Effect of a magnetic field on the structural phase transition in the Jahn-Teller crystal $TmVO_4$

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The magnetostriction and thermal expansion of the Jahn-Teller crystal $TmVO_4$ have been measured over the temperature range within which a structural phase transition (PT) occurs. The experimental data we obtained indicate that the structural PT is suppressed by a magnetic field $\mathbf{H}\|[001]$. We also observed that fields $\mathbf{H}\|[110]$ have a strong effect on the thermal expansion and magnetostrictive characteristics of $TmVO_4$. From these facts we conclude that the observed peculiarities of the magnetoelastic properties of $TmVO_4$ crystals arise from two mechanisms: (1) reorientation of crystallographic (Jahn-Teller) domains in a magnetic field, and (2) "true" magnetostriction of single-domain crystals, whose large value is treated to softening of the elastic modulus C_{66} at the structural PT.

In rare-earth compounds with zircon structure RXO_4 (R = Tm, Tb, Dy; X = V, As, P) the large electron-phonon interaction gives rise to structural phase transitions (PT) due to the cooperative Jahn-Teller effect (CJTE). According to the theory presented in Refs. 1 and 2, this interaction is caused by the large magnetostrictive effects in Jahn-Teller (JT) crystals with zircon structure. In these crystals, the magnetostrictive characteristics will be qualitatively different, depending on whether the JT distortion-induced ordering and magnetic ordering enhance each other (e.g., in $DyVO_4$ or $TbVO_4$) or suppress each other (e.g., in $TmVO_4$ or $TmAsO_4$),[(1)] Magnetostriction in the first group of zircons was investigated recently for the case of $DyVO_4$ (Ref. 3); experimental studies of the magnetoelastic properties of the second group of zircons are lacking.

In this paper we present the results of thermal expansion and magnetostriction measurements made on single-crystal $TmVO_4$ for temperatures in the vicinity of the structural phase transition,[4] i.e., $T_c = 2.1$ K. Crystals of $TmVO_4$ were grown from solution in a melt, having average dimensions of $1\times1\times2$ mm^3. We measured the thermal expansion and magnetostriction in terms of $\Delta l(T)/l_0 = [l(T) - l_0]/l_0$ and $u = \Delta l(T,H)/l_0$, respectively, where l_0 is the length of the crystal along the measurement direction for $H = 0$ and $T = 6$ K, i.e., in the undistorted tetragonal phase.

To make the measurements, we used an apparatus with a capacitive strain pickup, including a cryogenic generator (frequency ~ 1.5 MHz) in the oscillating circuit loop. Temperatures in the range 1.7 K and to 6 K were measured with a carbon resistance thermometer. The external magnetic field was created by two superconducting magnetic systems, allowing us to apply a field parallel ($H\leqslant 40$ kOe) and perpendicular ($H\leqslant 25$ kOe) to the measured deformation.

In Fig. 1 we show the temperature dependence of the relative thermal expansion of the $TmVO_4$ crystal along the [110] axis; this is the direction of the spontaneous rhombic distortion of the lattice, which appears as a consequence of the CJTE below T_c. It is clear that for $H = 0$ (Fig. 1a) anomalies are observed in the dependence of $\Delta l(T)/l_0$ due to the structural PT. The PT temperature determined from the maximum of the sample's coefficient of linear expansion $-\alpha = [d\Delta l(T)/dT]/l_0$, was found to be $T_c = (2.15 \pm .05)$ K. This value agrees well with the value of T_c determined previously in Refs. 6–8.

Above T_c, up to $T\approx 3T_c$ the function $\Delta l(T)/l_0$ exhibits a noticeable "tail," indicating the presence of a considerable tetragonal distortion in the $TmVO_4$ crystal lattice above T_c, Because the characteristics of the λ-anomaly[6] in the specific heat of $TmVO_4$ suggest that contributions from any short-range order effects are insignificant for $T\gtrsim T_c$, it is reasonable to assume that the tail observed in $\Delta l(T)/l_0$ is related to elasticity-induced deformations (EID) of B_{2g} symmetry. In our view, one specific cause of this deformation could be a small uniaxial stress arising as a result of gluing the crystal onto the measuring capacitor. Actually, near T_c even an insignificant mechanical stress applied to the sample can significantly affect the physical JT properties of the crystal, due to the considerable softening of the elastic moduli.[8]

Experiments show that the sign of the anomaly in $\Delta l(T)/l_0$ and its magnitude depend on the details of the sample's division into crystallographic (JT) domains below T_c. These domains are regions in which equivalent rhombic axes, e.g., a' ($a' < b'$) are directed along the various twofold axes in the basal plane of the tetragonal unit cell of the crystal. We note that in $TmVO_4$ the rhombic axes a' and b' are rotated at angle 45° relative to the a and b axes of the undistorted tetragonal lattice. In particular, for the sample used to make the measurement presented in Fig. 1, the b' axis of most domains was oriented along the direction of measurement Δl.

Figure 1b illustrates the suppression effect on the structural PT due to a magnetic field $\mathbf{H}\|[001]$. It is clear that the field noticeably decreases the value of the lattice deformation in $TmVO_4$ near T_c, and lowers the PT temperature, which agrees qualitatively with previous measurements of the magnetic[6] and elastic[7] properties of $TmVO_4$ crystals.

However, our observations, indicating that a magnetic field $\mathbf{H}\|[110]$ can have a strong effect on the thermal expan-

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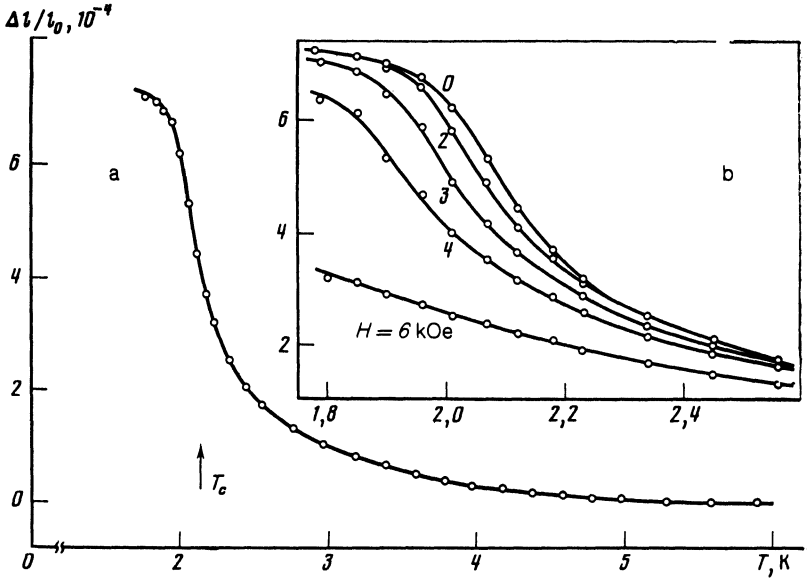

FIG. 1. Thermal expansion of the crystal $TmVO_4$ along the [110] axis for $H = 0$ (a) and in an external magnetic field $\mathbf{H}\|[001]$ (b).

sion of $TmVO_4$, were quite unexpected. The reason this is surprising is that the magnetic susceptibility in the basal plane of $TmVO_4$ is almost two orders of magnitude smaller than along the c-axis: from data in Ref. 6. $\chi_a = \chi_b \approx 0.025\chi_c$ at 4.2 K. Nevertheless, as follows from our measurements (Fig. 2), cooling the crystal in a field $\mathbf{H}\|[110]\|\Delta l$ decreases the value of the positive anomaly in $\Delta l(T)/l_0$, while in a field $\mathbf{H}\|[110]\perp\Delta l$ cooling increases it. This implies that in $TmVO_4$ the field $\mathbf{H}\|\langle 110\rangle$ gives rise to a preferred orientation of the a' axes of domains lying along the field direction.

We will assume that a magnetic field gives rise to these effects as a consequence of the following mechanism: axes a' and b', which are equivalent in the tetragonal $TmVO_4$ lattice, become nonequivalent in the rhombic phase (below T_c). Hence, the magnetic susceptibility becomes anisotropic in the basal plane perpendicular to the [001] axis, i.e., $\chi_{a'} \neq \chi_{b'}$. When $H = 0$, the energies of the two types of domains—$a'\|[110]$ and $a'\|[1\bar{1}0]$—are equal, and occur with equal probability. In a field $\mathbf{H}\|\langle 110\rangle$ the energy is smaller for those domains with the larger χ along the field; therefore a field $H \neq 0$ will assist in establishing a preferred domain orientation. When $\mathbf{H}\|[110]\|\Delta l$, the anomaly in $\Delta l(T)/l_0$ is negative; this implies that the magnetic field will align the short axis a' of the domains along the measurement direction Δl, i.e., for $TmVO_4$ below T_c, the case $\chi_{a'} > \chi_{b'}$ obtains.

Let us now consider the results of magnetostriction measurements on $TmVO_4$. In Fig. 3, we show isotherms of the transverse magnetostriction ($u_\perp$) for $\mathbf{H}\|[001]$ and

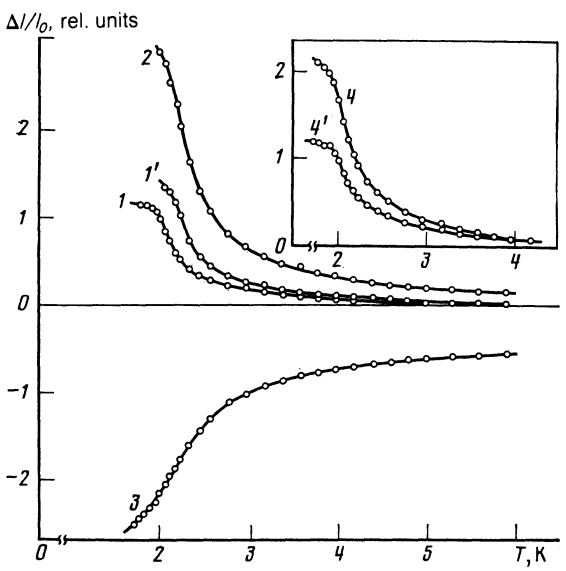

FIG. 2. The effect of a magnetic field on the thermal expansion of $TmVO_4$ along the [110] axis: 1—$H = 0$, 1'—the same function after cooling the crystal in a field $\mathbf{H}\perp\Delta l(H = 20$ kOe), 2—$\mathbf{H}\|[110]\perp\Delta l(H = 20$ kOe), 3—$\mathbf{H}\|\Delta l(H = 40$ kOe), 4—$h = 0$, 4'—the same function after cooling in a field $\mathbf{H}\|\Delta l(H = 40$ kOe). Curves 1 and 4 correspond to two different experiments.

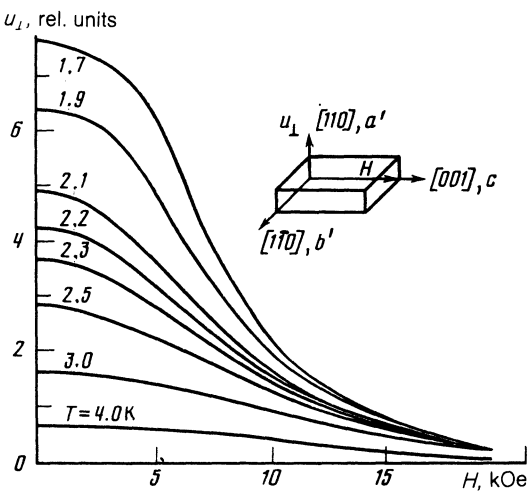

FIG. 3. Isotherms of the transverse magnetostriction of $TmVO_4$ ($\mathbf{H}\|[001], \Delta l\|[110]$) and the measurement geometry. The variation of $u_\perp$ with temperature for $H = 0$ reflects the thermal expansion of the sample.

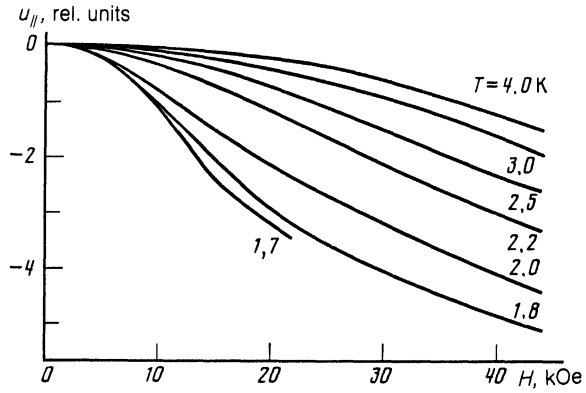

FIG. 4. Isotherms of the longitudinal magnetostriction ($\mathbf{H}\|[011]\|\Delta l$).

$\Delta l\|[110]$, For $T<T_c$, we observe a sharp increase in $u_\perp$ along the isotherms, connected with the restoration of the tetragonal phase in a magnetic field $H_c(T)$. We note that the signs of the jump in the magnetostriction as H increases and the thermal expansion as the crystal is cooled below T_c are different, i.e., the magnetic field causes the reverse transition from the rhombic to the tetragonal phase. The reestablishment of tetragonal symmetry by a magnetic field for $T<T_c$ is due to the fact that the magnetic energy of the undistorted phase is smaller than that of the distorted phase. Therefore, for a certain magnetic field H_c at which the difference in magnetic energies of the two phases equals the energy lowering due to the CJTE in the crystal, the tetragonal phase becomes energetically favorable.

From Fig. 3, it is clear that the PT in a magnetic field has a "washed out" character and differs significantly from the behavior predicted by theory for the function $u_\perp(H)$. In particular, according to Ref. 1, for $T<T_c$ the magnetostriction coefficient $D_\perp = du_\perp/dH \to \infty$ as $H\to H_c$, and $D_\perp = 0$ for $H>H_c$; for $T>T_c$, $D_\perp = 0$. A possible cause of the discrepancy between theory and epxeriment is the presence in the crystal of an EID for $T>T_c$, which is indicated by the thermal expansion data in this paper.

The field dependence of the longitudinal magnetostriction $u_\parallel$ measured in the geometry $\mathbf{H}\|[110]\|\Delta l$ is presented in Fig. 4. The longitudinal magnetostriction of $TmVO_4$ in a field $H = 40$ kOe at $T = 1.8$ K can be quite large (for a paramagnet): $u_\parallel \sim 10^{-3}$. As the temperature rises, $u_\parallel$ decreases; however, it stays rather large even when $T>T_c$. Only in the region $T\approx 3T_c$, where the contribution from the EID becomes insignificant, does the magnitude of the magnetostriction drop below 10^{-5}. We also note the characteristic dependence of $u_\parallel(H)$, which in the $TmVO_4$ crystals we investigated has a tendency to saturate for temperatures $T<T_c$.

We can explain the magnetostriction $u_\parallel$ by invoking two possible mechanisms. The first one is reorientation of JT domains in the magnetic field, whose cause is the anisotropy of χ in the basal plane of the crystal arising from the CJTE. We note that the Tm^{3+} ion has a low-lying isolated doublet for $T>T_c$ or a quasidoublet for $T<T_c$ (the next excited level lies at a distance of $\sim 50\ cm^{-1}$), and its χ along the a' and b' axes is of Van Vleck form, i.e., is due to admixture of excited levels. Since the magnitude of χ in the basal plane is small, the field which reorients the domains is larger than, e.g., in $DyVO_4$ (Ref. 3), and even for $H = 40$ kOe the sample still has not reached the single-domain state. A second mechanism is "true" magnetostriction of a single-domain crystal along the easy-magnetization direction in the basal plane. This magnetostriction also has the Van Vleck form, and can attain appreciable values near T_c where the elastic modulus C_{66} softens.

In principle, the two contributions to magnetostriction in $TmVO_4$ mentioned above can be distinguished if we calculate the magnitude of the "true" magnetostriction, along with its dependence on H and T. However, such calculation are not available at this time. In our views, the basic contribution to magnetostriction in $TmVO_4$ for $\mathbf{H}\|[110]$ is given by reorientation of JT domains, because the magnetostriction is large only in the range of temperatures where a lattice distortion exists. In addition, the function $u_\parallel(H)$ below T_c has a tendency to saturate, which is characteristic of domain-related magnetostriction.

In conclusion, we note that the magnitude of the magnetostriction in $TmVO_4$ below T_c is of the same order of magnitude as the spontaneous lattice deformation caused by the CJTE. In the tetragonal phase, the magnetostriction is considerably smaller. In this regard, $TmVO_4$ differs qualitatively from zircons in which mutual enhancement of the JT and magnetic correlations occurs; in these compounds one observes the opposite situation, as measurements on crystals of $DyVO_4$ have shown.[3]

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[1)] In these compounds, the magnetic order appears in an external field, and is not due to dipole or exchange interactions.

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