Magnetic-field-induced structural phase transition in the virtual Jahn–Teller elastic material $TmPO_4$

B. G. Vekhter, A. Z. Kazeĭ, M. D. Kaplan, and Yu. F. Popov
M. V. Lomonosov Moscow State University, 119899, Moscow

(Submitted 14 October 1991)
Pis'ma Zh. Eksp. Teor. Fiz. **54**, No. 10, 575–578 (25 November 1991)

A structural phase transition of a new type—a stimulated cooperative Jahn–Teller effect—has been observed experimentally and studied in rare-earth Jahn–Teller compounds. The type of transition, the order parameter, and the threshold magnetic field for this type of structural phase transition have been determined from measurements of the magnetostriction of the virtual Jahn–Teller elastic material $TmPO_4$ along various crystallographic directions in a pulsed magnetic field.

In rare-earth Jahn–Teller systems, an external magnetic field has a pronounced effect on a structural phase transition, i.e., on the transition temperature and the other parameter. The magnitude and nature of the effect are determined by the symmetry of the wave functions and by the spectrum of low-lying electronic states of the rare-earth ion in the crystal field. The effect of a magnetic field on systems with the simplest enery spectrum, consisting of an isolated orbital doublet ($TmVO_4$; Ref. 1) or two Kramers doublets separated by a gap ($DyVO_4$; Refs. 2 and 3), has now been studied in some detail for the special cases of rare earth compounds with the zirconium structure.

The most complex and at the same time the most interesting case, on the other hand, is that of a four-level singlet-doublet-singlet system, like that in (for example) the virtual Jahn–Teller elastic material $TmPO_4$. The behavior of a system of this type is known to be governed by the ratio A/Δ, where Δ is the gap between the ground singlet and the excited doublet, and the parameter A describes the Jahn–Teller correlations between the rare-earth ions.[4] For the Tm^{3+} ion in $TmPO_4$, this ratio is $A/\Delta = 0.67$; a structural phase transition therefore does not occur in $TmPO_4$ in the absence of a magnetic field.[5] An external magnetic field in the orientation $H \| [100]$ alters the spectrum and wave functions of the Tm^{3+} ion in such a way that the ratio A/Δ increases. At a certain critical field, the necessary condition for the structural phase transition becomes satisfied. This is the physical reason why an external magnetic field can induce a structural phase transition in compounds of this sort.

An unusual behavior of Jahn–Teller elastic materials with a singlet-doublet-singlet system of electronic levels in an external magnetic field has been predicted[6] theoretically for rare-earth compounds with the zirconium structure. More generally, a magnetic field stimulates a structural phase transition in such systems; i.e., it raises the temperature of the phase transition, without smearing the transition (in this regard, these systems are fundamentally different from systems of the $DyVO_4$ type). In this letter we are reporting an experimental study of this problem in the particular case of the virtual elastic material $TmPO_4$.

We studied the magnetostriction of the $TmPO_4$ crystal along various crystallographic directions in pulsed magnetic fields at liquid-helium temperatures. The $TmPO_4$ single crystals, with dimensions of $2\times1\times1$ mm, were grown by spontaneous crystallization from a molten solution with the help of a lead pyrophosphate flux. The crystals were oriented within $\sim1°$ by an x-ray method. The experimental geometry is shown in Fig. 1. The magnetostrictive deformation (extension–compression) U was measured with quartz piezoelectric gauges 3 (thin silver-plated quartz plates cut perpendicular to the x axis, with the pressure-sensitive axis along the y axis in the plane of the plate), cemented in the appropriate way to the crystal (1). The crystal was mounted on a holder (2), which made it possible to vary the orientation of the magnetic field H with respect to the crystal axes. The signal which appeared across the electrodes on the quartz, V, in a pulsed magnetic field was displayed on an oscilloscope screen.

Measurements on paramagnetic crystals in pulsed magnetic fields at liquid-helium temperatures are complicated by the heating of the sample which results from a magnetocaloric effect. We estimated the extent of the heating of the sample by comparing the magnetizations measured in pulsed and static magnetic fields. For rare-earth zirconia, with H oriented along the maximum value of the g-factor, the heating of the sample for a 100-kOe field pulse amounts to $\sim(2–3)°$ and has no fundamental effect on the experimental results.

Figure 2 shows $U(H)$ for a $TmPO_4$ crystal along the [110] axis for the case in which H is directed approximately along the [100] axis, at $T=4.5$ K (the experimental geometry is shown in Fig. 1 and also in the inset in Fig. 2), at two angular deviations of the magnetic field. Note the unusual behavior of $U(H)$ for this geometry: The magnetostriction does not exceed 10^{-4} in fields below the critical field $H_c\simeq50$ kOe, while it increases sharply at $H>H_c$, reaching a huge value $\sim10^{-3}$. The magnitude

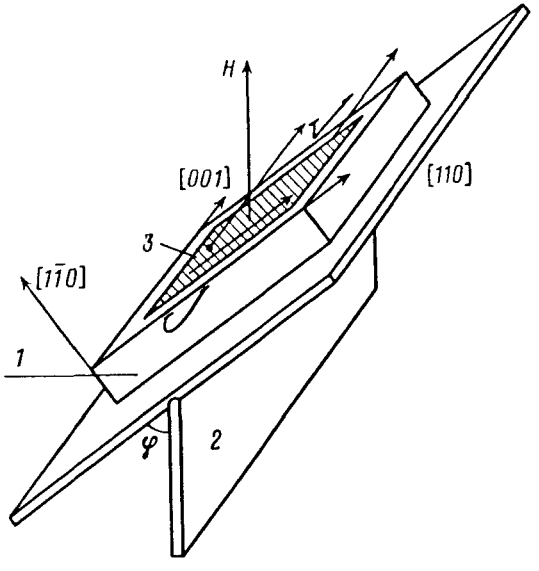

FIG. 1. Experimental geometry. 1—Test sample; 2—sample holder; 3—quartz piezoelectric gauge (the arrow indicates the direction of the pressure sensitivity of the transducer).

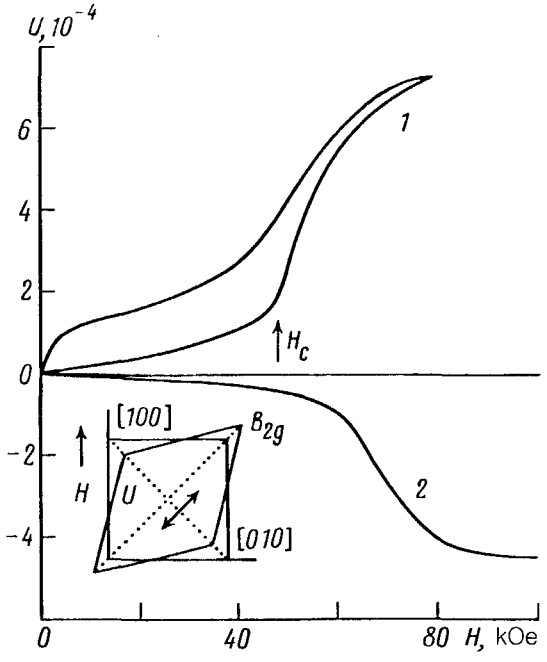

FIG. 2. Field dependence of the extension–compression deformation of the $TmPO_4$ crystal along the [110] axis for the case in which the magnetic field is oriented nearly along the [110] axis, at various angular deviations $\Delta\varphi$ from this axis. 1—$\Delta\varphi > 0$; 2—$\Delta\varphi < 0$ (Fig. 3).

and sign of U depend strongly on the angular deviation of the magnetic field from the [100] axis. When the sign of this deviation is changed, the sign of the magnetostriction changes. For the same field orientation, $H \| [100]$, the magnetostriction along the [100] direction is lower by two orders of magnitude ($U \sim 10^{-5}$), consistent with the results of measurements in static fields.[7]

The symmetry of the magnetostrictive deformation induced by a magnetic field $H \| [100]$ is crucial to an interpretation of the experimental results. In tetragonal zirconia, the interaction of Jahn–Teller ions with deformations and phonons of B_{1g} and B_{2g} symmetry is predominant. A deformation of the B_{1g} type corresponds to an orthorhombic deformation (extension) along the [100] or [010] axis. A deformation of the B_{2g} type corresponds to an orthorhombic deformation (extension) along the [110] or [$1\bar{1}0$] axis (in the original coordinate system of the crystal, a B_{2g} deformation is monoclinic). The experimental results show that with $H \| [100]$ the longitudinal magnetostriction (a B_{1g} deformation) is small, while the deformation along the [110] direction (a B_{2g} deformation) reaches the value of the spontaneous deformation during the structural phase transitions in rare-earth zirconia. The meaning here is that a magnetic field $H \| [100]$ actually causes a B_{2g} deformation in the *ab* plane, and the symmetry of the magnetostrictive deformation is not the same as the symmetry of the magnetic field. A B_{2g} deformation causes a very slight ($\sim U^2$) extension–compression deformation along the [100] direction, just as is observed experimentally.

In other words, an external magnetic field $H \| [100]$ not only causes a magneto-

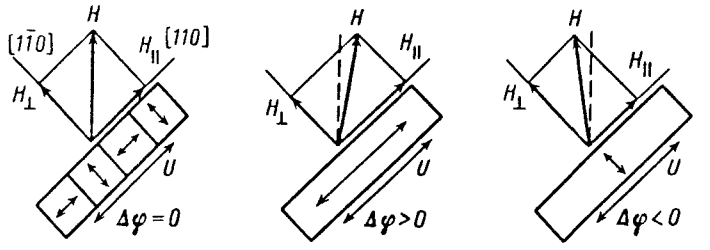

FIG. 3. Schematic diagram of the domain state of the $TmPO_4$ crystal in fields above the critical field H_c, for the case in which the magnetic field is oriented nearly along the [100] axis, for various values of the angular deviation of the field from this axis, $\Delta\varphi$.

strictive deformation but also induces a B_{2g} structural phase transition in $TmPO_4$. The type of transition is attributable to the fact that in $TmPO_4$ the interaction with B_{2g} deformations is predominant; the elastic constant C_{66}, which is the conjugate of the B_{2g} deformation, therefore undergoes a pronounced softening (by 80%) as the temperature is lowered.[8] At $H = 0$, however, the Jahn–Teller correlation parameter A is below the critical value, and the magnetic field gives rise to a more favorable electronic structure and induces a cooperative B_{2g} Jahn–Teller effect.

Confirmation for this interpretation comes from the strong dependence of the magnetostriction along [110] on the angular deviation of H from the [100] axis. The reasoning here is that in the course of a structural phase transition the crystal usually breaks up into Jahn–Teller or structural domains, and the magnitude and sign of the resultant deformation of the crystal depend on the actual domain structure.[2] The crystal can be put in a single-domain state by a weak magnetic field (~ 5 kOe) oriented along the spontaneous-deformation direction, i.e., along [110] or [1$\bar{1}$0] in our case.

When the magnetic field is oriented exactly along the [100] direction, the field projections onto the [110] and [1$\bar{1}$0] axes are identical. In addition, the distribution of domains is equiprobable, and the resultant macroscopic deformation of the crystal is much lower than the deformation in a domain (Fig. 3). If the angular deviation of the magnetic field from the [100] axis in the ab plane is small $\Delta\varphi \simeq (3-5)°$, a field $H_d = |H_{\parallel}| - H_{\perp}| \simeq \sqrt{2}H\Delta\varphi$, parallel or perpendicular to the direction in which the magnetostriction is measured tends to put the sample into a single-domain state. The crystal goes into such a state, with a magnetic easy axis (an axis with a maximum magnetic susceptibility) along the direction of the field H_d, which puts the sample in the single-domain state.

In summary, these experimental results show unambiguously that a magnetic field $H \| [100]$ induces a B_{2g} structural phase transition in the virtual Jahn–Teller elastic material $TmPO_4$. The nature of the $U(H)$ curve is determined to a large extent by the quality of the crystal and by the precision of the orientation. In the best case we observed a sharp, nearly discontinuous increase in $U(H)$ at a threshold field $H_c \simeq 50$ kOe. As the crystal quality is lowered, and as the precision of the orientation is lowered, the sharp change on the $U(H)$ curve becomes smeared. The value of the

critical field H_c agrees well with theoretical estimates derived for $TmPO_4$ in the mean-field approximation.[6]

The compound $TmPO_4$ is not the only crystal in which a stimulated structural phase transition can occur. Effects similar to those described above should be observed in dilute $Tb_xGd_{1-x}VO_4$ crystals. In this sytem, on can adjust the value of the parameter A/Δ at will by varying the concentration (x) of the Jahn–Teller Tb^{3+} ions, and one can thus carry out a more detailed study of this elegant physical effect: the magnetic-field-induced cooperative Jahn–Teller effect.

[1]A. H. Cooke, S. J. Swithenby, and M. R. Wells, Solid State Commun. **10**, 265 (1972).
[2]Z. A. Kazeĭ, Fiz. Tverd. Tela (Leningrad) **28**, 3194 (1986) [Sov. Phys. Solid State **28**, 1800 (1986)].
[3]R. T. Harley, C. H. Perry, and W. Richter, J. Phys. C **10**, L187 (1977).
[4]R. J. Elliott, R. T. Harley, W. Heyes, and S. R. P. Smith, Proc. R. Soc. A **238**, 217 (1972).
[5]K. D. Knoll, Phys. Status Solid B **45**, 553 (1971).
[6]B. G. Vekhter, V. N. Golubev, and M. D. Kaplan, Pis'ma Zh. Eksp. Teor. Fix. **45**, 136 (1987) [JETP Lett. **45**, 168 (1987)].
[7]I. A. Bondar', B. G. Vekhter, Z. A. Kazeĭ *et al.*, Zh. Eksp. Teor. Fiz. **94** (7), 288 (1988) [Sov. Phys. JETP **67**, 1460 (1988)].
[8]R. T. Harley and D. I. Manning, J. Phys. C **11**, L633 (1978).

Translated by D. Parsons