Magnetostriction of paramagnetic terbium molybdate in fields up to 150 kOe

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The magnetostriction of a single-crystal sample of the metastable, ferroelectric, ferroelastic, orthorhombic β' phase of $Tb_2(MoO_4)_3$ has been measured at 78 K in pulsed magnetic fields up to 150 kOe. In fields from 80 to 100 kOe directed along the [100] axis, a strain on the order of 6×10^{-3} arises because of a switching of the spontaneous electric polarization.

The material studied in these experiments is the metastable orthorhombic β' phase of $Tb_2(MoO_4)_3$. Its symmetry space group is *Pba*2, its point group is *mm*2, and it is ferroelectric and ferroelastic. Its ferroelectric Curie point is $T_C = 160°C$.[1] At $T < T_N = 0.45$ K, an antiferromagnetic order arises.[2]

The test sample was a cube with dimensions of $2.5\times2.5\times2.5$ mm, with sides parallel to the [110], [1$\bar{1}$0], and [001] crystallographic axes. In its initial state the sample contained a large number of structural domains of two types, differing in the orientation of the [100] and [010] axes. The spontaneous polarization vectors in the domains were antiparallel, directed along the [001] axis.[1] In such cases, the x-ray method can tell us only two mutually perpendicular geometric directions along which the [100] and [010] axes of the different structural domains may be oriented. We call these the X and Y directions.

The crystal structure of rare-earth molybdates is sensitive to a stress in the basal plane. The lattice constants along the [100] axis (a) and the [010] axis (b) are different, with $b > a$. A sufficiently strong compression along [010] causes a change in the twin structure: Ferroelectric domains with [100] axis along the compression direction become favored from the energy standpoint and grow at the expense of the less favored domains, in which the long [010] axis is oriented along the compression direction.

Before the measurements, the sample was subjected to compression along the X direction to cause saturation of the domain structure. This process was monitored visually in polarized light. The single-domain state persisted after the compressional stress was ended. The X direction thus coincided with the [100] crystallographic axis before the measurements were begun.

The magnetostriction was measured by the procedure described in Ref. 3. The length of the magnetic field pulse was 0.01 s. The measurements were carried out at a temperature of 78 K. The strain was measured by a thin (0.1-mm) X-cut quartz piezoelectric plate cemented to the sample. The potential difference which appeared

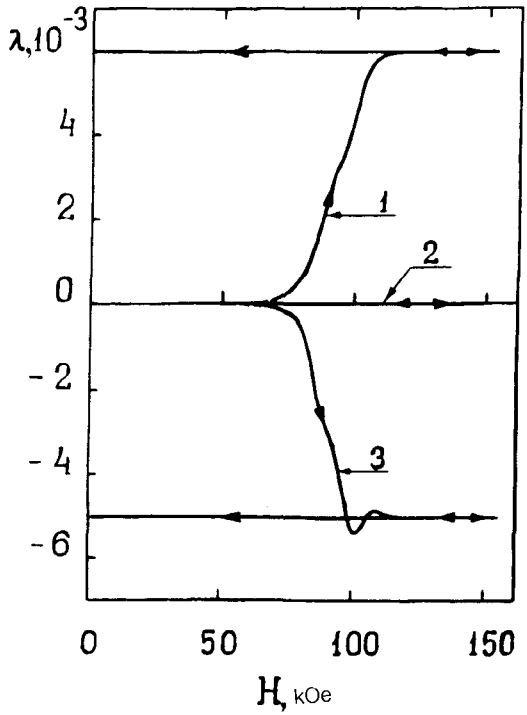

FIG. 1. Magnetostrictive strain along the geometric X direction in a $Tb_2(MoO_4)_3$ sample versus the magnetic field for various orientations of this field, at 78 K. *1*—The field was along the X direction, this was the first application, and X was along the [100] axis; *2*—the field was along X, this was the second application, and X was along the [010] axis; *3*—the field was along Y, which coincided with the [100] axis.

across the electrodes on the quartz plate when the sample was strained was fed to an electrometer cascade with an input resistance which imparted a time constant on the order of 1 s to the input circuit. This time is much longer that the field pulse and ensures an essentially undistorted reproduction of the signal.

The position of the quartz gauge with respect to the sample was not changed during the experiment.

Figure 1 shows the field dependence of the magnetostriction. All three curves show the strain along the same geometric direction in the sample, which coincided with the [100] crystallographic axis (the X geometric direction) before the measurements. Curve *1* shows the magnetostrictive strain measured on a sample in its original state (the [100] axis coincides with X) in a magnetic field along X. In weak fields, the strain is zero at the sensitivity of these measurements. At 70 kOe there is a positive strain on the order of 10^{-4}–10^{-3}. Between 80 and 100 kOe the strain rises sharply, by $\Delta\lambda \simeq +6\times 10^{-3}$, and then reaches saturation, remaining constant up to 150 kOe. When the field is reduced to zero, the strain remains constant.

When the field in the given orientation is reapplied directly after the measurement of curve *1*, there is no strain along the geometric X direction. Curve *2* shows the field dependence of the magnetostriction along X upon the repeated application of a field directed along X. We see that the magnetostriction is zero at the sensitivity of these measurements.

After curve *2* was measured, the magnetic field was directed along the geometric

Y direction, and the magnetostrictive strain was measured along X. The results of these measurements are shown by curve *3*. The field dependence of the magnetostriction in this case is seen to be similar to that along the X direction during the first application of the field, but the sign is the opposite.

Two aspects of these results distinguish $Tb_2(MoO_4)_3$ sharply from ordinary paramagnets.

First, the magnetostriction of $Tb_2(MoO_4)_3$ is not only anomalously large but also a nonlinear function of the field. Such a large magnetostriction, with a strongly nonlinear field dependence, has not previously been seen in a paramagnetic material at such a high temperature ($T=78$ K $= 173T_N$).

Second, the magnetostriction does not arise during a repeated application of the field.

The reason for these results is that the source of the observed strain is not attributable exclusively or even predominantly to magnetostriction. The primary source is instead a change stimulated in the ferroelectric twin domain structure by the magnetostriction, with an interchange of the [100] and [010] axes . The magnetostrictive strain is playing the same role here as ordinary mechanical strain, whose effect was described above on the basis of data from a review.[1] Let us examine this case in more detail.

The magnetic properties of $Tb_2(MoO_4)_3$ are governed by Tb^{3+} ions.[2] These ions have a nonzero orbital moment, so the charge cloud of the magnetically active $4f$ electrons of these ions is spatially anisotropic. The orientation of this charge cloud is tied rigidly to the magnetic moment of the ion by the strong spin–orbit coupling. When the orientation of the magnetic moment of the ion is altered by a magnetic field, the anisotropic charge cloud of the $4f$ electrons thus also changes orientation, causing a deformation of the lattice (this is magnetostriction). The magnitude of the magnetostrictive deformation is on the order of 10^{-4}–10^{-3} in materials containing $3+$ ions of rare earths with a nonzero orbital moment (even in the paramagnetic state). These are well-known experimental facts.[4–6]

When the magnetic field is in the appropriate orientation, magnetostrictive strain can play the same role as is played by the ordinary mechanical strain which we used to saturate the domain structure of the sample.

When the magnetostriction reaches a certain critical level, those ferroelectric domains in which the long [010] axis is oriented along the direction of the positive magnetostriction become favored from the energy standpoint. These domains grow at the expense of the less favored domains, in which the short [100] axis is oriented along the extension direction.

If the magnetostrictive strain of the appropriate sign in a single-domain sample reaches a sufficiently high level, the [100] and [010] axes should thus trade places, and the direction of the spontaneous electric polarization should change by 180°.

Our previous study[7] of the magnetoelectric effect in $Tb_2(MoO_4)_3$ supports that explanation: It was established by direct visual observation that the magnetization of a ferroelectrically single-domain sample along the [100] axis leads to reversed ferro-

electric domains, and measurements of the electric polarization show that at a magnetic field of 100 kOe the spontaneous electric polarization vector reverses direction.

If this is indeed the case, then the [100] and [010] axes trade places in the measurement of curve *1*, leading to an elongation $\Delta\lambda$ along the X direction. This elongation should be $\Delta\lambda = (b - a)/a$ in order of magnitude.

In $Tb_2(MoO_4)_3$ at 300 K, the lattice constant along the [100] direction is $a = 10.352$ Å, and that along the [010] direction is $b = 10.381$ Å.[1] Upon an interchange of a and b axes, the strain is $\Delta\lambda(300\ \text{K}) = (b - a)/a = 0.029/10.352 \simeq 3 \times 10^{-3}$. This figure agrees in order of magnitude with the results of our measurements. Our experimental value $\Delta\lambda(78\ \text{K}) = 6 \times 10^{-3}$ is slightly larger than this figure. It is quite possible that the difference stems from thermal expansion.

In summary, after curve *1* is measured, the [010] crystallographic axis is along the geometric X direction, and the [100] axis is along Y. The absence of a magnetostriction upon repeated applications of the field after the measurement of curve *1* supports our explanation: If, after the measurement of curve *1*, the lattice remains unchanged, a repeated application of the field would lead to the same result as the first application. It follows that curve *3* describes the deformation along the [010] axis in a magnetic field parallel to the [100] axis. The negative sign of the deformation in this case agrees completely with experiments on the polarization reversal of $Tb_2(MoO_4)_3$ by mechanical compression along [010] and also with the results we found in Ref. 7: The negative magnetostrictive deformation along the [010] axis, caused by a field parallel to [100], switches the spontaneous electric polarization and causes the [100] and [010] axes to trade places. These effects are manifested in our measurements as a negative jump in the size of the sample along the geometric X direction, which coincides with the [010] axis before the application of the field.

It was not our purpose in this study to determine the critical magnetic field or the critical strain for switching. These topics will be pursued in the future.

We should point out that the shape of the steep section of the magnetostriction curve, which is associated with the growth of reversed ferroelectric domains, generally depends on the rate at which the field is increased. The reason is the rather slow motion of domain walls.

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