformation. For example, the effect of a negative magnetostrictive deformation along the [010] axis on our sample is completely analogous to the effect of mechanical compression. We used compression to put the sample in a single-domain state before the beginning of the experiment. A positive magnetostrictive deformation along the [100] axis should have precisely the effect on the domain structure which we observe experimentally.

Magnetostrictive deformation at the beginning of the experiment (curves 1 and 2 in Fig. 2b; the field is parallel to X) promote the growth of ferroelectric domains with

the reversed polarization. At the end of the experiment (curves 1–6 in Fig. 2c; field along Y), these deformations annihilate domains with the reversed polarization.

As a boundary moves through a sample, it may encounter barriers. The applied field may not be strong enough to overcome these barriers. For this reason, the fraction of the sample which has undergone restructuring may vary with the defect structure of the sample. Clearly, this is a random factor. If a complete polarization reversal of the sample had occurred in a field parallel to the X axis in our experiments, the value of the polarization on curve 2 in Fig. 2b would have been on the same order of magnitude as that for curve 6 in Fig. 2c, with the opposite sign. Visual observation of the domain structure revealed that the polarization reversal of the sample was not complete. This result might be due to the presence of fairly high potential barriers in the path of the domain walls—barriers which could not be overcome under our experimental conditions (i.e., for the particular quality of the sample, for the particular magnetic field strength, and for the particular temperature). When a domain structure reaches a potential barrier which it cannot surmount under the given conditions, it comes to a stop, and visual inspection reveals that the sample is in a state of a partial polarization reversal. The opposite polarization reversal in this sample went to completion, i.e., to the point that the initial single-domain state was restored.

We wish to thank V. A. Borodin, S. N. Rossolenko, I. S. Pet'kov, I. M. Shmyt'ko, and I. K. Bdikin for useful discussions and for assistance in the preparation for the experiments.

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Translated by D. Parsons