

MAGNETISM
AND FERROELECTRICITY

Anomalies in Thermal Expansion of DyVO₄ Induced by Quadrupolar Ordering

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Abstract—The thermal expansion of the DyVO₄ crystal has been experimentally and theoretically investigated in the range of the Jahn–Teller structural phase transition. The manifestation of totally symmetric magnetoelastic interactions upon this transition has been studied for the first time. It is found that the temperature dependences of the unit-cell and thermal expansion parameters along the nonactive Jahn–Teller direction in the basal plane for the DyVO₄ crystal exhibit characteristic magnetoelastic anomalies at $T < T_c$ due to the ordering of quadrupole moments of Dy³⁺ ions. The magnetoelastic contributions of the totally symmetric $\epsilon^{\alpha 1}$ and $\epsilon^{\alpha 2}$ and symmetry-lowering ϵ^γ modes to the thermal expansion are calculated within the general crystal-field formalism. The total quadrupolar coefficient G^γ and magnetoelastic coefficient B^γ are determined from the spectroscopic and spontaneous deformation data. It is demonstrated that the thermal expansion of the DyVO₄ crystal in the tetragonal and orthorhombic phases is well described in the framework of the unified model using a common set of interaction parameters for both phases. © 2000 MAIK “Nauka/Interperiodica”.

1. It is well known that rare-earth oxide compounds RXO₄ (X = V, P, or As; R is the rare-earth ion) with a tetragonal zircon structure are characterized by considerable single-ion magnetoelastic and quadrupolar pair interactions. The interaction parameters for totally symmetric and symmetry-lowering modes were determined in detailed investigations of the thermal expansion and magnetostriction in the tetragonal phase with allowance made for all the features of crystal field [1, 2]. These interactions are responsible for appreciable magnetoelastic effects and, in a number of cases (TbVO₄, DyVO₄, and TmVO₄), bring about the spontaneous ordering of quadrupole moments of rare-earth ions [3], which is accompanied by the orthorhombic strain of a crystal lattice. In essence, such a quadrupolar ordering consists in the Jahn–Teller structural phase transitions in rare-earth zircons.

The low-symmetry phases in rare-earth zircons are usually treated on the basis of a model pseudospin Hamiltonian. This approach is applicable for describing only the dominant magnetoelastic effects arising upon ordering of quadrupole moments of rare-earth ions, but fails to carry out consistent comparative analysis of the low-symmetry and tetragonal phases. However, comparison of magnetoelastic interactions of different symmetry for the zircon structure demonstrates that totally symmetric interactions are not negligibly small [4] and also should lead to the magnetoelastic effects observed upon quadrupolar ordering. In particular, according to our investigations of TbVO₄ [5], the ordering of quadrupole moments of rare-earth ions is accompanied not only by an orthorhombic distortion of

the crystal structure, but also by a change in the volume and a change in the degree of lattice tetragonality. It is of special interest to examine similar magnetoelastic effects arising upon quadrupolar ordering in DyVO₄ and to compare these effects for two crystals with different types of lattice distortion.

2. The contribution of rare-earth ions to the thermal expansion in the tetragonal and orthorhombic phases in the presence of magnetic field can be calculated with the use of the Hamiltonian $H = H_{CF} + H_{ME} + H_Q + H_Z$, where H_{CF} is the crystal-field Hamiltonian, H_{ME} and H_Q describe the magnetoelastic and quadrupolar pair interactions in terms of the equivalent Stevens operators O_n^m , and H_Z represents the Zeeman coupling to the external magnetic field, that is,

$$H_{CF} = \alpha_J B_2^0 O_2^0 + \beta_J (B_4^0 O_4^0 + B_4^4 O_4^4) + \gamma_J (B_6^0 O_6^0 + B_6^4 O_6^4), \quad (1)$$

$$H_{ME} = -\alpha_J [(B^{\alpha 1} \epsilon^{\alpha 1} + B^{\alpha 2} \epsilon^{\alpha 2}) O_2^0 + B^\gamma \epsilon^\gamma O_2^2 + B^\delta \epsilon^\delta P_{xy}], \quad (2)$$

$$H_Q = -\alpha_J^2 (K^\alpha \langle O_2^0 \rangle O_2^0 + K^\gamma \langle O_2^2 \rangle O_2^2 + K^\delta \langle P_{xy} \rangle P_{xy}), \quad (3)$$

$$H_Z = g_J \mu_B J H, \quad \left(P_{xy} = \frac{1}{2} (J_x J_y + J_y J_x) \right). \quad (4)$$

In these relationships, α_J , β_J , and γ_J are the Stevens parameters; B_n^m are the crystal-field parameters (their

number for the tetragonal symmetry is equal to five); B^μ are the magnetoelastic coefficients; K^μ are the quadrupolar pair interaction constants; g_J is the Lande factor; J is the angular momentum operator for the rare-earth ion; and μ_B is the Bohr magneton. In the H_{ME} and H_Q Hamiltonians, only the actual invariants for the magnetoelastic effects under consideration are written in an explicit form. The ε -symmetry invariants are omitted, because in the absence of external stresses of the corresponding symmetry for DyVO_4 , they make no contribution.

The minimization of the free energy with the respect to the strains gives the equilibrium strains expressed in terms of observable quantities of the corresponding quadrupolar operators. The substitution of these equilibrium strains for the ε^μ strains in the magnetoelastic Hamiltonian makes H_{ME} similar to the H_Q Hamiltonian, and both terms can be reduced to the generalized quadrupolar Hamiltonian

$$H_{QT} = H_Q + H_{ME} \\ = -\alpha_J^2 (G^\alpha \langle O_2^0 \rangle O_2^2 + G^\gamma \langle O_2^2 \rangle O_2^2 + G^\delta \langle P_{xy} \rangle P_{xy}). \quad (5)$$

The total quadrupolar coefficients G^μ involves the contributions of the single-ion magnetoelastic interaction B^μ and the quadrupolar pair interaction K^μ

$$G^\mu = G_{ME}^\mu + K^\mu = \frac{(B^\mu)^2}{C_0^\mu} + K^\mu \quad (\mu = \gamma, \delta), \quad (6)$$

where C_0^μ is the lattice background elastic constant in the absence of interactions. Note that, for rare-earth zirconates, the single-ion magnetoelastic contribution G_{ME}^μ , as a rule, is dominant, and, in the absence of interaction through optic phonons, the relationship $K^\mu/G_{ME}^\mu = -1/3$ is valid for each mode [6].

In the H_{QT} Hamiltonian, the term $\alpha_J^2 G^\gamma \langle O_2^2 \rangle O_2^2$ corresponding to the strain of the $\gamma = (B_{1g})$ symmetry is nonzero only either in the presence of external factors, for example, the magnetic field along the [100] axis, or in a low-symmetry phase. In the latter case, there is the spontaneous phase transition followed by the ordering of the quadrupole moments of rare-earth ions $Q_2 = \alpha_J \langle O_2^2 \rangle = \alpha_J (1/Z) \sum_i \langle i | O_2^2 | i \rangle \exp(-E_i/k_B T)$, where E_i are the energy levels of a rare-earth ion that are calculated using the Hamiltonian $H = H_{CF} + H_{QT}$, and Z is the statistical sum. This implies that, at $T < T_c$, the thermal average of $Q_2(T)$, which is computed in a self-consistent manner, is nonzero in the absence of external magnetic field. The necessary condition of existing this quadrupolar ordering is a sufficiently large value of the total quadrupolar coefficient G^γ and also the appropriate electronic structure of a rare-earth ion with low-lying "quadrupolar" levels. It is these conditions for the

Q_2 quadrupole moment that are realized in DyVO_4 . The ordering of the Q_2 quadrupole moments is attended by the orthorhombic lattice distortion of the B_{1g} type, which is defined as

$$\varepsilon^\gamma = \alpha_J B^\gamma \langle O_2^2 \rangle / C_0^\gamma = A^\gamma Q_2 \quad (A^\gamma = B^\gamma / C_0^\gamma).$$

The contribution of rare-earth ions to the thermal expansion can be determined in the conventional way, i.e., by minimizing the free energy, involving magnetoelastic and elastic terms with respect to the strain tensor components. The calculations similar to those conducted in [1] demonstrate that, in the absence of external magnetic field, the contribution to the thermal expansion in the distorted phase along the tetragonal axis is associated only with the totally symmetric modes, namely, the isotropic $\varepsilon^{\alpha 1}$ and tetragonal $\varepsilon^{\alpha 2}$ modes. Moreover, along the [100], [010], and [110] axes, there is the contribution of the spontaneous orthorhombic strain ε^γ , which, for the nonactive Jahn-Teller direction [110] $\equiv a'$, is quadratic in the spontaneous strain, that is,

$$\frac{\Delta c_{ME}}{c} = A_1 \Delta Q_0, \quad \frac{\Delta a'_{ME}}{a} = A_2 \Delta Q_0 - \frac{3}{4} (A^\gamma Q_2)^2, \\ \frac{\Delta a_{ME}}{a} = A_2 \Delta Q_0 + \frac{A^\gamma Q_2}{\sqrt{2}}, \quad (7) \\ \frac{\Delta b_{ME}}{b} = A_2 \Delta Q_0 + \frac{A^\gamma Q_2}{\sqrt{2}},$$

where $Q_0(T) = \alpha_J \langle O_2^0 \rangle = \alpha_J (1/Z) \sum_i \langle i | O_2^0 | i \rangle \exp(-E_i/k_B T)$. The expressions for the A_1 and A_2 coefficients that depend on the magnetoelastic and elastic coefficients take the same form as for the tetragonal phase [1].

3. The experiments were performed with single-crystal samples. The crystals were grown from the melt in platinum crucibles by the well-known method of spontaneous crystallization from solution. The magnetoelastic anomalies in the thermal expansion of the DyVO_4 crystal upon structural phase transition were investigated using wire strain and capacity-type strain gauges. The relative accuracy of measurements was no worse than 10^{-6} . The measurements were carried out in the presence and absence of magnetic field, which made it possible to control the changes in the domain structure of the sample below the T_c temperature.

4. The lattice distortion and magnetoelastic anomalies of the parameters upon quadrupolar ordering in DyVO_4 are considerably less than those in TbVO_4 , which requires the use of more sensitive techniques. In order to investigate the orthorhombic strain of the B_{1g} symmetry $\varepsilon^\gamma = (b - a) / \sqrt{2} a_0$ (Fig. 1), the thermal expansion $\Delta l/l$ of the DyVO_4 crystal along the [100] axis was measured with a capacity-type strain gauge in

the magnetic field $H = 20$ kOe, which was parallel and perpendicular to the direction of measuring Δl . In this field, the crystal becomes single-domain with the easy magnetization axis aligned along the magnetic field. Therefore, the thermal expansion was measured along the orthorhombic a axis for $\mathbf{H} \parallel [100] \parallel \Delta l$ and along the b axis for $\mathbf{H} \parallel [010] \perp \Delta l$ (in the latter case, according to the standard setting for an orthorhombic structure, $a < b$). As can be seen from Fig. 1, the lattice in the absence of magnetic field undergoes a distortion at the temperature $T_c \sim 14$ K (see the inset in Fig. 1), and the orthorhombic strain ϵ^γ at $T = 0$ K is equal to 36.8×10^{-4} , which is in good agreement with the available data [7].

The anomaly in the thermal expansion of the DyVO₄ crystal along the [100] axis at $H = 0$ is equal to 7×10^{-4} , which is substantially less than the spontaneous lattice strain. This means that, in the absence of external magnetic field, the sample at temperatures below T_c is in a polydomain state and exhibits only a slight preferred orientation of the b axes of domains along the direction of measuring Δl . Note also the presence of an appreciable “tail” $\Delta l(T)/l$ at $T > T_c$. This suggests that there exists a distortion of the B_{1g} symmetry above T_c , likely, due to mechanical stresses. Earlier [8], similar effects were observed and discussed for the TmVO₄ crystal. The measurements of the thermal expansion in the magnetic field make it possible to stabilize the domain structure and to examine the temperature dependences of the spontaneous strain for a single-domain sample. However, the magnetic field leads to an increase in the transition temperature and a substantial extension of the transition range in the vicinity of T_c . This is consistent with both the results obtained by numerical calculations of the temperature dependence of the lattice distortion for the DyVO₄ crystal in magnetic field within the pseudospin formalism [9] and with our computations in the framework of the more general crystal-field formalism (cf. curves 1 and 2 in Fig. 1).

The anomalies observed in the unit-cell parameters $\Delta c/c$ and $\Delta a'/a'$ due to the $\epsilon^{\alpha 1}$ and $\epsilon^{\alpha 2}$ totally symmetric magnetoelastic modes upon quadrupolar ordering in the DyVO₄ crystal are substantially less than the ϵ^γ spontaneous orthorhombic strain and, hence, call for special conditions of observation against the background of effects associated with the reorientation of the Jahn–Teller domains. The thermal expansion $\Delta c(T)/c$ along the tetragonal axis of the DyVO₄ crystal was measured with strain gauges cemented in the $(a-c)$ and $(a'-c)$ crystal planes. Both dependences show a similar anomalous behavior, which manifests itself in an increase in the $\Delta c/c$ parameter with a decrease in the temperature from 30 K down to $T_c = 14$ K (Fig. 2, curve 1) in accord with the theoretical calculations. An increase in $\Delta c/c$ is retarded in the vicinity of T_c , and, below the critical temperature, the parameter $\Delta c/c$ for two measurement conditions exhibits different behav-

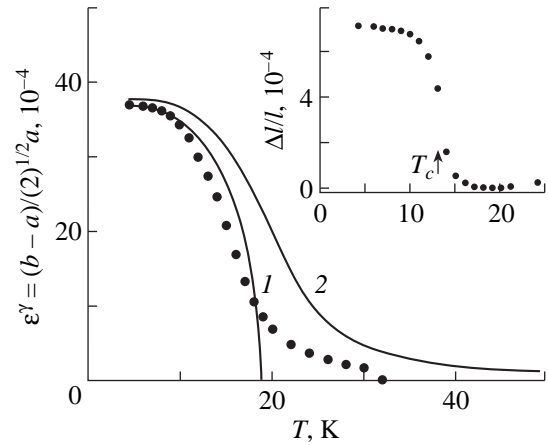


Fig. 1. Experimental (points, $H = 20$ kOe) and calculated [curves (1) $H = 0$ and (2) $H = 20$ kOe] temperature dependences of the orthorhombic distortion of the γ symmetry for the DyVO₄ crystal. The inset shows the temperature dependence of $\Delta l/l$ along the [010] direction in the absence of magnetic field for the polydomain sample.

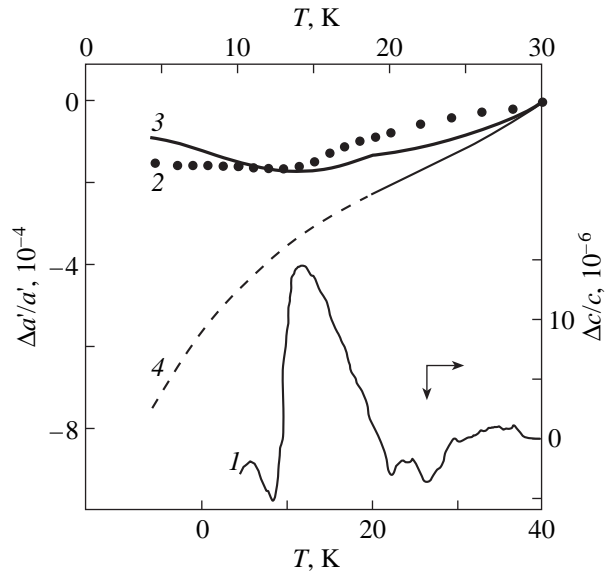


Fig. 2. Experimental temperature dependences of the relative change in the parameters (1) $\Delta c/c$ ($H = 0$) and (2) $\Delta a'/a'$ ($H = 30$ kOe, $\mathbf{H} \parallel [110]$) for the DyVO₄ crystal and theoretical curves of the relative change in the parameter $\Delta a'/a'$ at (3) $H = 30$ kOe ($\mathbf{H} \parallel [110]$) and (4) $H = 0$, calculated in the presence and absence of structural transition, respectively.

ior, which, in turn, disagree with the theoretical predictions. Evidently, such a disagreement is caused by the rearrangement of the domain structure in the crystal below the T_c temperature.

During the rearrangement of domain structure, the a and b orthorhombic axes in a domain exchange places with each other, which is accompanied by the tensile-compressive local strain of a gauge in the perpendicular direction $\epsilon \sim (b - a)/a \sim 5 \times 10^{-3}$. Note that, since the length of perpendicular closing links in a wire strain

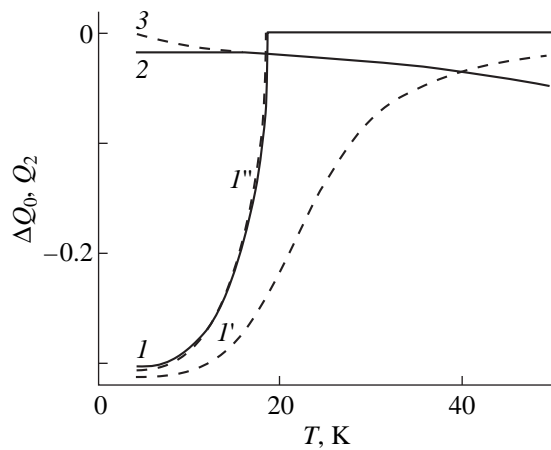


Fig. 3. Calculated temperature dependences of (I , I' , I'') the quadrupole moment Q_2 and the dependences $\Delta Q_0(T) = Q_0(T) - Q_0(0)$ for (2) orthorhombic and (3) tetragonal phases of the DyVO_4 crystal. Magnetic field H , kOe: (I) 0, (I') 30 ($\mathbf{H} \parallel [100]$), and (I'') 30 ($\mathbf{H} \parallel [110]$).

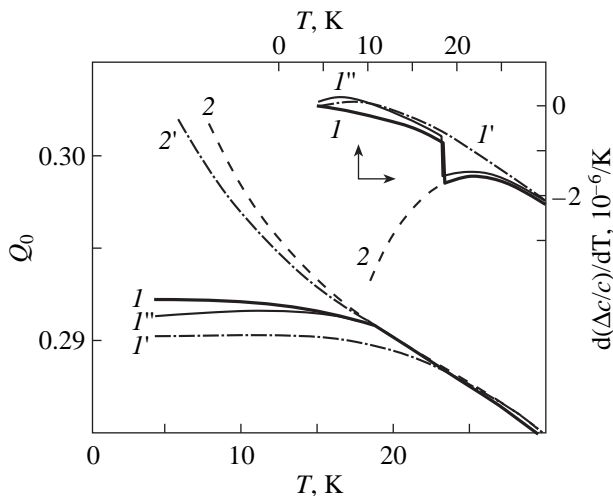


Fig. 4. Calculated temperature dependences of the quadrupole moment $Q_0(T, H)$ in the magnetic field (I , 2) $H = 0$, (I' , 2') $H = 30$ kOe ($\mathbf{H} \parallel [100]$), and (I'') $H = 30$ kOe ($\mathbf{H} \parallel [110]$) for (I , I') orthorhombic and (2, 2') tetragonal phases of the DyVO_4 crystal. The inset shows the calculated temperature dependences of thermal expansion coefficient $d(\Delta c/c)/dT$ along the tetragonal axis under the same conditions.

gauge is equal to $\sim 5\%$ of the length of “operating” links, the strain $\varepsilon \sim 5 \times 10^{-3}$ should result in an anomaly of an order of 25×10^{-5} in the $\Delta c(T)/c$ curve for the single-domain sample along the tetragonal axis. For the polydomain sample in the absence of external magnetic field, the contribution of domain processes is substantially (by about one order of magnitude) less and equal to $\sim 20 \times 10^{-6}$ (Fig. 2). When measuring even in a rather weak magnetic field of 10–20 kOe that stabilizes the domain structure, the jumps in the $\Delta c/c$ dependences disappear. However, the observed behavior of the ther-

mal expansion along the c axis is inconsistent with the theoretical calculations. Therefore, the wire strain gauges do not ensure reliable measurements of the anomalies in the $\Delta c/c$ or $\Delta a'/a'$ parameters, which are induced $\varepsilon^{\alpha 1}$ and $\varepsilon^{\alpha 2}$ totally symmetric modes.

The measurements performed with a capacity-type strain gauge are *a priori* more reliable, because they in principle are not affected by the perpendicular strain component (Fig. 2). Actually, the dependence of the $\Delta a'/a'$ parameter along the $[110]$ direction below T_c shows a characteristic anomaly in the form of a plateau (curve 2), which is in qualitative agreement with the behavior predicted by the crystal-field calculations (curve 3, see below). In the absence of structural transition at $H = 0$, the thermal expansion of the DyVO_4 crystal along the a' axis should change with the increasing derivative $d(\Delta a'/a')/dT$ down to 4 K (curve 4). In order to stabilize the domain structure, the measurements were performed in the constant magnetic field $H = 30$ kOe, which was parallel to the measured strain. In the DyVO_4 crystal, the magnetic field $\mathbf{H} \parallel [110]$ does not give rise to a single-domain structure, but induces extended thin strip domains [10] whose boundaries are perpendicular to the magnetic field and run along planes of the (110) type.

5. The features of the thermal expansion in the DyVO_4 crystal upon quadrupolar ordering can be described by the Hamiltonian $H = H_{CF} + H_{QT} + H_Z$ with the use of a common set of interaction parameters for the tetragonal and orthorhombic phases. At present, the problem of the crystal field in DyVO_4 is far short of the final solution, since the required spectroscopic data on the Dy^{3+} ion in the tetragonal and orthorhombic phases of DyVO_4 are unavailable. The crystal-field parameters available in the literature, for example, in [11], do not describe the known spectroscopic data and, in particular, lead to the splitting of two low-lying Kramers doublets in the tetragonal phase by a magnitude of less than 1.5 cm^{-1} as compared to the experimental value of 9 cm^{-1} [12, 13].

From the available experimental data, we determined the crystal-field parameters ($B_2^0 = -114 \text{ K}$, $B_4^0 = 50$, $B_4^4 = 973$, $B_6^0 = -59$, and $B_6^4 = 182 \text{ K}$), which adequately describe the experimental data and agree closely with the sets of parameters for other rare-earth vanadates, for example, HoVO_4 [14] whose crystal field is regarded as reliably established. In further calculations, we used these crystal-field parameters, coefficients $A_1 = 0.31 \times 10^{-2}$ and $A_2 = -0.39 \times 10^{-2}$ calculated for the DyVO_4 crystal from the anomalies of the thermal expansion in the tetragonal phase [1], and the elastic modulus $C_0^y = 1.24 \times 10^6 \text{ K}$ taken for DyVO_4 from [15]. As is customary, we consider the orthorhombic phase of DyVO_4 as a small distortion ($\varepsilon^y \sim 10^{-3}$) of the tetragonal phase. Then, it is expedient to use the

same coefficients for the calculation of the magnetoelastic contribution to the thermal expansion in the orthorhombic phase. The orthorhombic parameter of the crystal field $B_2^2 = -\alpha_J G^J \langle O_2^2 \rangle = 57.9$ K was chosen in such a way as to account for the experimental spectral changes in the phase with the quadrupolar ordering [12, 13]. It is known that, at $T > T_c$, two low-lying Kramers doublets of the Dy³⁺ ion in dysprosium vanadate are separated by 9 cm⁻¹ (the other excited states are separated by a considerable gap), and, below T_c , the separation between the doublets increases up to 27 cm⁻¹.

With the above parameters, we calculated the temperature dependence of the order parameter of phase transition $Q_2 = \alpha_J \langle O_2^2 \rangle$ (Fig. 3) and determined the critical temperature $T_c = 18.7$ K. This value substantially exceeds the T_c temperature, which was experimentally obtained in the present work and has been known from the literature [16]. It is characteristic that the critical temperature is primarily determined by the gap between the doublets in the orthorhombic phase, and different sets of crystal-field parameters, including the set obtained within the pseudospin formalism, result in virtually the same T_c temperatures. The problem of the overestimated, theoretically calculated transition temperature for DyVO₄ is well known in the literature (see, for example, [17]) and concerns the applicability of the mean-field approximation to this crystal. The calculated dependence $Q_2(T)$ reflects the variation in the ϵ^J orthorhombic distortion with temperature (Fig. 1, curve 1). The experimental value of $\epsilon^J = 36.8 \times 10^{-4}$ at 0 K leads to the magnetoelastic coefficient $B^J = 15 \times 10^3$ K.

The dependence $Q_2(T)$ provides a means of calculating the changes in the spectrum and wave functions of the Dy³⁺ ion below T_c and, then, the temperature dependences of the quadrupole moment $Q_0(T)$ in the orthorhombic (Fig. 3, curve 2) and tetragonal (Fig. 3, curve 3) phases. For the Q_0 quadrupole moment, which is non-zero even in the tetragonal phase, the ordering of the quadrupole moments Q_2 is attended by a jump in the dQ_0/dT derivative (Fig. 4), which, in turn, is responsible for the jump in the temperature dependence of the thermal expansion coefficient along the tetragonal axis $d(\Delta c/c)/dT$ or along the nonactive Jahn–Teller direction $d(\Delta a'/a)/dT$. The above-determined values of the B_2^2 parameter and the B^J magnetoelastic coefficient allow us to calculate the total quadrupolar coefficient $\alpha_J^2 G^J = 7.6$ mK and the magnetoelastic contribution $\alpha_J^2 G_{ME}^J = 7.3$ mK to this coefficient. Therefore, for the DyVO₄ crystal, the contribution of the pair quadrupolar interaction K^J is close to zero (positive, within the limits of experimental error), and the theoretical relationship $K^J/G_{ME}^J = -1/3$ is not valid, which can point to a sizable contribution of optic phonons.

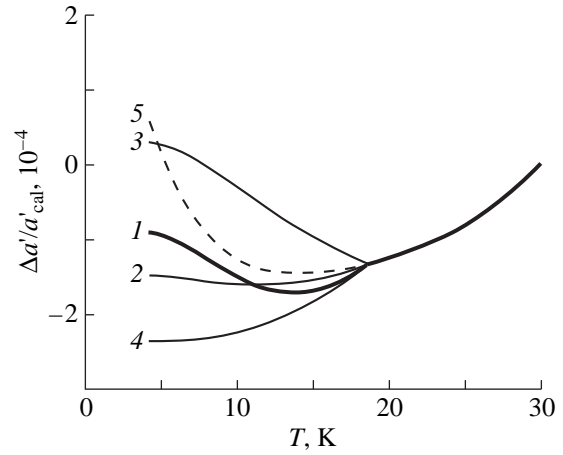


Fig. 5. Calculated contributions to the temperature dependence of (1) $\Delta a'/a'$ for the DyVO₄ crystal at $\mathbf{H} \parallel [110]$ in the presence of structural transition: (2) totally symmetric $\epsilon^{\alpha 1}$ and $\epsilon^{\alpha 2}$, (3) orthorhombic ϵ^{δ} , and (4) orthorhombic ϵ^J strain modes. (5) The sum of contributions from the totally symmetric $\epsilon^{\alpha 1}$ and $\epsilon^{\alpha 2}$ and orthorhombic ϵ^{δ} strain modes in the absence of structural transition.

Figures 3 and 4 also demonstrate the calculated dependences $Q_2(T, H)$ and $Q_0(T, H)$ at $H = 30$ kOe ($\mathbf{H} \parallel [100]$, curves 1' and 2'; $\mathbf{H} \parallel [110]$, curves 1''), which illustrate how the magnetic field orientation affects the critical temperature, order parameter, and magnetoelastic anomalies of the thermal expansion. It is seen that the H field aligned along the direction of the spontaneous orthorhombic strain leads to a smearing of the anomalies in the dependences of the quadrupole moments $Q_2(T, H)$ and $Q_0(T, H)$ and a considerable increase in the transition temperature. The field $\mathbf{H} \parallel [110]$ with the symmetry different from that of the order parameter produces a different, substantially weaker effect. As can be seen, the transition temperatures slightly decrease (by 0.2 K at a field of 30 kOe), but the anomalies in both dependences $Q_2(T, H)$ and $Q_0(T, H)$ remain pronounced. Specifically, the jump in the temperature dependence of the thermal expansion coefficient along the tetragonal axis $d(\Delta c/c)/dT$ in the field $\mathbf{H} \parallel [110]$ remains as abrupt as before (see the inset in Fig. 4).

The dependences $Q_2(T, H)$, $Q_{xy}(T, H) = \alpha_J \langle P_{xy} \rangle(T, H)$, and $Q_0(T, H)$ furnish an opportunity to separate different contributions to the thermal expansion of the DyVO₄ crystal along the nonactive Jahn–Teller direction $\Delta a'/a'$ (Fig. 5). For the tetragonal phase in the magnetic field $\mathbf{H} \parallel [110]$, there are only the contributions $(\Delta a'/a')_{\alpha} = A_2 \Delta Q_0$ and $(\Delta a'/a')_{\delta} = A^{\delta} Q_{xy} / \sqrt{2}$, which are brought about by the totally symmetric $\epsilon^{\alpha 1}$ and $\epsilon^{\alpha 2}$ and orthorhombic ϵ^{δ} modes, respectively. The sum of these contributions above T_c in the presence of structural transition is shown in Fig. 5 by curve 1 and by the dashed line below T_c in the absence of transition. The quadrupolar ordering leads to the change in these con-

tributions (curves 2, 3) and gives rise to the additional contribution $(\Delta a'/a')_\gamma = -3(\varepsilon^\gamma)^2/4$ from the ε^γ orthorhombic mode (curve 4). Resultant curve 5 reasonably well describes the experimental data along the a' axis and, in particular, the characteristic anomaly in the form of a plateau below T_c . Thus, the quadrupolar ordering in DyVO_4 is characterized by an inflection point in the $\Delta a'/a'$ curve at the T_c temperature and the change in the sign of $d(\Delta a'/a')/dT$ at lower temperatures. The anomaly at T_c in the experimental dependence of $\Delta a'/a'$ (as in the dependence of $\Delta a/a$ at $H=0$) is smeared by internal stresses in the crystal, but the change in the sign of the thermal expansion coefficient at a lower temperature is clearly observed (Fig. 2). It is worth noting that the calculated dependence of $\Delta a'/a'$ unexpectedly well quantitatively describes the experimental data, even though the thermal expansion was experimentally measured with respect to the reference sample without corrections for its thermal expansion because of the lack of these data at low temperatures.

It is of interest to compare the magnetoelastic anomalies in the thermal expansion of the DyVO_4 and TbVO_4 crystals upon quadrupolar ordering [5]. For the DyVO_4 crystal, the Q_2 or Q_{xy} spontaneous quadrupole moments responsible for the orthorhombic strain are two times larger and the ε^γ orthorhombic strain, on the contrary, is substantially (approximately five times) less than those for the TbVO_4 crystal. This is primarily due to the fact that the elastic constant C_0^γ is larger than the C_0^δ constant for the zircon structure. By contrast, the change in the Q_0 quadrupole moment in the orthorhombic phase with respect to the tetragonal phase (the difference between curves 2 and 3) for the DyVO_4 crystal is two times less than that for the TbVO_4 crystal. However, as is seen from Fig. 2, the magnetoelastic anomalies in the thermal expansion upon quadrupolar ordering, which are induced by the totally symmetric interactions and described by the Q_0 quadrupole moment, remain pronounced in the DyVO_4 crystal.

6. In the present work, the anomalies observed in the thermal expansion of the DyVO_4 crystal due to the ordering of the Q_2 quadrupole moments of the Dy^{3+} ions were studied experimentally and theoretically. The experimental data for the tetragonal and orthorhombic phases are adequately described by the theoretical curves calculated with a common set of interaction parameters for both phases. The magnetoelastic coefficient $B^\gamma = 15.1 \times 10^3$ K for the DyVO_4 crystal is close to the values of B^γ for DyPO_4 (10.4×10^3 K) and HoVO_4 (9.9×10^3 K), which were determined in complex investigations of magnetoelastic effects in the tetragonal phase of these zircons [4, 18]. It was found that, for the DyVO_4 crystal, the total quadrupolar coefficient $\alpha_j^2 G^\gamma$ is equal 7.6 mK, and the magnetoelastic contri-

bution $\alpha_j^2 G_{ME}^\gamma$ to this constant is 7.3 mK. Therefore, the contribution of the quadrupolar pair interaction K^γ is close to zero, and the theoretical relationship $K^\gamma/G_{ME}^\gamma = -1/3$ is not valid, which can indicate a significant role of optic phonons. It should be mentioned that, in the zircon family, DyVO_4 is the sole crystal characterized by the quadrupolar ordering of the γ symmetry, which explains increased interest in this crystal.

In summary, it should be emphasized that, in the present work, unlike the majority of works dealing with the investigation of distorted phases in rare-earth zircons, the calculations were performed within the framework of the general crystal-field model. In the earlier works, the contribution to the thermal expansion of rare-earth zircons with the cooperative Jahn–Teller effect included only the dominant Jahn–Teller mode, and the contribution of the totally symmetric modes was ignored. Moreover, it was assumed that the ordering of quadrupole moments is accompanied by only the orthorhombic distortion of a crystal in the basal plane and, hence, brings about neither volume nor tetragonal strains. The latter contribution was found to be substantially less than the former contribution due to the hierarchy of magnetoelastic and elastic coefficients in the zircon structure. Nonetheless, we established that the contribution of the totally symmetric modes gives rise to the observable magnetoelastic effects. The calculation of this contribution proportional to the change in the Q_0 quadrupole moment is outside the province of the pseudospin formalism and requires consideration of all the features of mixing in the crystal field. In particular, for the quadrupole moment $Q_0(T)$ that is nonzero even in the tetragonal phase, the ordering of the Q_2 quadrupole moments is attended by the manifestation of the feature in the derivative dQ_0/dT , which, in turn, is responsible for the jump-type anomalies in the temperature dependence of the thermal expansion coefficient along the tetragonal axis or along the nonactive Jahn–Teller direction a' in the basal plane.

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