Manifestation of the magnetoelastic and Jahn–Teller interactions in elastic and structural characteristics of rare-earth phosphates RPO (R=Y, Tb–Yb)

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The first systematic experimental and theoretical investigations were made of the contribution of the rare-earth ions to the temperature dependences of the Young modulus and the lattice parameters of phosphates with the formula RPO_4, where R = Y, Tb–Yb. An anomalous, compared with YPO_4, behavior of the Young modulus and the lattice parameters of the investigated phosphates was observed. It was also found that the Young modulus of the Tb and Tm phosphates exhibited strong "softening" as a result of cooling. These anomalies of the Young modulus were described satisfactorily by temperature dependences of the deformation susceptibilities of the rare-earth ions calculated using the known parameters of the crystal field, while the thermal expansion anomalies were accounted for by the temperature dependences of the quadrupole moment. The magnetoelastic coefficients were estimated. The strong softening of the Young modulus of the Tb and Tm phosphates was demonstrated to be due to a correlation enhancement of the relevant deformation susceptibility.

1. INTRODUCTION

Rare-earth phosphates belong to the class of the rare-earth Jahn–Teller (JT) elastic materials which are attracting intense interest. They have the zircon structure with the general formula RXO_4, where R is a rare-earth ion and X is an ion of V, As, or P. The majority of the compounds belonging to this class exhibits a stronger or weaker JT interaction and studies have been made of the manifestation of the JT effect in the various cases of degeneracy in the rare-earth ion spectrum.[1] The least known among the JT interactions are those in rare-earth phosphates. An investigation of these interactions is reported below.

All the rare-earth compounds, including those exhibiting the JT effect, are characterized by a strong magnetoelastic interaction which distorts the immediate environment of the rare-earth ion when its state is altered by an external magnetic field, variation of temperature, etc. Two extreme cases are possible. If the spectrum of the rare-earth ion is degenerate, a strong electron–phonon interaction results in a strong intercenter (JT) interaction between the rare-earth ions and a correlation between local distortions of the rare-earth ion environment throughout a crystal (manifested by certain characteristics of various physical properties, including the elastic properties); if the interaction is sufficiently strong, it can induce a structural phase transition. When there is no interaction between the rare-earth ions, the local distortions do not influence each other and the effect is purely of the single-ion nature, but when summed over the whole crystal it can make a considerable contribution to the elastic, magnetoelastic, and structural characteristics.

The object of our investigation was the contribution of the magnetoelastic interaction to the elastic and structural characteristics of a rare-earth phosphate in the presence and in the absence of the JT correlations. Similar systematic experimental and theoretical investigations have already been made for many rare-earth intermetallic cubic compounds with different structures. References to the numerous and sometimes very comprehensive investigations can be found in, for example, Refs. 2 and 3.

However, such systematic experimental investigations of the elastic and structural characteristics are lacking in the case of rare-earth oxides. One can mention Ref. 4, reporting the temperature dependences of the lattice parameters of rare-earth aluminate and gallate garnets for the whole heavy rare-earth ion series. In our opinion, rare-earth phosphates are very promising objects for the investigation because the local symmetry of the environment of the rare-earth ion is tetragonal (point symmetry group $\bar{4}m2$), as is the symmetry of the whole crystal (space symmetry group $I4_1/amd$). In this respect the phosphates differ conveniently from rare-earth garnets whose low (orthorhombic) local symmetry of the environment of the rare-earth ion is averaged out to the cubic symmetry for the whole crystal because of the presence of nonequivalent sites.

We synthesized and investigated rare-earth phosphates with elements from Tb to Yb and the phosphate of the nonmagnetic Y, which all crystallize in the zircon structure; the phosphates with the light rare-earth ions crystallize in the monoclinic structure of monazite, which will not be considered by us. Our task was carried out by determination of the temperature dependences of the elastic moduli and the unit cell parameters of these compounds, because these properties were the most sensitive to the magnetoelastic and JT interactions.

2. THEORETICAL ANALYSIS

2.1. Hamiltonian and free energy

In the calculation of the contribution of the rare-earth ion to the temperature dependences of the elastic constants and crystal lattice parameters we shall use the Hamiltonian

$$H = H_{\rm cf} + H_{\rm me} + H_Q. \qquad (1)$$

In the case of a crystal with the tetragonal symmetry the crystal field Hamiltonian $H_{\rm cf}$ has the familiar form

$$H_{\rm cf}=\alpha_J B_2^0 O_2^0+\beta_J(B_4^0 O_4^0+B_4^4 O_4^4)+\gamma_J(B_6^0 O_6^0+B_6^4 O_6^4), \qquad (2)$$

where α_J, β_H, and γ_J are the Stevens parameters; B_n^m are the crystal field parameters; O_n^m are the equivalent operators.

The magnetoelastic Hamiltonian $H_{\rm me}$ considered in the quadrupole approximation is linear[5] in components of the strain tensor ε^{μ} (harmonic approximation) and it can be described by five independent magnetoelastic coefficients B^{μ}:

$$H_{\text{me}}=\alpha_J[-(B^{\alpha1}\varepsilon^{\alpha1}+B^{\alpha2}\varepsilon^{\alpha2})O_2^0-B^{\gamma}\varepsilon^{\gamma}O_2^2-B^{\delta}\varepsilon^{\delta}Q_{xy}-B^{\varepsilon}(\varepsilon_1^{\varepsilon}Q_{zx}+\varepsilon_2^{\varepsilon}Q_{zy})]. \tag{3}$$

The two-ion quadrupole Hamiltonian H_Q, describing the JT correlations in the molecular field approximation, can be written in the form (see, for example, Ref. 6):

$$H_Q=\alpha_J^2[-K^{\alpha}\langle O_2^0\rangle O_2^0-K^{\gamma}\langle O_2^2\rangle O_2^2-K^{\delta}\langle Q_{xy}\rangle Q_{xy}-K^{\varepsilon}(\langle Q_{zx}\rangle Q_{zx}+\langle Q_{zy}\rangle Q_{zy})]. \tag{4}$$

The following notation is used in Eqs. (2)–(4):

$$O_2^0=3Q_{zz}=3J_z^2-J(J+1),\quad O_2^2=J_x^2-J_y^2,$$

$$Q_{ij}=\frac{1}{2}(J_iJ_j+J_jJ_i)\quad (ij=xy,\ zx,\ zy).$$

We shall use the Hamiltonian (1) to calculate the free energy

$$F=F_y-k_BT\ln Z. \tag{5}$$

The dependences of the energy levels E_n of the rare-earth ions on the deformation via the magnetoelastic interactions ($H_{\text{me}}+H_Q$) are allowed for in the partition function

$$Z=\sum_n \exp(-E_n/k_BT)$$

using the second order of perturbation theory. Clearly, in the case of the non-Kramers ion, which in the tetragonal symmetry case has doublets in the spectrum, the energy corrections are different for degenerate and nondegenerate levels.

The elastic energy of a tetragonal crystal defined in terms of the symmetrized components of the strain tensor are as follows:[5]

$$E_e={}^1\!/_2C_0^{\alpha1}(\varepsilon^{\alpha1})^2+C_0^{\alpha12}\varepsilon^{\alpha1}\varepsilon^{\alpha2}+{}^1\!/_2C_0^{\alpha2}(\varepsilon^{\alpha2})^2+{}^1\!/_2C_0^{\gamma}(\varepsilon^{\gamma})^2+{}^1\!/_2C_0^{\delta}(\varepsilon^{\delta})^2+{}^1\!/_2C_0^{\varepsilon}[(\varepsilon_1^{\varepsilon})^2+(\varepsilon_2^{\varepsilon})^2], \tag{6}$$

where C_0^{μ} are the symmetrized elastic constants of the lattice considered ignoring the magnetic interactions. The relationship between ε^{μ} and C^{μ} and the Cartesian components ε_{ij} and C_{ij} can be found, for example, in Ref. 6.

2.2. Contribution of the rare-earth ions to the elastic constants

The expression for the contribution of the magnetoelastic interaction to the temperature dependences of the elastic constants can be obtained as in Ref. 7, i.e., by calculating the elastic constant C^{μ} as the second derivative of the free energy F with respect to the appropriate components of the strain tensor ε^{μ} (see also Ref. 6):

$$\begin{gathered}C^{\alpha1,\alpha2}=C_0^{\alpha1,\alpha2}-(B^{\alpha1,\alpha2})^2\frac{\chi_\alpha}{1-K^{\alpha}\chi_\alpha},\\ C^{\mu}=C_0^{\mu}-(B^{\mu})^2\frac{\chi_\mu}{1-K^{\mu}\chi_\mu},\quad \mu=\gamma,\delta,\varepsilon.\end{gathered} \tag{7}$$

In these expressions the deformation or strain susceptibilities χ_μ are defined by the following expression ($\mu=\alpha,\gamma,\delta,\varepsilon$):

$$\chi_\mu=\alpha_J^2\Bigg[\frac{1}{Z}\sum_n\exp\left(-\frac{E_n}{k_BT}\right)\Bigg(\frac{|\langle n|Q|n\rangle|^2}{T}-2\sum_{m\neq n}\frac{|\langle n|Q|m\rangle|^2}{E_n-E_m}+\delta_{\mu,\delta}\sum_{m\neq n}\frac{|\langle n|Q|m\rangle|^2}{T}\delta_{E_n,E_m}\Bigg)-\frac{\langle Q\rangle^2}{T}\Bigg], \tag{8}$$

where

$$Q=\begin{cases}O_2^0, & \mu=\alpha,\\ O_2^2, & \mu=\gamma,\\ Q_{xy}, & \mu=\delta,\\ Q_{zx}, & \mu=\varepsilon.\end{cases}$$

The deformation susceptibility χ_α governs the renormalization of the elastic constants due to an elastic strain $\varepsilon^{\alpha1}$ and a tetragonal strain $\varepsilon^{\alpha2}$; χ_γ and χ_δ are related to the orthorhombic strains ε^{γ} and ε^{δ}, respectively, whereas χ_ε is related to the monoclinic strain $\varepsilon^{\varepsilon}$.

In the interpretation of the experimental results obtained for polycrystalline samples we can carry out the usual (see, for example, Ref. 8) averaging, which gives the following expression for the Young modulus anomaly in the tetragonal symmetry case:

$$\frac{\Delta E}{E_0}=-\Bigg\{[\eta_1(B^{\alpha1})^2+\eta_2(B^{\alpha2})^2]\frac{\chi_\alpha}{1-K^{\alpha}\chi_\alpha}+\eta_2(B^{\gamma})^2\frac{\chi_\gamma}{1-K^{\gamma}\chi_\gamma}+\eta_2(B^{\delta})^2\frac{\chi_\delta}{1-K^{\delta}\chi_\delta}+2\eta_2(B^{\varepsilon})^2\frac{\chi_\varepsilon}{1-K^{\varepsilon}\chi_\varepsilon}\Bigg\}, \tag{9}$$

where the average compliances η_1 and η_2 are given by

$$\eta_1=\frac{0{,}1(C_0^{\alpha2}+C_0^{\gamma}+C_0^{\delta}+2C_0^{\varepsilon})}{C_0^{\alpha1}[C_0^{\alpha1}+0{,}1(C_0^{\alpha2}+C_0^{\gamma}+C_0^{\delta}+2C_0^{\varepsilon})]},$$

$$\eta_2=\frac{C_0^{\alpha1}}{(C_0^{\alpha2}+C_0^{\gamma}+C_0^{\delta}+2C_0^{\varepsilon})[C_0^{\alpha1}+0{,}1(C_0^{\alpha2}+C_0^{\gamma}+C_0^{\delta}+2C_0^{\varepsilon})]}.$$

Since all the deformation susceptibilities $\chi_{\alpha,\gamma,\delta,\varepsilon}$ are, by definition, positive quantities, it follows that the magnetoelastic interaction, like the pair quadrupole interaction, always "softens" the lattice, i.e., they both reduce the Young modulus. The actual form of the temperature dependence of the Young modulus is governed by the ratio of the values of the various deformation susceptibilities of a given rare-earth compound and by the nature of their temperature dependences.

2.3. Contribution of the rare-earth ions to the thermal expansion

The rare-earth contribution to the temperature dependences of the lattice parameters can be found in the usual way from the expression for the magnetoelastic and elastic energies. In the case of the tetragonal lattice parameters a and c, we obtain

$$\Delta c_{\text{RE}}(T)=3^{1/2}c_0\frac{B^{\alpha1}(C_0^{\alpha2}-2^{1/2}C_0^{\alpha12})+B^{\alpha2}(2^{1/2}C_0^{\alpha1}-C_0^{\alpha12})}{C_0^{\alpha1}C_0^{\alpha2}-(C_0^{\alpha12})^2}Q_0(T), \tag{10}$$

$$\Delta a_{\text{RE}}(T)=3^{1/2}a_0\frac{B^{\alpha1}(C_0^{\alpha2}+C_0^{\alpha12}/2^{1/2})-B^{\alpha2}(C_0^{\alpha1}/2^{1/2}+C_0^{\alpha12})}{C_0^{\alpha1}C_0^{\alpha2}-(C_0^{\alpha12})^2}Q_0(T),$$

where

$$Q_0(T)=\alpha_J\langle Q_{zz}\rangle=\frac{1}{3}\alpha_J\langle O_2^0\rangle'=\frac{1}{3}\alpha_J\frac{1}{Z}\sum_n\langle n|O_2^0|n\rangle\exp\left(-\frac{E_n}{k_BT}\right).$$

It therefore follows that the rare-earth contribution to the thermal expansion of a crystal is governed by the quadrupole moment Q_0 of the rare-earth ion and we can expect that in the case of major changes in the quadrupole moment with temperature, particularly at low temperatures, there will be anomalies in the temperature dependences of the lattice parameters.

2.4. Numerical calculation of the deformation susceptibilities and of the quadrupole moment of rare-earth phosphates

It therefore follows that in order to determine the magnitudes and the temperature dependences of the rare-earth contributions to the anomalies of the Young modulus and the crystal lattice parameters of rare-earth phosphates we have to know the deformation susceptibilities and the quadrupole moments of the rare-earth ions in these compounds. These quantities can be calculated numerically using the expressions given above, because for the majority of the heavy rare-earth ions we know the crystal field parameters, which have been determined from fairly extensive spectroscopic and other data.

In the case of almost all the rare-earth ions there are data on the crystal field in the compounds YPO and $LuPO_4$, which are doped with these ions, and for some of them there are also data on the concentrated compounds. We carried out calculations for all the known sets of the crystal field parameters. In most cases the different sets gave similar temperature dependences of the elastic constants and lattice parameters for a given rare-earth ion, with the differences purely of quantitative nature. The deformation susceptibilities and the quadrupole moments plotted in our figures were calculated for the optimal (in our opinion) sets of the crystal field parameters taken from the following sources: Tb (Ref. 9), Ho (Ref. 10), Er (Ref. 11), Tm (Ref. 12), Yb (Ref. 13). It must be mentioned that the crystal field parameters are given in different systems of coordinates. We employed the crystallographic coordinate system, which corresponds to the $\bar{4}m2$ symmetry. The crystal field parameters of $DyPO_4$ are not known; the only information is that in Refs. 14 and 15, and it applies to the lower excited levels of the Dy^{3+} ion. We therefore described the Dy^{3+} ion using the crystal field parameters of Tb^{3+} taken from Ref. 9, because it is known (see, for example, Ref. 10) that in the case of the adjacent rare-earth ions the crystal field parameters are similar for the same compound.

3. SAMPLES AND MEASUREMENT METHOD

The elastic properties were investigated using polycrystalline samples, whereas the thermal expansion was determined using single crystals ($TbPO_4$,$TmPO_4$) as well as polycrystalline samples. The polycrystalline rare-earth phosphates PPO_4 with the zircon structure were synthesized by the ceramic technology including double firing in air; the components of the original charge were R_2O_3 oxides (in the case of $TbPO_4$ we used Tb_4O_7) and $NH_4H_2PO_4$. The characteristic features of the solid-phase synthesis of rare-earth phosphates required a special heating during the first firing of the charge. A sample was first heated slowly (in order to prevent NH_3 and H_2O, released on decomposition of $NH_4H_2PO_4$, from cracking a pellet) to $T\approx 300\,^\circ C$; this was followed by fast heating to the synthesis temperature $T_1 = 1400\,^\circ C$ in 1.5–2 h (in order to minimize the loss of the volatile P_2O_5 before it was bound to form RPO_4). The second firing improved the homogeneity and mechanical properties of the ceramic and it again took place at $T_2 = 1400\,^\circ C$.

Among the heavy rare-earth phosphates the compound $TbPO_4$ is a special case: it can exist in two crystalline modifications, a low-temperature monoclinic (monazite structure) and a high-temperature tetragonal (zircon structure). A single-phase $TbPO_4$ sample with the zircon structure was obtained when the first and second firings took place at $T_1 = T_2 = 1200\,^\circ C$. At higher temperatures ($T> 1300\,^\circ C$) an impurity phase appeared in the sample and we were unable to identify it.

The phase composition was monitored by x-ray diffraction using a Geigerflex diffractometer with an accuracy to within $\sim 1\%$. Samples of RPO_4 with the rare-earth ions ranging from Tb to Tm or Y were single-phase, as tested by x-ray diffraction; $YbPO_4$ contained $\sim 3\%$ Yb_2O_3. The tetragonal unit cell parameters a and c deduced from the (116) and (552 + 712) reflections agreed well with the published data. The density of the ceramic samples was 65–75% of the x-ray value. We also used $TbPO_4$, $DyPO_4$, and $TmPO_4$ crystals grown by spontaneous crystallization from the melt.

We determined the temperature dependences of the elastic properties (2.0–100 K) and of the unit cell parameters (10–300 K) of rare-earth phosphates. The Young modulus E and the internal friction coefficient q^{-1} were determined by the compound resonator (pendulum) method at frequencies of ~ 150 kHz in magnetic fields up to 40 kOe. The x-ray diffraction determination of the unit cell parameters was carried out using the Geigerflex diffractometer with a continuous-flow CF-108 (Oxford Instruments) cryostat.

The temperature dependences of the tetragonal unit cell parameters a and c of $TbPO_4$ and $TmPO_4$ were obtained for single-crystal plates with the (100) and (001) orientations employing the (800) reflection (Co K_β radiation, intensity $I\approx 4\times 10^3$ pulses/s, $2\theta\approx 140°$) and the (008) reflection (Cu K_β radiation, intensity $I\approx 2\times 10^3$ pulses/s, $2\theta\approx 135°$). The parameters a and c of polycrystalline samples were found from the single reflections (116) and ($2\theta\approx 103°$) and (552 + 712) ($2\theta\approx 113°$) characterized by the intensity $I\approx (2\text{–}8)\times 10^2$ pulses/s using Cu $K_{\alpha 1}$ radiation. The thermal contact between a polycrystalline sample and the heat sink of the cryostat was improved by mixing a finely ground sample with a Ramsay vacuum grease. It was found that solidification of this grease resulted in a slight misalignment of the sample and an additional shift of the reflections by $(0.02\text{–}0.03)°$ in the temperature range 220–300 K. This effect was allowed for by introducing a correction on the basis of the measurements carried out on a sample without recourse to the grease.

4. EXPERIMENTAL RESULTS

4.1. Young modulus and internal friction

It is well known that the elastic moduli are most sensitive to the presence of the JT interaction between the rare-

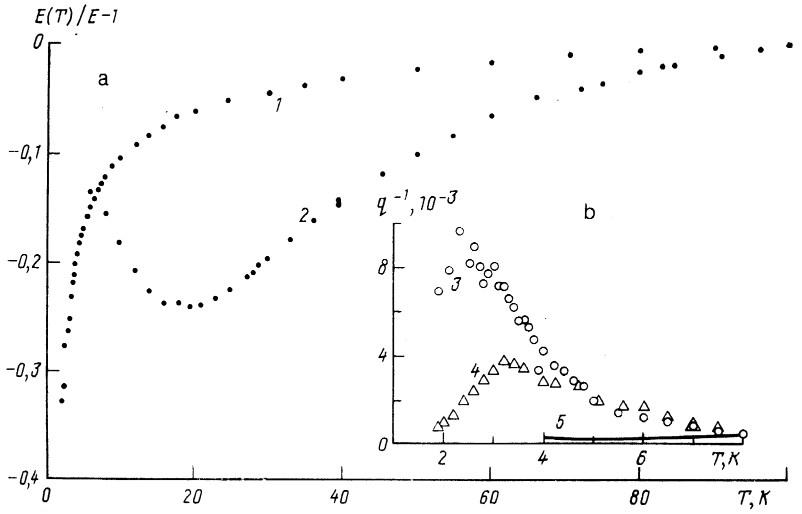

FIG. 1. Temperature dependences of the relative value of the Young modulus $E(T)/E - 1$ (a) and of the internal friction q^{-1} (b) of polycrystalline samples of $TbPO_4$ ($H = 0$ for curves *1* and *3* and $H = 30$ kOe for curve *4*) and $TmPO_4$ ($H = 0$ for curves *2* and *5*).

earth ions and that the degree of softening of the Young modulus as a result of cooling can be used to judge the JT correlations. According to the results, the investigated rare-earth phosphates can be divided into two groups in accordance with the magnitude of the JT correlations.

Figure 1 shows the temperature dependences of the relative value of the Young modulus $\Delta E(T)/E = E(T)/E - 1$ (a) and $\Delta E(T) = E(T) - E, E = T(T = 100\text{ K})$ and internal friction coefficient q^{-1} (b) of the Tb and Tm phosphates. It is clear that in the case of $TbPO_4$ at $T < 100$ K a strong softening of the Young modulus begins as a result of cooling and it reaches $\Delta E/E \approx 0.33$ at $T \approx 2$ K (curve 1). At lower temperatures the softening $\Delta E(T)/E$ slows down, but the Young modulus does not pass through a minimum right down to 1.9 K, which we reached in our experiments. A discontinuity of $\Delta E(T)/E$ is observed at 2.5 K, superimposed on a monotonically falling dependence. The internal friction q^{-1} of $TbPO_4$ exhibits two absorption maxima in $H = 0$: a weak one at $T \approx 3.5$ K and a strong one ($\sim 10^{-2}$) at $T \approx 2.5$ K (curve 3).

The Young modulus of $TmPO_4$ passes through a minimum at $T \approx 20$ K as a result of cooling (curve 2), which is also true of the elastic constant C_{66} reported for single crystals in Ref. 16. The internal friction shows no singularities at low temperatures and remains at $\sim 10^{-4}$ (curve 5).

The application of a magnetic field has a strong influence on the anomalies of $\Delta E(T)/E$ and $q^{-1}(T)$ exhibited by $TbPO_4$. A static magnetic field of $H = 30$ kOe reduces strongly the softening of the Young modulus $\Delta E(T)/E$ as a result of cooling, which now amounts to ≈ 0.14; moreover, there is a clear anomaly at $T = 3.5$ K. A magnetic field also reduces strongly the absorption maximum at $T = 2.5$ K, so that an additional maximum amounting to $q^{-1} \approx 4 \times 10^{-3}$ appears clearly at $T = 3.5$ K, but the latter maximum is not affected greatly by the magnetic field (curve 4). The change in the Young modulus, i.e., the $\Delta E(H)$ effect, is positive in the case of $TbPO_4$ and it amounts to $\Delta E(H)/E(H = 0) \approx 0.32$ for $H = 40$ kOe at $T = 2.6$ K, and it decreases on increase in temperature.

The influence of an external magnetic field on the Young modulus of $TmPO_4$ is qualitatively different from the influence on $TbPO_4$ (Fig. 2). At low temperatures ($T = 4.2$ K) the application of fields up to 40 kOe reveals a negative $\Delta E(H)$ effect of ≈ 0.07 magnitude. When temperature of this compound is increased ($T = 10$, 15, 20 K) the magnitude of the $\Delta E(H)$ effect decreases and in high fields there is a reversal of the sign of the effect to positive. At $T > 25$ K in the full range of the investigated fields the $\Delta E(H)$ effect in $TmPO_4$ is positive.

The temperature dependences of the Young modulus in the second group of phosphates are qualitatively and quantitatively different. The temperature dependence of the Young modulus of the phosphates of Dy, Ho, Er, Yb, and Y, are plotted in Fig. 3 (curves from top to bottom, respectively). For clarity, the dependences $\Delta E(T)/E$ obtained for different phosphates are shifted relative to one another along the ordinate. The most typical dependence $\Delta E(T)/E$ is observed for $DyPO_4$. We can see that cooling from 100 K first softens the Young modulus by $\approx 5 \times 10^{-3}$ and further cooling below 50 K begins to increase $\Delta E(T)/E$. The small low-temperature anomaly of the Young modulus shown in the inset is associated with the antiferromagnetic ordering of the Dy^{3+} ions.

A similar (but less pronounced) temperature dependence of the Young modulus is exhibited also by the other rare-earth phosphates belonging to this group. The softening of the Young modulus as a result of cooling is less for the Ho–Yb phosphates and, therefore, it cannot be detected against the background of the Debye dependence $\Delta E(T)/E$. The small, $\sim 10^{-3}$, softening of the Young modulus of $HoPO_4$ is observed below 10 K and it is also manifested by the smaller temperature coefficient of the modulus in the

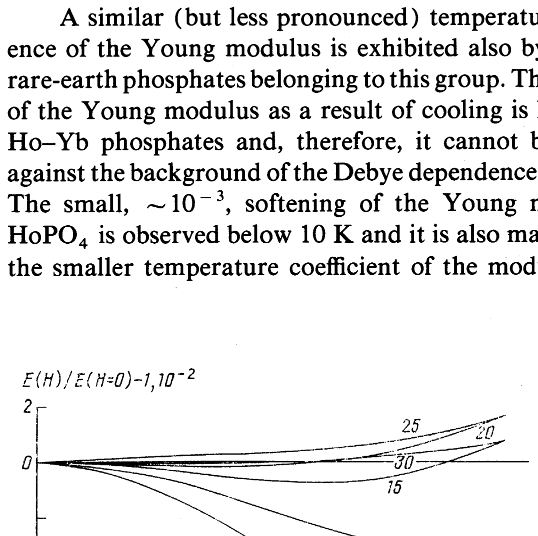

FIG. 2. Field dependences of the relative value of the Young modulus of a polycrystalline sample of $TmPO_4$ determined at low temperatures.

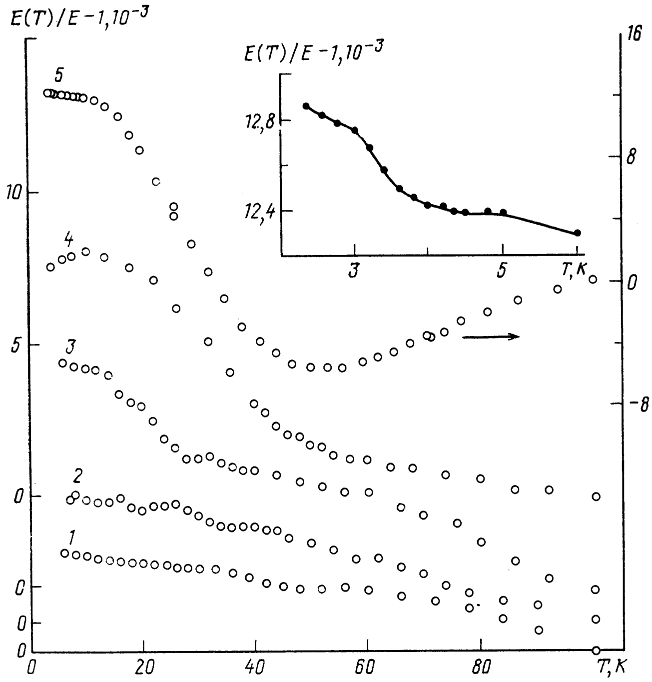

FIG. 3. Temperature dependences of the relative Young modulus of polycrystalline samples of YPO_4 (1), $YbPO_4$ (2), $ErPO_4$ (3), $HoPO_4$ (4), and $DyPO_4$ (5). The inset shows the behavior of the Young modulus of $DyPO_4$ at low temperatures.

range $T > 50$ K, compared with the phosphates of Er, Yb, and Y.

A distinguishing feature of the dependences $\Delta E(T)/E$ obtained for the phosphates of Ho, Er, and Yb (Fig. 3) is a strong rise in the rigidity of the lattice as a result of cooling below 50 K. A small anomaly of this type is exhibited also by $YbPO_4$, as indicated by an increase in the difference between the dependences $\Delta E(T)/E$ obtained for the Yb and Y phosphates as a result of cooling. The low-temperature anomaly becomes smaller and the characteristic temperatures ($T \approx 50$–0 K) increase somewhat in the series from Dy to Yb (with the exception of Er). Clearly, these anomalies are of common origin for all the RPO_4 compounds and are associated with the rare-earth ions because in the case of the Y phosphate that does not contain the magnetic ions the changes in the Young modulus as a result of cooling are of the conventional nature.

4.2. Thermal expansion

A fuller picture of the low-temperature behavior of the investigated rare-earth phosphates was obtained by determination of the temperature dependences of their unit cell parameters. For the majority of the phosphates containing magnetic rare-earth ions it was found that the temperature dependences of the unit cell parameters were similar (Figs. 4–6).

We shall consider in greater detail the thermal expansion singularities of rare-earth phosphates taking $TbPO_4$ as the example. Figure 4 shows the temperature dependences of the parameters a and c (curves 1 and 2) and also of the volume V (curve 3) of the tetragonal unit cell of $TbPO_4$. For convenience of comparison we plotted the relative changes in these parameters normalized to their values at room temperature: $\Delta a/a = a(T)/a - 1$, $\Delta c/c = c(T)/c - 1$, and $\Delta V/V = V(T)/V - 1 = 2\Delta a/a + \Delta c/c$, where $a = a(290\ \text{K})$, $c = c(290\ \text{K})$, and $V = V(290\ \text{K})$. Curve 4 shows the temperature dependence of the relative values of the parameters a and c of the Y phosphate, which exhibits the usual Debye behavior and shows no thermal expansion anisotropy.

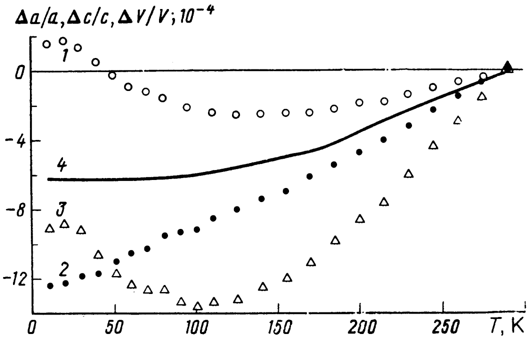

FIG. 4. Temperature dependences of the relative unit cell parameters $\Delta a/a$ [curve 1, $a(290\ \text{K}) = 6.9428$ Å], $\Delta c/c$ [curve 2, $c(290\ \text{K}) = 6.0712$ Å], of the volume $\Delta V/V$ (curve 3) of the tetragonal unit cell of $TbPO_4$, and of the relative value of the parameter $\Delta a/a$ of YPO_4 (curve 4).

When compared with YPO_4, the parameters a and c and the unit cell volume V of $TbPO_4$ behave anomalously when temperature is varied. The reduction in the parameter a as a result of cooling slows down at $T \approx 140$ K and changes to a rise at lower temperatures. The lattice parameter c of $TbPO_4$ also behaves anomalously at low temperatures: in the range $T \leqslant 80$ K the dependence does not slow down, as one would expect for the Debye temperature dependence, but becomes steeper. It should be stressed that if $TbPO_4$ does

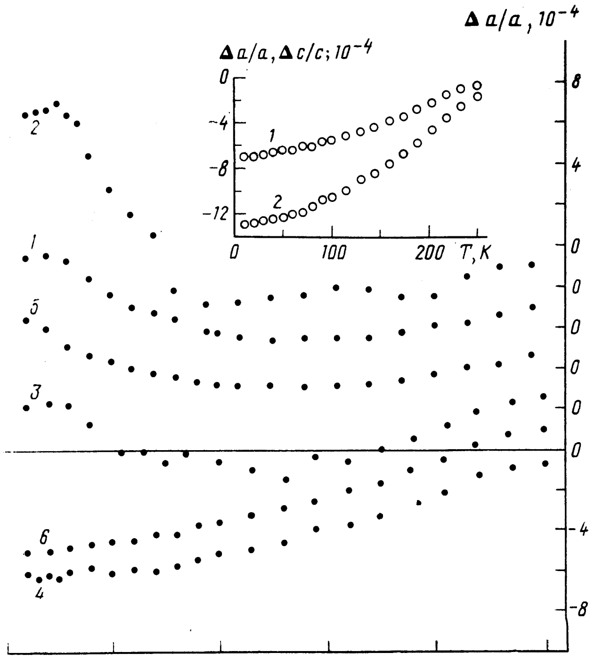

FIG. 5. Temperature dependences of the relative parameters $\Delta a/a$ of the tetragonal unit cell of the following rare-earth phosphates: 1) $TbPO_4$ [$a(290\ \text{K}) = 6.9428$ Å]; 2) $DyPO_4$ [$a(290\ \text{K}) = 6.9109$ Å]; 3) $HoPO_4$ [$a(290\ \text{K} = 6.8884$ Å]; 4) $ErPO_4$ [$a(290\ \text{K}) = 6.8635$ Å]; 5) $TmPO_4$ [$a(290\ \text{K}) = 6.8411$ Å]; 6) $YbPO_4$ [$a(290\ \text{K}) = 6.8173$ Å]. The inset shows the anisotropy of the thermal expansion of $YbPO_4$ at right-angles (1) and along (2) the tetragonal c axis.

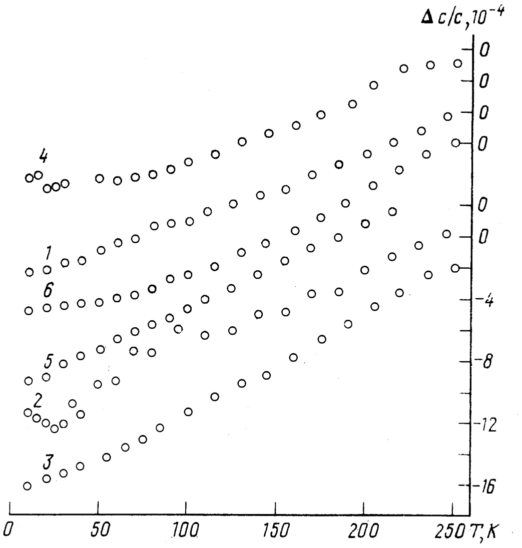

FIG. 6. Temperature dependences of the relative parameters $\Delta c/c$ of the tetragonal unit cell of rare-earth phosphates: 1) $TbPO_4$ [c(290 K) = 6.0712 Å]; 2) $DyPO_4$ [c(290 K) = 6.0378 Å]; 3) $HoPO_4$ [c(290 K) = 6.0214 Å]; 4) $ErPO_4$ [c(290 K) = 6.0100 Å]; 5) $TmPO_4$ [c(290 K) = 5.9878 Å]; 6) $YbPO_4$ [c(290 K) = 5.9727 Å].

not undergo a structural phase transition in the investigated range of temperatures right down to 10 K, the lattice remains tetragonal, and only the degree of tetragonality changes. Anomalies of the dependences $\Delta a(T)/a$ and $\Delta c(T)/c$ are responsible for the positive volume anomaly of $\Delta V(T)/V$.

Systematic experimental data on the thermal expansion of rare-earth phosphates are not available in the published literature: one can only mention Ref. 17, which reports an x-ray diffraction investigation of the temperature dependences of the tetragonal cell parameters a and c of polycrystalline $TbPO_4$. Our dependence $a(T)$ is in good agreement with Ref. 17, but the parameter $c(T)$ reported at low temperatures in Ref. 17 exhibits the usual Debye behavior. The reason for this discrepancy is not clear; one should mention however the relatively large (compared with the magnitude of the anomaly) error in the determination of the parameter c reported in Ref. 17, compared with the error of our data.

In quantitative estimates the anomalies $\Delta a(T)/a$, $\Delta c(T)/c$, and $\Delta V(T)/V$ for $TbPO_4$ (and other rare-earth phosphates) were found by us using as comparison standards the unperturbed curves representing the corresponding dependences of YPO_4. It should be pointed out that the molecular weights of YPO_4 and the heavy rare-earth phosphates are quite different, which may result in some systematic error in the determination of the anomalies. A rough estimate of this error based on the Debye thermal expansion model shows that the unperturbed dependence $\Delta a(t)/a$ [and also $\Delta c(T)/c$] of RPO_4 compared with that for YPO_4 should pass $\approx(1\text{–}3)\times 10^{-4}$ lower at $T = 0$ K [when $\Delta a(T)/a$ is normalized to $a = a(T = 290\text{ K})$].

If the dependences $\Delta a(T)/a$, $\Delta c(T)/c$, and $\Delta V(T)/V$ for YPO_4 are used as the comparison standard, it is found that the anomalies of the unit cell parameters volume of $TbPO_4$ at 10 K are 8×10^{-4}, -6×10^{-4}, and 10×10^{-4}, respectively.

Similar anomalies of the lattice parameters and volume are observed also for $DyPO_4$, $HoPO_4$, and $TmPO_4$ phosphates (Figs. 5 and 6), which differ only in respect of the magnitude of the anomaly and the characteristic temperature. For convenience and clarity of comparison, the dependences $\Delta a/a$ and $\Delta c/c$ are shifted in Figs. 5 and 6 relative to one another along the ordinate; in each case the shift is 2×10^{-4} and they are arranged in accordance with the magnitude of the anomaly. The large error in the determination of the lattice parameters of the phosphates of Dy, Ho, Er, and Yb is due to the fact that the measurements were carried out on polycrystalline samples.

The thermal expansion anomalies, i.e., an increase in the parameter as a result of cooling below 100 K, are exhibited most clearly by the dependences $\Delta a/a$ for our rare-earth phosphates (Fig. 5). In the case of the parameter c the contribution of the rare-earth ion to the thermal expansion has the opposite sign and produces a stronger (compared with the pure phonon mechanism) reduction in the parameter as a result of cooling. Therefore, the existence and magnitude of the anomaly of the parameter c can be judged (Fig. 6) on the basis of the temperature dependence of the difference between the dependences $\Delta c/c$ for YPO_4 (or $ErPO_4$, in which case the rare-earth contribution is negligible) and for the rare-earth phosphate under investigation.

A special feature of the thermal expansion of $DyPO_4$ is the stronger nature of the anomalies $\Delta a(T)/a$, $\Delta c(T)/c$, and $\Delta V(T)/V$. The thermal expansion anomalies of $DyPO_4$ are as follows: $\delta(\Delta a/a) = 13\cdot 10^{-4}$, $\delta(\Delta c/c) = -8\times 10^{-4}$, and $\delta(\Delta V/V) = 19\cdot 10^{-4}$, i.e., they are 1.5 times greater than the corresponding anomalies of $TbPO_4$. In the case of $HoPO_4$ the thermal expansion anomalies decrease and they amount to $\delta(\Delta a/a) = 4\cdot 10^{-4}$, $\delta(\Delta c/c) = -10\cdot 10^{-4}$, and $\delta(\Delta V/V) = (0\pm 1)\cdot 10^{-4}$, whereas in the case of $TmPO_4$ they rise again: $\delta(\Delta a/a) = 7\times 10^{-4}$, $\delta(\Delta c/c) = -9\cdot 10^{-4}$, and $\delta(\Delta V/V) = 5\cdot 10^{-4}$.

The x-ray diffraction measurements failed to reveal the thermal expansion anomalies in the case of the Er and Yb phosphates. Among the singularities of these phosphates one should mention the considerable anisotropy of the thermal expansion along and at right-angles to the tetragonal c axis exhibited by $YbPO_4$ (Fig. 5).

5. DISCUSSION OF RESULTS

5.1. Thermal expansion of rare-earth phosphates

It is well known that at sufficiently high temperatures the unit cell (crystal lattice) parameters rise with temperature, which is a consequence of the anharmonicity of the crystal lattice vibrations (phonon–phonon interaction). At low temperatures the lattice parameters of the majority of crystals cease to depend on temperature if there are no phase transitions. In the case of the rare-earth ions however there are additional anomalies (reduction or increase in the lattice parameters), which are due to the magnetoelastic interaction of the aspherical electron cloud of the 4f shell of the rare-earth ion with the lattice. Cooling gradually freezes out the excited levels and changes the asphericity of the electron shell, which results—via the magnetoelastic interaction—in an additional increase or reduction in the lattice parameters. Anomalies of this type have been investigated experimentally and theoretically for rare-earth aluminate and gallate garnets.[4]

It follows from the expressions in Eq. (10) that the con-

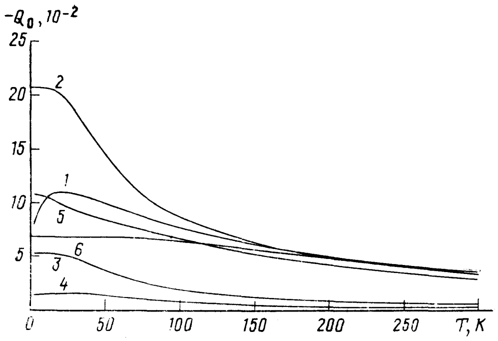

FIG. 7. Calculated temperature dependences of the quadrupole moment Q_0 of the following rare-earth phosphates: 1) $TbPO_4$; 2) $DyPO_4$; 3) $HoPO_4$; 4) $ErPO_4$; 5) $TmPO_4$; 6) $YbPO_4$.

tribution of the rare-earth ion to the thermal expansion is independent of the magnitude of the JT correlations, but is governed by the magnetoelastic coefficients $B^{\alpha 1}$ and $B^{\alpha 2}$, and by the change in the quadrupole moment $Q_0 = \frac{1}{3}\alpha_J \langle O_2^0 \rangle$ with temperature. Then, the experimental evidence shows no significant difference between the thermal expansion of the rare-earth phosphates with strong ($TbPO_4$, $TmPO_4$) or weak ($DyPO_4$, $HoPO_4$) JT interactions. The temperature dependences of the contributions of the rare-earth ions to the lattice parameters (which can be found by subtracting the phonon contribution deduced from measurements on the nonmagnetic analog in the form of yttrium phosphate) repeat the temperature dependence of the quadrupole moment Q_0 calculated by us for the known electron structures of the rare-earth ions in the phosphates (Fig. 7).

The experimentally observed contribution of the rare-earth ions to the thermal expansion agrees with the changes, along the rare-earth phosphate series, in the calculated temperature dependences of the quadrupole moment Q_0. This allows us to draw the conclusion that, in the zeroth approximation, the magnetoelastic coefficients $B^{\alpha 1}$ and $B^{\alpha 2}$ are not too different along the rare-earth phosphate series. In this approximation the calculated quadrupole moments Q_0 account for the changes in the thermal expansion anomalies along the rare-earth phosphate series. For example, the anomaly of $\Delta a/a$ observed experimentally in the temperature range 10–50 K (where there is no phonon contribution to the thermal expansion) is three times greater for $DyPO_4$ than for $TbPO_4$ and it is due to the three times greater changes in the value of Q_0 for $DyPO_4$ than for $TbPO_4$ in this temperature range.

We shall now consider some characteristics of the variation of the quadrupole moments along the rare-earth phosphate series (Fig. 7). We can find the relationship between this behavior and the specific electron structures of the rare-earth ions by separating the contributions made to the total quadrupole moment Q_0 by the various levels of the rare-earth ions at different temperatures. The largest value and the strongest temperature dependence of Q_0 is exhibited by $DyPO_4$ for which the ground-state doublet of the Dy^{3+} ion is characterized by a strongly anisotropic g tensor ($g_z = 19.5, g_x = g_y \lesssim 0.3$) and by a large contribution to the quadrupole moment. The total contribution to Q_0 by the higher doublets is small, so that the temperature dependence of the quadrupole moment of the Dy^{3+} ion is governed by the reduction in the population of the ground-state doublet on increase in temperature and at $T < 70$ K it can be described by the usual Boltzmann dependence. The quadrupole moment of $HoPO_4$ is approximately four times less, but it has a similar temperature dependence. The dependence $Q_0(T)$ for $TmPO_4$ is less steep and this is due to a considerable contribution made to the quadrupole moment by the "anisotropic" excited levels. The reduction in the quadrupole moment of $TbPO_4$ as a result of cooling below 10–15 K is due to a reduction in the population of the excited singlet of the Tb^{3+} ion, which makes the largest contribution to the moment. The quadrupole moment of $ErPO_4$ is small and in the case of $YbPO_4$ the change in this moment is small below 100 K, so that the thermal expansion anomalies are not observed for these compounds. However, the considerable change in the quadrupole moment of $YbPO_4$ in the range 0–300 K is responsible for the observed thermal expansion anisotropy [see Eq. (10)].

Since we do not know the elastic constants C_0^{μ}, we cannot determine accurately the magnetooptic coefficients $B^{\alpha 1}$ and $B^{\alpha 2}$. However, in the case of the relationships between the elastic constants typical of the rare-earth compounds with the zircon structure, a comparison of the theoretical expressions with the experimentally determined temperature dependence of $\Delta a/a$ and $\Delta c/c$ indicates that the magnetoelastic coefficient $B^{\alpha 1}$ should be a negative quantity, which does not differ too much from the absolute value of $B^{\alpha 2}$. This conclusion applies to the phosphates of Tb, Dy, Ho, and Tm. In the case of the phosphates of Er and Yb we cannot draw conclusions about the magnitude of the magnetoelastic coefficients because there is practically no theoretical or experimental information on the contribution of the rare-earth ions in these compounds to the low-temperature thermal expansion.

Using the values of the elastic constants of $TmVO_4$ given in Ref. 18, we can estimate the magnetoelastic coefficients of the rare-earth phosphates using the thermal expansion anomalies. In the case of $TmPO_4$ these coefficients are $B^{\alpha 1} = -2.1 \times 10^3$ K/ion and $B^{\alpha 2} = 6.4 \times 10^3$ K/ion, whereas for $DyPO_4$ they are $B^{\alpha 1} = -4.3 \times 10^3$ K/ion and $B^{\alpha 2} = 4.1 \times 10^3$ K/ion.

5.2. Magnetoelastic contribution to the Young modulus of rare-earth phosphates

For the majority of these compounds the elastic (rigidity) constants increase as a result of cooling and this increase slows down at sufficiently low temperatures. The temperature dependences of the elastic constants, like those of the lattice parameters, are a consequence of the anharmonicity of the crystal lattice vibrations.

We can suggest a number of reasons why the behavior of the elastic constants can deviate from the usual Debye dependence. Firstly, the elastic constants have anomalies near various phase (structural, magnetic, ferroelectric, etc.) transitions. In the case of the rare-earth compounds with the zircon structure the cooperative JT effect is known to be accompanied by vanishing of one of the components of the matrix of the elastic moduli $C_{11}-C_{12}$ or C_{66}, depending on the nature of the distortion caused by a structural phase transition. If the concentration of the JT ions is below the critical value, the JT interaction results in softening, i.e., it reduces the elastic moduli as temperature is lowered and this is observed even at concentrations of these ions which are one or two orders of magnitude less than the critical value.

The magnetoelastic interaction makes an additional contribution to the elastic constants of rare-earth compounds. The magnitude and the temperature dependence of these contributions are different for different rare-earth ions and are governed by the characteristics of their electron structure. They can be described by the deformation susceptibilities χ_μ ($\mu = \alpha, \gamma, \delta, \varepsilon$). It follows from Eqs. (7) and (9) that the JT correlations, the magnitude of which is governed by the constant K^μ in the adopted formalism, can enhance greatly the single-ion magnetoelastic contribution described by the deformation susceptibility χ_μ, so that the elastic constant for which the corresponding value of K^μ is large.

Numerical calculations for the whole rare-earth phosphate series showed that the deformation susceptibility χ_α is the largest and it is included in the resultant correction to the Young modulus twice with the magnetoelastic coefficients $B^{\alpha 1}$ and $B^{\alpha 2}$ [see Eq. (9)]. Therefore, in the case of comparable magnetoelastic coefficients and in the absence of the correlation-induced enhancement, the net magnetoelastic contribution to the Young modulus and its temperature dependence are governed primarily by the deformation susceptibility χ_α.

The calculated temperature dependences of χ_α are plotted in Fig. 8. We can see that the deformation susceptibilities χ_α of the Tb, Dy, Tm, and Yb ions are comparable. Since the softening of the Young modulus of the Tb and Tm phosphates is an order of magnitude greater than the change in $\Delta E(T)/E$ of the Dy and Yb phosphates, we may conclude that the JT correlations are particularly important in $TbPO_4$ and $TmPO_4$ and they enhance the single-ion magnetoelastic contribution. The results of our determination of the elastic moduli of the rare-earth phosphates allow us to divide them, depending on the strength of the JT interaction, into two groups and it is more convenient to discuss the elastic properties of these two groups separately.

The characteristic features of the acoustic properties of $TbPO_4$ confirmed that it exhibits a structural phase transition and that the low-temperature maximum of the absorption of sound is due to relaxation of JT domains at temperatures $T < T_c$. As in the case of the other rare-earth phosphates with the zircon structure, the minimum of the dependence $\Delta E(T)/E$ obtained for a polycrystalline sample of this compound occurs at a temperature slightly lower than the temperature T_c of the structural phase transition and this is clearly due to an additional "domain" contribution to the elastic modulus at $T < T_c$. The application of a magnetic field reduces considerably, as expected, the domain maximum q^{-1}, because it maintains the single-domain state of those crystallites whose easy magnetization axes are oriented along the field so that they make no contribution to the relaxation-induced absorption of sound.

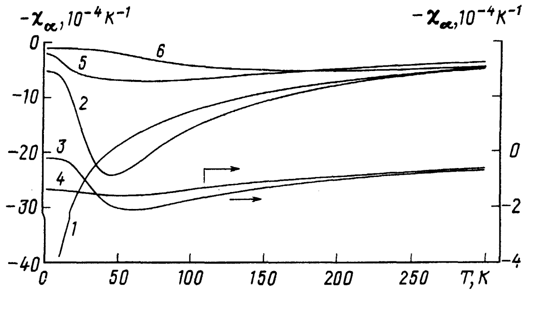

FIG. 8. Calculated temperature dependences of the deformation susceptibility χ_α of the following rare-earth phosphates: 1) $TbPO_4$; 2) $DyPO_4$; 3) $HoPO_4$; 4) $ErPO_4$; 5) $TmPO_4$; 6) $YbPO_4$.

A structural phase transition does not occur in $TmPO_4$, as deduced from the weak absorption of sound at low temperatures, but a strong softening of the Young modulus demonstrates the existence of the JT correlations. Therefore, a comparison of the acoustic properties of these two phosphates shows that $TbPO_4$ is a real JT elastic, whereas $TmPO_4$ is a virtual one.

Experiments on single crystals have shown that the elastic constant $C^\delta = 2C_{66}$ of $TmPO_4$ exhibits strong softening.[18] In the case of $TbPO_4$ it follows from the published experimental data that a strong softening affects the elastic constant $C^\varepsilon = 2C_{44}$ and possibly also $C^\delta = 2C_{66}$. In fact, the deformation susceptibilities χ_δ of $TmPO_4$ and the susceptibilities χ_δ and χ_ε of $TbPO_4$ are not small and exhibit the expected temperature dependences (Fig. 9).

A comparison of the experimental and theoretical dependences $\Delta E(T)/E$ obtained for $TmPO_4$ and substitution of the elastic constants C_0^μ of $TmVO_4$ from Ref. 16, yield estimates of the values of B^δ and K^δ for the Tm phosphate and allows us to study the influence of the JT correlations on the nature of the dependence $\Delta E(T)/E$. If we assume that $K^\delta = 0$, we find that $|B^\delta| = 1.4 \cdot 10^4$ K/ion, which is far too large compared with $|B^{\alpha 1}|$, and $|B^{\alpha 2}|$, determined from the thermal expansion anomalies (in the case of the rare-earth intermetallic compounds it is reported in Ref. 3 that $B^\mu \approx 10^3$ K/ion).

The JT correlations [see Eq. (7)] enhance (if $K^\delta > 0$) the softening of the elastic constant C^δ, and this effect is particularly strong near the maximum χ_δ. An increase in the correlation constant K^δ increases the depth of the minimum $C^\delta(T)$ and at a critical value of K^δ the elastic constant C^δ vanishes, which corresponds to a structural phase transition. It should be noted that an increase in K^δ distorts the dependence $C^\delta(T)$ and changes in particular the relationship between $C^\delta_{\min}$ and C^δ (0 K) (curves *3, 4,* and *5* in Fig. 9). The value of K^δ is estimated from the minimum value of $\Delta E(T)/E$.

If $K^\delta = 1.4 \times 10^3$ K/ion, which represents $\approx 80\%$ of the critical value,[19] we have $|B^\delta| = 3.8 \cdot 10^3$ K/ion. For

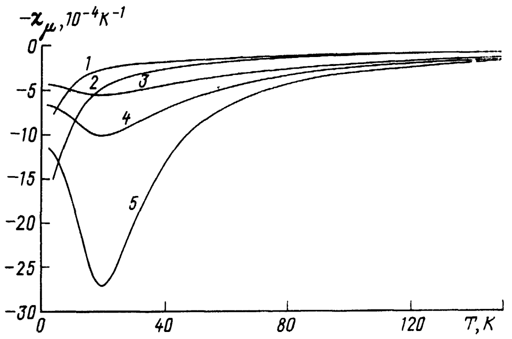

FIG. 9. Calculated dependences of the deformation susceptibilities χ_δ (1) and χ_ε (2) of $TbPO_4$ and of $\chi_\delta^{\rm corr} = \chi_\delta/(1 - K^\delta \chi_\delta)$ calculated for $TmPO_4$ assuming different values of the correlation constant K^δ: 3) $K^\delta = 0$; 4) $K^\delta = 0.8 \times 10^3$ K/ion; 5) $K^\delta = 1.4 \times 10^3$ K/ion.

these values of the parameters we find however that the calculated dependence $\Delta E(T)/E$ lies well above the experimental value at temperatures $T < 20$ K. A better agreement between the calculated and experimental dependences $\Delta E(T)/E$ in the range 10–100 K is observed if we assume that $K^{\delta} = 0.8 \times 10^3$ K/ion, when we have $|B^{\delta}| = 8.3 \cdot 10^3$ K/ion (curve 4 in Fig. 9).

The second and more numerous group of the phosphates includes also those for which the JT correlations are not that important and the renormalization of the elastic moduli can be described by the single-ion magnetoelastic interaction. As pointed out already, the main contribution to the Young modulus of this group of phosphates comes from the deformation susceptibility χ_{α} with the temperature dependences shown in Fig. 8. We can see that in the case of the Dy, Ho, Er, and Yb phosphates the temperature dependences $-\chi_{\alpha}(T)$ pass through a minimum in the region of 50 K, like the experimental dependences obtained for the same compounds (after subtraction of the phonon contribution deduced for YPO_4). In agreement with the experimental results, there is an increase in the temperatures of an extremum of $-\chi_{\alpha}$ (representing a steep rise of the Young modulus as a result of cooling) and a reduction in the anomalies of the magnetoelastic contribution to the modulus characterized by $\chi_{\alpha}^{\min} - \chi_{\alpha}(0)$, as we go from the Dy to the Ho, Er, and Yb phosphates.

The quantitative changes in the anomalies of the Young modulus along the rare-earth phosphate series are described less satisfactorily (compared with the thermal expansion) by changes solely in the electron structure of the rare-earth ions. This may be due to the fact that the anomalies of $\Delta E(T)/E$ are proportional to the square of the magnetoelastic coefficients B^{μ} and the assumption about their constancy along the rare-earth ion series is in this case quite a coarse approximation. Moreover, there is no information on the JT correlations for the rare-earth phosphates of the second group. Finally, in the case of these compounds some contribution to the dependence $\Delta E(T)/E$ is made, apart from χ_{α}, by other deformation susceptibilities.

For example, the change of χ_{α} observed in the range 0–50 K for $DyPO_4$ is an order of magnitude greater than for $HoPO_4$, whereas the experimental anomalies of the Young modulus observed in this range of temperatures differ by only a factor of 3. This means that either the magnetoelastic coefficients of $HoPO_4$ are 1.5–2 times greater than those of $DyPO_4$ or in the case of $HoPO_4$ there is some correlation enhancement, which can be assumed, in principle, because the ground state of the Ho^{3+} ion is a non-Kramers doublet. One should point out also that if we assume constancy of the magnetoelastic coefficients along the rare-earth phosphate series, we find that the calculated anomalies of $\Delta E(T)/E$ are overestimated compared with the experimental values obtained for $YbPO_4$ and are underestimated in the case of $ErPO_4$.

The magnetoelastic coefficients $B^{\alpha 1}$ and $B^{\alpha 2}$, determined from the thermal expansion, allow us to estimate the low-temperature anomaly of the Young modulus $\Delta E(4.2\ K)/E - (\Delta E(T)/E)_{\min}$ from Eq. (9) using the calculated values of $\chi_{\alpha}(T)$. In the case of $DyPO_4$, we obtain 1.2×10^{-2}, whereas the experimental anomaly amounts to 1.8×10^{-2} (Fig. 3). Bearing in mind the approximate nature of our calculations, we can conclude that the agreement is very good.

6. CONCLUSIONS

We carried out a systematic experimental and theoretical investigation of the contribution of the rare-earth ions to the temperature dependences of the lattice parameters in the Young modulus of the phosphates RPO_4 of the heavy rare-earth ions. The main results can be formulated briefly as follows. It was found that the anomalies of the thermal expansion of these rare-earth phosphates were described, irrespective of the presence or absence of the JT correlations, quite satisfactorily by the temperature dependences of the quadrupole moments calculated from the known parameters of the crystal field of the rare-earth ions. The experimental values of the anomalies of the lattice parameters *a* and *c* were used to estimate the single-ion magnetoelastic constants $B^{\alpha 1} \approx -(2\text{–}4) \times 10^3$ K/ion and $B^{\alpha 2} \approx (4\text{–}6) \times 10^3$ K/ion, which are of the same order of magnitude as the corresponding constants of the rare-earth intermetallic compounds.

The anomalies of the Young modulus of the rare-earth phosphates were described satisfactorily by the calculated, using the same crystal field parameters, deformation susceptibilities $\chi_{\mu}(T)$ of different symmetry. In the absence of the JT correlations it was found that the magnetoelastic correction to the Young modulus was dominated by the deformation susceptibilities $\chi_{\alpha}(T)$ and the anomalies of the Young modulus were described well by the magnetoelastic coefficients $B^{\alpha 1}$ and $B^{\alpha 2}$ deduced from the thermal expansion data. In the presence of the JT correlations ($TbPO_4$, $TmPO_4$) the resultant behavior of the Young modulus is governed by the corresponding correlation-enhanced deformation susceptibility: χ_{δ} for $TmPO_4$ and χ_{ε} (and possibly also χ_{δ}) for $TbPO_4$.

We shall conclude by noting that the combined investigation of the temperature dependence of the structural and elastic characteristics provides mutually complementary results, because such investigations (particularly those carried out on single crystals) allow us to determine the complete set of the single-ion magnetoelastic and intercenter parameters of the interaction in a given compound.

The authors are deeply grateful to B. V. Mill' for supplying single crystals of rare-earth phosphates, and also for the help and valuable advice in the synthesis of polycrystalline RPO_4 samples.

[1] G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. **38**, 1 (1975).

[2] B. Luthi, M. Niksch, R. Takke *et al.*, in *Crystalline Electric Field Effects in f-Electron Magnetism* (Proc. Intern. Conf., Wroclaw, Poland, 1981, ed. by R. P. Guertin, W. Suski, and Z. Zotnierek), Plenum Press, New York (1982), p. 233.

[3] R. Aleonard and P. Morin, J. Magn. Magn. Mater. **84**, 255 (1990).

[4] N. P. Kolmakova, R. Z. Levitin, V. N. Orlov, and N. F. Vedernikov, J. Magn. Magn. Mater. **87**, 218 (1990).

[5] É. du Trémolet de Lacheisserie, Ann. Phys. (Paris) **5**, 267 (1970).

[6] P. Morin, J. Rouchy, and D. Schmitt, Phys. Rev. B **37**, 5401 (1988).

[7] B. Luthi, in *Dynamical Properties of Solids* (ed. by G. K. Horton and A. A. Maradudin), Vol. 3, Metals, Superconductors, Magnetic Materials, Liquids, North-Holland, Amsterdam (1980), p. 245.

[8] T. D. Shermergor, Theory of Elasticity of Microinhomogeneous Media [in Russian], Nauka, Moscow (1977), p. 37.

[9] W. Bohm, H. G. Kahle, and W. Wuchner, Phys. Status Solidi B **126**, 381 (1984).

[10] C. A. Morrison and R. P. Leavitt, in *Handbook on the Physics and Chemistry of Rare-Earths* (ed. by K. A. Gschneidner, Jr., and L. Eyring), Vol. 5, North-Holland, Amsterdam (1982), p. 461.

[11] T. Hayhurst, G. Shalimoff, N. Edelstein *et al.*, J. Chem. Phys. **74**, 5449 (1981).
[12] J. A. Hodges, J. Phys. (Paris) **44**, 833 (1983).
[13] P. C. Becker, T. Hayhurst, G. Shalimoff *et al.*, J. Chem. Phys. **81**, 2872 (1984).
[14] J. C. Wright and H. W. Moos, Phys. Rev. B **4**, 163 (1971).
[15] I. R. Jahn and S. H. Smith, Phys. Status Solidi B **18**, 531 (1975).
[16] R. T. Harley and D. I. Manning, J. Phys. C **11**, L633 (1978).
[17] F. Sayetat, Physica B + C (Utrecht) **86–88**, 1467 (1977).
[18] R. L. Melcher, in *Physical Acoustics: Principles and Methods* (ed. by W. P. Mason and R. N. Thurston), Vol. 12, Academic Press, New York (1976), p. 1.
[19] B. G. Vekhter and M. D. Kaplan, Zh. Eksp. Teor. Fiz. **87**, 1774 (1984) [Sov. Phys. JETP **60**, 1020 (1984)].

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