Quadrupole approximation in the theory of the magnetoelasticity of rare-earth compounds: magnetoelastic contribution to the thermal expansion of the rare-earth vanadates RVO_4

Z. A. Kazeĭ and N. P. Kolmakova

M. V. Lomonosov Moscow State University, 119899 Moscow, Russia

(Submitted 22 May 1995)
Zh. Éksp. Teor. Fiz. **109**, 1687–1703 (May 1996)

Systematic experimental and theoretical investigations of the thermal expansion of the rare-earth vanadates RVO_4 (R=Pr, Nd, Gd–Ho, and Tm) are carried out. Considerable magnetoelastic thermal-expansion anomalies are detected, and the magnetoelastic contributions are identified in the Debye model of thermal expansion with consideration of corrections for the variation of the phonon contribution along the RVO_4 series. The applicability of the quadrupole approximation to the totally symmetric modes is discussed on the basis of a comparison of calculated multipole moments of all orders for different rare-earth ions in the vanadate structure. It is shown that the magnetoelastic contribution to the thermal expansion of rare-earth vanadates is described well by the temperature dependences of the quadrupole moments of the rare-earth ions. The totally symmetric magnetoelastic coefficients for all the rare-earth ions investigated are determined from the experimental data on the magnetoelastic contributions, and comparisons are made for various rare-earth ions in the structure under consideration, as well as for the closely related phosphate structure.
[S1063-7761(96)01405-9]

1. INTRODUCTION

Rare-earth compounds, which are characterized by numerous interactions of varied nature and of comparable magnitude, viz., exchange, magnetoelastic, Jahn–Teller, and other interactions, are among the most complicated and important objects of study in the physics of magnetism. The magnetoelastic interaction, which is far stronger in rare-earth compounds than in compounds of transition elements with an unfilled *d* subshell and has a single-ion nature in oxides, plays an important role in shaping their magnetic behavior and magnetic characteristics. The form of the one-particle magnetoelastic Hamiltonian and the number of independent magnetoelastic coefficients are determined by the symmetry of the environment of the magnetic ion and the approximation used.

The complete magnetoelastic Hamiltonian in the multipole approximation[1–3] contains a large number of terms even for compounds of fairly high symmetry. In the case of tetragonal symmetry in the environment of the rare-earth ion, the number of terms in the one-particle Hamiltonian and thus the number of magnetoelastic coefficients both equal 24. Obviously, such Hamiltonians are essentially useless for interpreting experimental results. The treatment is usually restricted to the quadrupole approximation, which for tetragonal symmetry, for example, reduces the number of terms in the Hamiltonian to five. However, it is not clear whether the simple quadrupole approximation is adequate for faithfully describing the entire set of magnetoelastic effects in systems with a strong magnetoelastic interaction.

Various formalisms (the pseudospin, initial-susceptibility, and crystal-field formalisms[4,5]), which all operate within the quadrupole approximation, are used for systems with strong magnetoelastic and Jahn–Teller interactions. There have been very few studies devoted to the applicability of the quadrupole approximation in the theory of the magnetoelasticity of rare-earth compounds of different symmetry. The quadrupole approximation is widely used to describe cubic rare-earth intermetallic compounds (see, for example, the review in Ref. 4). It is substantiated by evaluations performed in the point-charge model,[6] which show that the principal magnetoelastic effects observed in an external magnetic field and/or after spontaneous deformation of the crystal are due to a second-order term in the magnetoelastic Hamiltonian, which is absent in the undistorted lattice of a cubic crystal.

It was concluded in Ref. 7 that the quadrupole approximation is applicable to the description of magnetostriction and the magnetoelastic contribution to the thermal expansion of oxide compounds with cubic symmetry, i.e., paramagnetic aluminates and gallate garnets with the heavy rare-earth ions from Tb to Yb (the local symmetry of the environment of the rare-earth ion in the structure of a garnet is orthorhombic). For the tetragonal phosphates RPO_4 with a zircon structure and rare-earth ions from Tb to Yb (Refs. 8 and 9), the anomalies in the thermal expansion and Young's modulus and the ΔE effect can be described within the quadrupole approximation. The successful description of all the experimental data supports the validity of the quadrupole approximation for the zircon structure, but there are no *a priori* arguments regarding its applicability.

The contributions of the multipole moments to various magnetoelastic effects depend both on their magnitude in comparison with the quadrupole moments and on the ratio between the quadrupole and multipole magnetoelastic coefficients. The most general treatment reveals that the multipole moments can be not only comparable in value, but also considerably greater than the corresponding quadrupole moments. The main difficulty in the theoretical investigation of magnetoelastic phenomena lies in calculating the magnetoelastic coefficients, since such calculations require knowledge of numerous structural and electronic parameters of the compound under investigation, such as ion–ion distances, bond angles, the electron-density distribution in the lattice, covalency effects, etc. Calculations in semiphenomenological models, for example, in the exchange-charge model,[10] which make it possible to express the magnetoelastic coefficients in the form of explicit functions of the structural parameters of the crystal and the charges and dipole moments of the ions, are of unquestionable interest. The number of fitting parameters decreases in this case, but the calculated coefficients have not yet been verified experimentally, and their values can be regarded only as estimates. The treatment of the magnetoelastic coefficients as phenomenological constants and their determination from comparisons with experimental data are more realistic approaches at the present time.

The conditions for applicability of the quadrupole approximation to totally symmetric and low-symmetry magnetoelastic modes, i.e., the relative contributions of the multipole moments of orders higher than the quadrupole moment to the magnetoelastic energy and the magnetoelastic effects, can be different, since the main magnetoelastic effect for the latter modes results from a corresponding nonzero quadrupole moment under the conditions of an external symmetry-lowering force.

The purpose of the present work is to investigate the totally symmetric magnetoelastic modes in the vanadate structure and the conditions for applicability of the quadrupole approximation to their description. Since the totally symmetric magnetoelastic modes for rare-earth zircons are relatively small, situations in which these modes are displayed in their pure form, i.e., not masked by low-symmetry magnetoelastic modes, are of greatest interest, especially in the experimental area. Such situations are realized for magnetoelastic thermal-expansion anomalies in an undistorted phase or for magnetostriction along high-symmetry directions in a crystal.

In the present work we investigated the magnetoelastic contribution to the thermal expansion of rare-earth vanadates. Similar investigations were previously carried out for a series of rare-earth phosphates having a zircon structure with heavy rare-earth ions.[8] The crystal-field parameters for rare-earth vanadates and phosphates differ appreciably, so that the same rare-earth ions have drastically different spectra and consequently behave totally differently in these closely related structures. Therefore, a systematic investigation of the magnetically ordered interactions for a series of rare-earth vanadates followed by a comparison with rare-earth phosphates with consideration of the difference between the crystal fields and structural parameters is of unquestionable interest.

2. SAMPLES AND MEASUREMENT METHOD

The measurements were performed on single-crystal samples grown by spontaneous crystallization from a solution with molten $PbO–PbF_2–V_2O_5–H_3BO_3$ as the solvent.

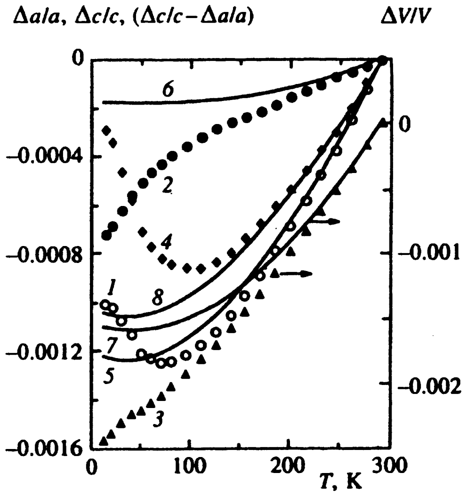

FIG. 1. Relative variation of the unit-cell parameters $\Delta c/c$ (*1*) and $\Delta a/a$ (*2*), the volume $\Delta V/V$ (*3*), and the tetragonality $(\Delta c/c-\Delta a/a)$ (*4*) of $HoVO_4$ with the temperature. The analogous dependences of $\Delta c/c$ (*5*), $\Delta a/a$ (*6*), $\Delta V/V$ (*7*), and $(\Delta c/c-\Delta a/a)$ (*8*) for $GdVO_4$ are shown for comparison.

The x-ray diffraction investigations of the parameters a and c of the tetragonal unit cell were performed on a Geigerfleks diffractometer with an Oxford Instruments CF-108 continuous-flow He cryostat on single-crystal wafers with natural (100) crystal faces using the (10.00) reflection (Cu K_β radiation $2\theta \sim 150–160°$) and the (008) reflection (Cu $K_{\alpha 1}$ radiation $2\theta \sim 152–160°$). The relative error in the measurements of a and c with respect to the temperature was $\delta a/a \approx \delta c/c \approx \cot\theta \cdot \Delta\theta \approx 10^{-5}$ ($\Delta\theta \approx 0.003°$). Due to the sharp increase in the flow rate of liquid helium in the continuous-flow cryostat, in several cases some loss of alignment of the crystal was observed at low temperatures ($<40–50$ K) with a resultant systematic error of $\sim 0.01°$. This systematic error makes contributions of comparable magnitude and opposite sign to the magnetoelastic anomalies along the a and c axes; therefore, it is preferable to use the averaged magnetoelastic contribution $\Delta l_{\mathrm{me}}/l$ to isolate the magnetoelastic contributions, calculate the magnetoelastic constants, and optimize the crystal field.

3. EXPERIMENTAL RESULTS

3.1. Thermal expansion of RVO_4 (R = Pr, Nd, Tb–Ho, and Tm)

Similar variation of the lattice constants with the temperature, differing only with respect to the magnitude of the magnetoelastic anomalies and the characteristic temperatures, was observed in most of the rare-earth vanadates (Figs. 1–3). Let us examine the features of the thermal expansion of the rare-earth vanadates in greater detail in the case of $HoVO_4$. Figure 1 presents experimental plots of the temperature dependence of a and c [$\Delta a/a=a(T)/a_0-1$, $\Delta c/c=c(T)/c_0-1$, $a_0=a(290\text{ K})$, $c_0=c(290\text{ K})$, curves *1* and *2*] and the volume [$\Delta V/V=V(T)/V_0-1$, $V_0=a_0^2c_0$, curve *3*] of the tetragonal $HoVO_4$ unit cell. The solid lines (curves *5*, *6*, and *7*) in this figure depict the analogous de-

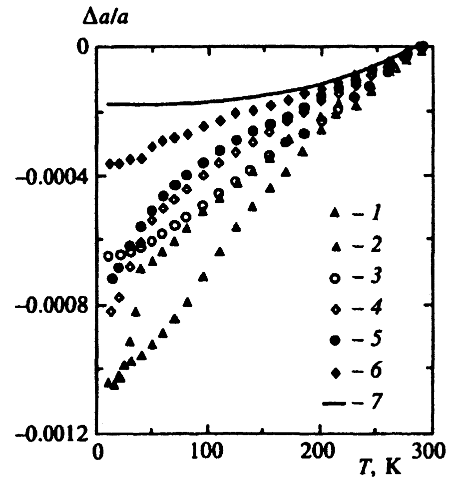

FIG. 2. Relative variation $\Delta a/a = a(T)/a_0 - 1$ of the tetragonal unit-cell parameter of rare-earth vanadates with the temperature $[a_0 = a(290\ \mathrm{K})]$: *1)* $DyVO_4$ ($a_0 = 7.1485$ Å), *2)* $TbVO_4$ ($a_0 = 7.1789$ Å), *3)* $TmVO_4$ ($a_0 = 7.0705$ Å), *4)* $PrVO_4$ ($a_0 = 7.3657$ Å), *5)* $HoVO_4$ ($a_0 = 7.1244$ Å), *6)* $NdVO_4$ ($a_0 = 7.3333$ Å), *7)* $GdVO_4$ ($a_0 = 7.2148$ Å).

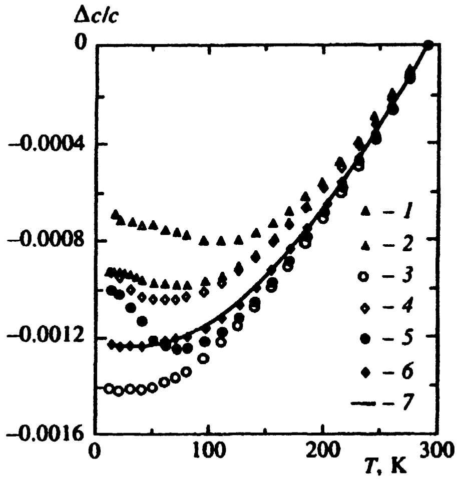

FIG. 3. Relative variation $\Delta c/c = c(T)/c_0 - 1$ of the tetragonal unit-cell parameter of rare-earth vanadates with the temperature $[c_0 = c(290\ \mathrm{K})]$: *1)* $DyVO_4$ ($c_0 = 6.3071$ Å), *2)* $TbVO_4$ ($c_0 = 6.3254$ Å), *3)* $TmVO_4$ ($c_0 = 6.2573$ Å), *4)* $PrVO_4$ ($c_0 = 6.4707$ Å), *5)* $HoVO_4$ ($c_0 = 6.2878$ Å), *6)* $NdVO_4$ ($c_0 = 6.4365$ Å), *7)* $GdVO_4$ ($c_0 = 6.3486$ Å).

pendences for $GdVO_4$, which can be used to determine the phonon contribution to the thermal expansion of other RVO_4 crystals.

The plot of $\Delta a/a$ for holmium vanadate passes below the corresponding curve for the Gd compound at all temperatures, the temperature dependence differing strongly from the Debye dependence, which is typified by saturation below 100–80 K. The plot of $\Delta a/a$ exhibits a feature like a point of inflection, and the maximum of the coefficient of thermal expansion $\alpha_a = (1/a)da/dT$ is at ~ 30 K.

With the accuracy of our experiment we did not detect any broadening of the (10.00) reflections, which would have attested to distortion of the tetragonal zircon structure to an orthorhombic or lower structure $(a/b - 1 < 4 \times 10^{-5})$. This means that the structure of $HoVO_4$ remains tetragonal over the entire temperature range investigated and that only the tetragonality, which is defined by the quantity $\Delta c/c - \Delta a/c$, varies with the temperature, this variation being nonmonotonic (curve *4*).

The temperature dependence of $\Delta c/c$ for holmium vanadate has a nonmonotonic character with a minimum in the vicinity of 80 K, the thermal expansion of $HoVO_4$ being greater than that of $GdVO_4$ at $T > 60$ K, but the relationship changes at lower temperatures. In our opinion, this attests to a difference between the phonon contributions in the Ho and Gd vanadates. The coefficient of thermal expansion along the tetragonal axis $\alpha_c = (1/c)dc/dT$ changes sign at $T \sim 80$ K and has an extremum at ~ 30 K, which coincides with the maximum of α_a. It is seen that the magnetoelastic contributions along both axes for $HoVO_4$ are insignificant at temperatures above 100 K, but increase sharply at lower temperatures. The anomalies in the plots of $\Delta a/a$ and $\Delta c/c$ for $HoVO_4$ cause a volume anomaly $\Delta V/V = \Delta c/c + 2\Delta a/a$ (compare curves *3* and *7*).

The vanadates $PrVO_4$, $NdVO_4$, $TbVO_4$, $DyVO_4$, and $TmVO_4$ exhibit similar anomalies of the lattice constants (Figs. 2 and 3), whose magnitude can be evaluated from the difference between the values of $\Delta a/a$ and $\Delta c/c$ for the particular rare-earth vanadate and $GdVO_4$. The magnetoelastic contribution for the vanadates investigated is negative at all temperatures for a, but positive, at least at low temperatures, for c. It is clearly seen from Figs. 2 and 3 that the magnetoelastic contribution is maximum for the Dy compound and decreases gradually for the Tb, Tm, Pr, Ho, and Nd compounds. The sharp anomaly in the plot of $\Delta a/a$ (more precisely, in the plot of the interplanar distance d_{100}) at $T \approx 35$ K for $TbVO_4$ is caused by the orthorhombic distortion of the crystal structure due to the cooperative Jahn–Teller effect, and its magnitude is related to the degree of distortion of the structure. There is also a small anomaly along the tetragonal axis for $TbVO_4$ at $T \approx 35$ K, although the cooperative Jahn–Teller effect generally causes lattice deformation only in the basal plane and is not accompanied by a change in volume. It is conceivable that this anomaly is the result of a change in the magnetoelastic contribution due to a change in the spectrum of the Tb ion in the orthorhombic phase.

The magnetoelastic contributions along the a axis for the Pr, Ho, and Tm compounds at low temperatures are comparable in value, but the contribution for $TmVO_4$ has a smoother temperature dependence. The thermal expansion along the c axis for neodymium vanadate is essentially identical to the plot of $\Delta c/c$ for $GdVO_4$, while the curve for Tm is considerably lower, attesting to variation of the phonon contribution to the thermal expansion along the c axis in the Nd compound and especially in the Tm compound.

There are no systematic experimental data on the magnetoelastic contribution to the thermal expansion of the rare-earth vanadates in the tetragonal phase and its analysis in the literature. Only the work in Ref. 11, in which the temperature dependences of a and c for polycrystalline $DyVO_4$ were presented, can be cited.

3.2. Thermal expansion of the vanadate lattice ($GdVO_4$)

The features of the thermal expansion of the vanadates RVO_4 are similar to those previously observed for rare-earth phosphates[8] and are governed by the magnetoelastic contribution of the rare-earth ion. The phonon contribution must be properly taken into account to isolate the magnetoelastic contribution to the thermal expansion in a pure form. The x-ray diffraction measurements of $GdVO_4$ make it possible to isolate the phonon contributions $\Delta c_{\mathrm{ph}}/c$ and $\Delta a_{\mathrm{ph}}/a$ for other RVO_4 lattices, and it is only necessary to make corrections for their variation along the series of rare-earth ions. The greatest uncertainty in isolating the magnetoelastic contribution arises for c, for which the phonon contribution and its variation along the series of rare-earth ions are significant and the magnitude of the magnetoelastic contribution is small compared with the phonon contribution. In some cases this restricts the accuracy of the determination of the magnetoelastic contribution and, consequently, the magnetoelastic constants. In our opinion, fairly rough models, for example, the Debye model of a solid, may be used to introduce a correction for the variation of the phonon contribution, which amounts to 10–15% of the contribution itself in most cases.

According to the Debye model, the total thermal expansion

$$\Delta c_{\mathrm{ph}}/c=\alpha_0 T_D\int_0^t \frac{C_v(t)}{3R}dt \tag{1}$$

is described by a universal expression for the specific heat at constant volume $C_v(t)$ as a function of the reduced temperature $t=T/T_D$ with two independent coefficients, viz., the Debye temperature T_D and the coefficient of thermal expansion at high temperatures α_0. There are no simple and reliable formulas for calculating the variation of these two coefficients along a rare-earth series of isomorphous compounds. If it is assumed, according to Ref. 12, that $T_D\sim(M_0V_0)^{-1/2}$, for rare-earth vanadates the decrease in T_D due to change in the molar mass M_0 would be compensated in practice by the increase due to the change in the molar volume V_0 resulting from the lanthanide contraction. The Debye temperature would then remain constant along the rare-earth series, and the variation of the thermal expansion due to α_0 would be equivalent to the simple variation of the scale of the plot of $\Delta c/c$ for $GdVO_4$.

It is more difficult to predict the variation of α_0 along the rare-earth series, which is determined by such parameters as the Grüneisen constant $-d\ln T_D/d\ln V$ and the bulk compressibility. Our analysis showed that for rare-earth vanadates both the Debye temperature T_D and the coefficient of thermal expansion α_0 vary over a 20–40% range. The most reliable method for determining T_D and α_0 is probably to measure the thermal expansion for several diamagnetic or isotropic (weakly anisotropic) rare-earth compounds with a given structure and to extrapolate the experimental values.

Figure 4 presents the experimental data for $GdVO_4$ and plots of $\Delta a_{\mathrm{ph}}/a$ and $\Delta c_{\mathrm{ph}}/c$ calculated from Eq. (1) for various values of T_D and α_0. It is seen that the thermal expansion of $GdVO_4$ along the tetragonal axis is described fairly well by the Debye formula with the coefficients $T_D=590$ K and $\alpha_0=9.7\times10^{-6}$ (curve *1*). A comparison of curves *1* and *2* ($T_D=650$ K, $\alpha_0=10.5\times10^{-6}$) reveals that the coupled pair of coefficients is generally determined to within the accuracy of our experiment: T_D and α_0 can simultaneously decrease or increase somewhat, so that the agreement remains satisfactory within the experimental error. Precision measurements at temperatures below 150 K are needed to determine the Debye temperature more accurately. The thermal expansion along the a axis is approximated by the Debye dependence with the parameters $T_D=690$ K and $\alpha_0=1.7\times10^{-6}$ (curve *5*). The calculation shows that as the Debye temperature varies within ±50 K, the variation of the phonon contribution is small compared with the magnetoelastic contribution along the a axis (curves *6–8*, $T_D=500$, 550, 600 K) and very significant along the tetragonal axis (curves *3* and *4*, $T_D=540$, 640 K). We stress that the Debye model is used below as a simple and convenient form for describing the thermal expansion of the RVO_4 lattice in order to make corrections for the variation of the phonon contribution and that the values of T_D and α_0 obtained are not used or discussed any further.

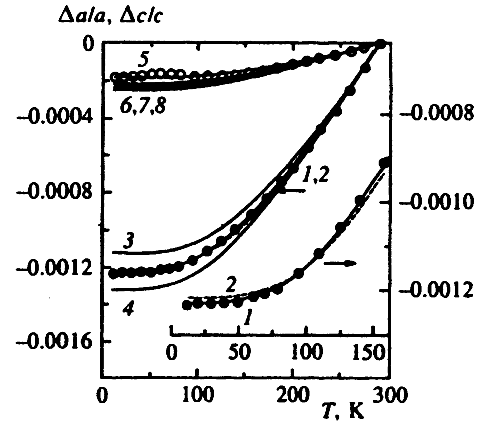

FIG. 4. Experimental ($GdVO_4$, points) relative variations $\Delta c/c$ (*1–4*) and $\Delta a/a$ (*5–8*) of the vanadate tetragonal unit-cell parameters with the temperature and analogous relative variations calculated from the Debye model. Calculation from Eq. (1) with various parameters: *1*) $\alpha_0=9.7\times10^{-6}$, $T_D=590$ K; *2*) $\alpha_0=10.5\times10^{-6}$, $T_D=650$ K; *3, 4*) $\alpha_0=9.7\times10^{-6}$, $T_D=540$, 640 K; *5*) $\alpha_0=1.7\times10^{-6}$, $T_D=690$ K; *6, 7, 8*) $\alpha_0=1.75\times10^{-6}$, $T_D=500$, 550, 600 K.

4. THEORETICAL TREATMENT

4.1. Magnetoelastic contribution to the thermal expansion of tetragonal compounds

To calculate the totally symmetric magnetoelastic modes (the rare-earth contribution to the thermal expansion and the magnetostriction in the high-symmetry directions in the crystal) we use a Hamiltonian which incorporates the crystal-field Hamiltonian H_{CF}, the Zeeman term H_Z, and the one-particle magnetoelastic Hamiltonian H_{ME}.

Since the ground-state multiplet is the actual space of functions for calculating thermodynamic properties, we write the crystal-field Hamiltonian in terms of the equivalent operators O_n^m in the form

$$H_{\mathrm{CF}}=\sum_{n,m} \alpha_n B_n^m O_n^m, \tag{2}$$

where $n=2, 4, 6$, $m=0, 4$ $(m \leqslant n)$, and $\alpha_2=\alpha_J$, $\alpha_4=\beta_J$, and $\alpha_6=\gamma_J$ are the Stevens parameters. The number of the crystal-field parameters B_n^m for tetragonal symmetry equals five.

The Zeeman interaction of a rare-earth ion with a magnetic field H is described by the Hamiltonian

$$H_Z=g_J\mu_B\mathbf{J}\cdot\mathbf{H}, \tag{3}$$

where g_J is the Landé factor, $\mathbf{J}$ is the angular momentum operator of the rare-earth ion, and μ_B is the Bohr magneton.

The one-particle magnetoelastic Hamiltonian which is linear with respect to the components of the strain tensor ε^{μ} (Ref. 13) (the harmonic approximation) for a rare-earth ion at a site with an environment having tetragonal symmetry contains 24 invariants. Five invariants contain second-rank tensor operators, eight invariants contain fourth-rank tensor operators, and 11 invariants contain sixth-rank tensor operators. We write down only the invariants that transform according to the totally symmetric representation in an explicit form in the magnetoelastic Hamiltonian, as they are significant for the totally symmetric modes being calculated:

$$H_{\mathrm{ME}}=-\sum_{n,m} \alpha_n O_n^m(B_{nm}^{\alpha1}\varepsilon^{\alpha1}+B_{nm}^{\alpha2}\varepsilon^{\alpha2}), \tag{4}$$

where $n=2, 4, 6$, $m=0, 4$ $(m \leqslant n)$, and the B_{nm}^{l} are the magnetoelastic coefficients. The symmetrized isotropic $(\varepsilon^{\alpha1})$ and tetragonal $(\varepsilon^{\alpha2})$ strains are expressed in terms of the Cartesian components of the strain tensor in the following manner

$$\varepsilon^{\alpha1}=(\varepsilon_{xx}+\varepsilon_{yy}+\varepsilon_{zz})/\sqrt{3},$$
$$\varepsilon^{\alpha2}=\sqrt{2/3}[\varepsilon_{zz}-(\varepsilon_{xx}+\varepsilon_{yy})/2]. \tag{5}$$

In many rare-earth compounds, including rare-earth zircons, there is also a fairly strong Jahn–Teller (or quadrupole) interaction, which is described for tetragonal symmetry by a two-particle quadrupole–quadrupole Hamiltonian of the type $K^{\gamma}\langle O_2^2\rangle O_2^2$. The rare-earth contribution to the totally symmetric magnetoelastic modes for an external magnetic field in the high-symmetry directions in the crystal does not depend on the low-symmetry pairwise quadrupole interactions.[8] As for the totally symmetric quadrupole interaction $K^{\alpha}\langle O_2^0\rangle O_2^0$, it can, in principle, make a contribution to the totally symmetric modes. Then both types of totally symmetric interactions, viz., the single-ion magnetoelastic interaction $(B^{\alpha1}, B^{\alpha2})$ and the pairwise quadrupole interaction K^{α}, make another contribution, in addition to the direct contribution, to the totally symmetry magnetoelastic modes by influencing the spectrum of the rare-earth ion. In fact, the resultant constant of the totally symmetric interactions

$$G^{\alpha}=\frac{(B^{\alpha1})^2C_0^{\alpha2}-2B^{\alpha1}B^{\alpha2}C_0^{\alpha12}+(B^{\alpha2})^2C_0^{\alpha1}}{C_0^{\alpha1}C_0^{\alpha2}-(C_0^{\alpha12})^2}+K^{\alpha} \tag{6}$$

stipulates a certain addition $G^{\alpha}\langle O_2^0\rangle O_2^0$ to the second-order crystal-field term $B_2^0O_2^0$ and, thus, spontaneous variation of the spectrum of the rare-earth ion with the temperature.

The real values of the single-ion and pairwise quadrupole interaction constants for rare-earth zircons, however, are such that the maximum value of this contribution at low temperatures does not exceed 5–7% of the static crystal-field parameter B_2^0 and can have an appreciable influence only on quasidegenerate low-lying levels of the rare-earth ion, as, for example, for the Tb ion in the structure of the phosphate.[14]

The totally symmetric magnetoelastic modes can be found in the usual way by minimizing the free energy. Using the actual Hamiltonian of the system we calculate the free energy

$$F=E_E-k_BT\ln Z. \tag{7}$$

In the partition function $Z=\Sigma_i\exp(-E_i/k_BT)$ it is sufficient to calculate the energy levels E_i for the rare-earth ion with consideration of the crystal-field Hamiltonian H_{CF} and the Zeeman term H_Z. When only the totally symmetric strains are taken into account, the elastic energy of a tetragonal crystal can be expressed in terms of the symmetrized components of the strain tensor in the following manner:[13]

$$E_E=\frac{1}{2}C_0^{\alpha1}(\varepsilon^{\alpha1})^2+C_0^{\alpha12}\varepsilon^{\alpha1}\varepsilon^{\alpha2}+\frac{1}{2}C_0^{\alpha2}(\varepsilon^{\alpha2})^2, \tag{8}$$

where the C_0^{μ} are the symmetrized elastic constants of the lattice without consideration of the magnetic interactions, whose relationship to the Cartesian components C_{ij} was given, for example, in Ref. 5.

For the magnetoelastic anomalies of the parameters a and c of the tetragonal lattice we obtain

$$\frac{\Delta c_{\mathrm{me}}(T)}{c}=\sum_{nm}\frac{B_{nm}^{\alpha1}(C_0^{\alpha2}-\sqrt{2}C_0^{\alpha12})+B_{nm}^{\alpha2}(\sqrt{2}C_0^{\alpha1}-C_0^{\alpha12})}{\sqrt{3}(C_0^{\alpha1}C_0^{\alpha2}-(C_0^{\alpha12})^2)}\times Q_{nm}(T,H), \tag{9}$$

$$\frac{\Delta a_{\mathrm{me}}(T)}{a}=\sum_{nm}\frac{B_{nm}^{\alpha1}(C_0^{\alpha2}+C_0^{\alpha12}/\sqrt{2})-B_{nm}^{\alpha2}(C_0^{\alpha1}/\sqrt{2}+C_0^{\alpha12})}{\sqrt{3}(C_0^{\alpha1}C_0^{\alpha2}-(C_0^{\alpha12})^2)}\times Q_{nm}(T,H), \tag{10}$$

where

$$Q_{nm}(T,H)=\alpha_n\langle O_n^m\rangle=\alpha_n(1/Z)\sum_i\langle i|O_n^m|i\rangle\times\exp(-E_i/k_BT).$$

The totally symmetric magnetoelastic modes $\varepsilon^{\alpha1}$ and $\varepsilon^{\alpha2}$ can be written in terms of the magnetoelastic anomalies $\Delta c_{\mathrm{me}}/c$ and $\Delta a_{\mathrm{me}}/a$ of the parameters using Eq. (5).

Thus, in the multipole approximation the totally symmetric magnetoelastic modes are determined by the variation of all the multipole moments Q_{nm} of the rare-earth ions with the temperature and/or the magnetic field, which can be calculated numerically from the known crystal-field parameters.

4.2. Multipole moments of rare-earth ions in vanadates and criteria for applicability of the quadrupole approximation

Unlike the rare-earth phosphates with a zircon structure $\mathrm{RPO_4}$, for which detailed inelastic neutron scattering investigations of the electronic structure of the rare-earth ions were recently published[15,16] and whose crystal-field param-

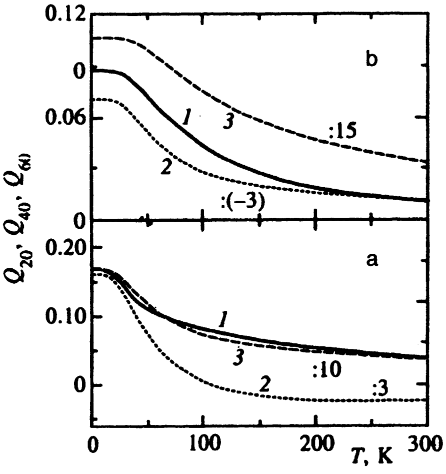

FIG. 5. Calculated temperature dependence of the multipole moments Q_{20} (*1*), Q_{40} (*2*), and Q_{60} (*3*) for the rare-earth vanadates $PrVO_4$ (a) and $NdVO_4$ (b). Values reduced by the indicated factors are presented for Q_{40} and Q_{60}.

eters can be considered reliably established, the crystal-field data for most of the rare-earth vanadates RVO_4 are meager. One exception is $HoVO_4$, whose crystal field has been the subject of several studies.[17,18]

The spectra of Nd, Er, and Tm ions implanted in a YVO_4 host were investigated in Refs. 19–21, and the crystal-field parameters were determined from them.[1,20,22] Guo, Aldred and Chan[23] obtained a set of crystal-field parameters for all the compounds RVO_4 with rare-earth ions from Ce to Yb from data on the magnetic susceptibility of polycrystalline samples using the available spectroscopic information and the procedure for determining the crystal field for a series of rare-earth ions developed by Morrison and Leavitt.[24] However, in some cases the values of these parameters do not seem to us to reflect the real picture of the crystal field in vanadates. For example, a calculation of the Stark splitting of the ground-state multiplet of the Dy ion in $DyVO_4$ using the crystal-field parameters from Ref. 23 gives a position of the second Kramers doublet at a distance of $<1.5\ \mathrm{cm}^{-1}$, while it is known from experiment[25] that the doublet is located at a distance of $9\ \mathrm{cm}^{-1}$.

Numerical calculations based on the known crystal-field parameters for RVO_4 show that the fourth- and sixth-order multipole moments are at least comparable ($TbVO_4$ and $DyVO_4$) and often 2–3 and 7–10 times, respectively, greater than the quadrupole moments. The temperature dependence of the three multipole moments Q_{20}, Q_{40}, and Q_{60} for all the ions investigated (Pr, Nd, Tb–Ho, and Tm) is presented in Figs. 5–7. For convenience in making comparisons, scaled values of Q_{40} and Q_{60} (reduced by approximately 3 and 10 times, respectively) are presented, and the magnitudes and signs of the scale factors were chosen such that Q_{20}, Q_{40}, and Q_{60} would be comparable. For all the ions investigated the multipole moments Q_{44} and Q_{64} and their temperature variations are far smaller than Q_{20} and therefore will not be discussed below. We note that, as a rule, Q_{20} and Q_{60} are positive and Q_{40} is negative. These signs of the multipole moments are specified by the fact that the second- and fourth-order crystal-field parameters in vanadates are negative and the fourth-order parameters are positive.

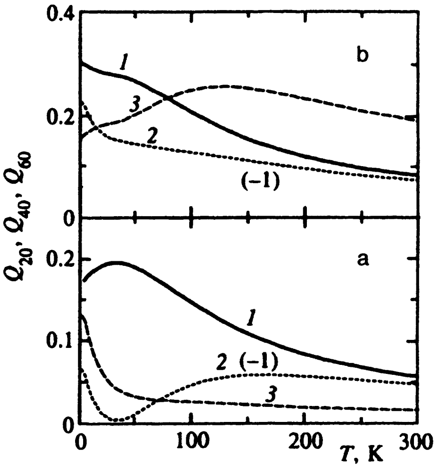

FIG. 6. Calculated temperature dependence of the multipole moments Q_{20} (*1*), Q_{40} (*2*), and Q_{60} (*3*) for the rare-earth vanadates $TbVO_4$ (a) and $DyVO_4$ (b).

An analysis of the temperature dependence of the multipole moments of the rare-earth ions and a comparison with experiment permit evaluation of the contributions of the different multipole moments to the thermal expansion despite the lack of information on the magnetoelastic coefficients of different orders. The criteria for applicability of the quadrupole approximation should be formulated differently for two groups of ions.

When the temperature dependences of all the moments are similar (Pr, Nd, and Tm), we can use at least an "effective" quadrupole approximation, for which the "effective" magnetoelastic coefficient is actually a certain combination of the quadrupole and multipole magnetoelastic coefficients. However, it is difficult to reach any conclusions regarding the contributions of the multipole moments of different or-

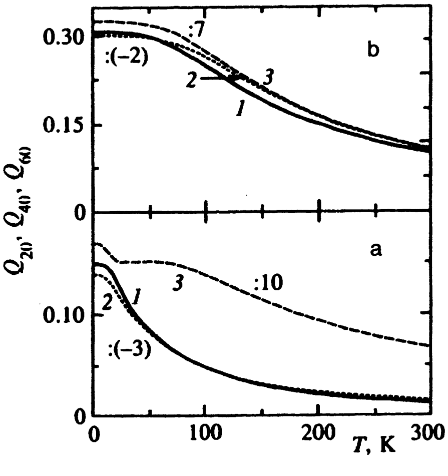

FIG. 7. Calculated temperature dependence of the multipole moments Q_{20} (*1*), Q_{40} (*2*), and Q_{60} (*3*) for the rare-earth vanadates $HoVO_4$ (a) and $TmVO_4$ (b). Values reduced by the indicated factors are presented for Q_{40} and Q_{60}.

ders to the totally symmetric magnetoelastic modes on the basis of the experimental data in this case.

If the temperature dependences of the multipole moments Q_{i0} differ strongly (Tb, Dy, and Ho), it is fairly simple to determine which of the moments makes the main contribution to the thermal expansion and to evaluate the actual magnetoelastic coefficients from a comparison with the experimental data. Then, if the contribution of the fourth- and sixth-order multipole moments to the magnetoelastic thermal-expansion anomalies is significant, several features corresponding to different multipole moments should be observed on the temperature dependences of $\Delta a_{\mathrm{me}}/a$ and $\Delta c_{\mathrm{me}}/c$. However, an analysis of the experimental data for $\mathrm{TbVO_4}$ and $\mathrm{DyVO_4}$ and especially for $\mathrm{HoVO_4}$ provides evidence that the decisive contribution is made by the quadrupole moments of the respective ions.

In fact, for $\mathrm{HoVO_4}$ the sixth-order multipole moment Q_{60} is almost an order of magnitude greater than the quadrupole moment, and it has a different temperature dependence with an additional anomaly at low temperatures. The proportionality of the magnetoelastic contributions $\Delta c_{\mathrm{me}}/c$ and especially $\Delta a_{\mathrm{me}}/a$ (for which the variation of the phonon contribution is insignificant) to the quadrupole moment Q_{20} in $\mathrm{HoVO_4}$ means that the sixth-order magnetoelastic coefficients $B_{60}^{\alpha 1}$ and $B_{60}^{\alpha 2}$ are one and a half or two orders smaller than the corresponding quadrupole magnetoelastic coefficients.

Since the crystal field for $\mathrm{HoVO_4}$ has been reliably determined by different methods, and the corrections to the phonon contribution does not have an appreciable influence on the character of the dependences of $\Delta c_{\mathrm{me}}/c$ and $\Delta a_{\mathrm{me}}/a$, the treatment presented and the conclusions for it are unequivocal. These conclusions are also fairly accurate for the Dy and Tb ions in the vanadate structure, since variations of the crystal-field parameters within 20–30% do not cause qualitative changes in the spectrum or wave functions of a rare-earth ion or, therefore, in the character of $Q_{i0}(T)$ over the range 10–290 K, and the variation of the magnitude of each of the multipole moments Q_{i0} does not exceed 10–15%.

Taking into account that the magnetoelastic coefficients do not vary very strongly along the series of rare-earth ions within the structure under discussion, it should probably be assumed that a similar relationship holds between the magnetoelastic coefficients of different orders for other rare-earth ions from the first group. Thus, an analysis of the experimental data on the thermal expansion of $\mathrm{RVO_4}$ leads us to believe that the quadrupole approximation is valid for the totally symmetric magnetoelastic modes in vanadates even in the case of the rare-earth ions for which the fourth- and sixth-order multipole moments significantly exceed the quadrupole moments.

5. MAGNETOELASTIC CONTRIBUTION TO THE THERMAL EXPANSION OF $\mathrm{RVO_4}$ (R = Pr, Nd, Tb–Ho, and Tm)

To isolate the magnetoelastic contribution and make corrections for the variation of the phonon contribution in $\mathrm{RVO_4}$ we used an optimization procedure, in which the parameters of the Debye model T_D and α_0 were varied over the range corresponding to ±40% of their values for $\mathrm{GdVO_4}$, so that the resultant magnetoelastic contribution would be proportional to the quadrupole moment calculated for the known crystal field and the phonon thermal expansion along the c axis for the test and Gd vanadates would differ at most (at low temperatures) by some given quantity $\delta(\Delta c/c)_0$. The value of $\delta(\Delta c/c)_0$ varies for different rare-earth ions more strongly, the further the particular rare-earth ion is from Gd along the series. Depending on the situation, we used two different versions of the optimization procedure, in which the magnetoelastic contributions along the a and c axes were isolated either separately (the first version) or simultaneously (the second version).

TABLE I. Values of $A_1=3(\Delta c/c)_{\mathrm{me}}/\Delta Q_{20}$ and $A_2=3(\Delta a/a)_{\mathrm{me}}/\Delta Q_{20}$ and the magnetoelastic coefficients $B^{\alpha 1}$ and $B^{\alpha 2}$ for rare-earth vanadates [$(\Delta c/c)_{\mathrm{me}}$, $(\Delta a/a)_{\mathrm{me}}$, and ΔQ_{20} are the magnetoelastic contributions to thermal expansion along the c and a axes and the variation of the quadrupole moment, respectively, in the temperature range 10–290 K].

$\mathrm{RVO_4}$	A_1 10^{-2}	A_2 10^{-2}	$B^{\alpha 1}$ 10^{-3} K/f.u.	$B^{\alpha 2}$ 10^{-3} K/f.u.
$\mathrm{PrVO_4}$	0.97	−1.31	−6.89	6.57
$\mathrm{NdVO_4}$	0.56	−0.42	−0.90	2.95
$\mathrm{TbVO_4}$	0.75	−1.02	−5.40	5.13
$\mathrm{DyVO_4}$	0.93	−1.16	−5.79	6.10
$\mathrm{HoVO_4}$[a)]	0.93	−1.03	−4.57	5.76
$\mathrm{HoVO_4}$[b)]	1.14	−1.12	−4.31	6.71
$\mathrm{HoVO_4}$[c)]	1.13	−1.13	−4.36	6.70
$\mathrm{TmVO_4}$	0.49	−0.59	−2.80	3.14

Note. a) For the temperature range 10–80 K (Ref. 29). b) First version of the optimization procedure. c) Second version of the optimization procedure.

The procedure was tested on $\mathrm{HoVO_4}$, for which there is a reliable crystal field[17] and the magnetoelastic contribution has a clearcut anomaly at low temperatures. Calculations of the magnetoelastic contribution and, accordingly, of the magnetoelastic coefficients were performed by various methods. First, taking into account that for $\mathrm{HoVO_4}$ the bulk of the variation of the magnetoelastic contribution occurs at temperatures below 80 K, we can (as in Ref. 26) isolate the contribution and determine the coefficients in that temperature range, where the variation of the phonon contribution may be neglected. At the same time, we also performed calculations for the 10–290 K range using the two different versions of the optimization procedure. The magnetoelastic coefficients for $\mathrm{HoVO_4}$ determined by different methods agree with one another to within 10–15% (see Table I). They are also in good agreement with the coefficients determined in Ref. 27 from measurements of the parastriction for a magnetic field along the tetragonal axis and with the totally symmetric magnetoelastic coefficient B^{zz} determined in Ref. 28, where the elastic properties of $\mathrm{HoVO_4}$ were investigated by ultrasonic methods.

The calculations employing the optimization procedure show that the correction to the phonon contribution along the c axis for the rare-earth vanadates has several common features and a systematic variation along the series of rare-earth ions. The correction for all the vanadates investigated is negative (at least at low temperatures) and has a characteristic temperature dependence with a point of inflection, which attests to variation of the Debye temperature T_D. The absolute value of the correction at 10 K increases from $\sim 1\times 10^{-4}$ for the Tb vanadates to $\sim 5\times 10^{-4}$ for the Tm vanadates, respectively. The correction to the phonon contribution for the vanadates with light rare-earth ions (Nd and Pr) is positive at high temperatures, but changes sign at lower temperatures, and its absolute value does not exceed 1×10^{-4}.

The proportionality coefficients between the magnetoelastic contributions and the quadrupole moment presented in Table I were determined as a result of the optimization: $\Delta c_{\rm me}/c = A_1 Q_{20}/3$, $\Delta a_{\rm me}/a = A_2 Q_{20}/3$ [see Eqs. (9) and (10)]. The magnetoelastic contributions along the c and a axes and the calculated quadrupole moments for the rare-earth vanadates are presented in Fig. 8. For convenience in making comparisons, the magnetoelastic contributions along the a axis and the quadrupole moment are given with the corresponding factors $A\Delta a_{\rm me}/a$ and A_1/Q_{20} ($A = A_1/A_2 \sim -1$ and $A_1 \sim 10^{-2}$, see Table I), and the dependences for the different rare-earth ions are shifted relative to one another along the vertical axis successively by 1.5×10^{-4}. As we have already noted, only parameters obtained by extrapolation from neighboring rare-earth ions according to the procedure developed by Morrison and Leavitt[24] or for doped compounds in yttrium vanadate or lutetium vanadate hosts[20,22,23] can be found in the literature for most of the vanadates. An acceptable description of the spectrum and the magnetoelastic contribution can be obtained using an extrapolated crystal field only for $TbVO_4$. The characteristic temperatures of the points of inflection in the plots of $\Delta l_{\rm me}/l = (\Delta c_{\rm me}/c + A\Delta a_{\rm me}/a)/2$ and Q_{20} for the other vanadates differ appreciably, and, therefore, a restricted optimization of the crystal field within a 20–30% range was also performed for them using the available spectroscopic information.

As for the Pr, Nd, and Tm ions, there are spectroscopic data only for the doped compounds YVO_4:R. However, our data on the magnetoelastic contribution show that the positions of the lowest levels of the rare-earth ion, which determine the main magnetoelastic contribution to the thermal expansion, differ considerably for pure and strongly diluted vanadates. In particular, the first excited level determined from the spectroscopic data in a YVO_4 host or calculations based on an extrapolated crystal field is considerably higher (by 40–50 $\rm cm^{-1}$) for the Nd and Pr ions and lower (by 90 $\rm cm^{-1}$) for Tm than that following from our data for the corresponding concentrated RVO_4. Of course, in the absence of spectroscopic information for the Pr, Nd, and Tm ions in concentrated RVO_4 hosts, complete optimization of the crystal field cannot be performed, and a single reliable set of parameters cannot be obtained. Therefore, our data from optimization of the crystal field should be regarded as preliminary.

6. DISCUSSION

As follows from Eqs. (9) and (10), if the quadrupole approximation is valid, the contribution of the rare-earth ions to the thermal expansion is determined by the quadrupole magnetoelastic coefficients $B_{20}^{\alpha 1} = B^{\alpha 1}$ and $B_{20}^{\alpha 2} = B^{\alpha 2}$ and the variation of the quadrupole moment Q_{20} with the temperature. We note several features of the temperature dependences of the magnetoelastic contribution of Q_{20} along the series of rare-earth vanadates (Fig. 8). In accordance with experiment, the strongest variation of Q_{20} in the range 10–290 K is observed for $DyVO_4$. The calculation shows (see Fig. 5) that in the temperature range below 40 K there is a sharp increase in the quadrupole moment for the Dy compound, and, conversely, the value for the Tb compound decreases with decreasing temperature. Due to structural phase transitions these additional low-temperature thermal-expansion anomalies are not observed for the concentrated compounds $DyVO_4$ and $TbVO_4$, but they can be investigated in the corresponding diluted compounds.

The variations of the quadrupole moments and, accordingly, of the magnetoelastic contributions over the temperature range 10–290 K for $HoVO_4$ and $PrVO_4$ (curves *4* and *5*) are similar and are characterized by an abrupt increase at low temperatures. In accordance with experiment, the magnetoelastic contribution for $NdVO_4$ is small, so that for the c axis it essentially coincides with the correction to the variation of the phonon contribution (curves *6* and *7* in Fig. 3); therefore, the data for the Nd compound should be considered approximate. This is also true for $TmVO_4$, for which the correction for the variation of the phonon contribution along the c axis is almost twice the corresponding magnetoelastic contribution.

The magnitude of the experimentally observed magnetoelastic contribution to the thermal expansion for the series of rare-earth vanadates correlates with the variation of the calculated temperature dependences of the quadrupole moment Q_{20}. This suggests that in a first approximation the magnetoelastic coefficients $B^{\alpha 1}$ and $B^{\alpha 2}$ do not differ excessively along the rare-earth series. Using the elastic constants C_{11}, C_{12}, and C_{33} for $HoVO_4$ from Ref. 28 in the calculation and setting $C_{12} \approx C_{13}$, we obtained the following values for the symmetrized elastic constants used in Eqs. (9) and (10) (in units of 10^5 K/f.u.): $C_0^{\alpha 1} = 25$, $C_0^{\alpha 2} = 11$, $C_0^{\alpha 12} = 1.7$. The results of the calculation of the magnetoelastic contributions and the quadrupole magnetoelastic coefficients for all the rare-earth vanadates investigated are presented in Table I. We note that the values of $B^{\alpha 1}$ and $B^{\alpha 2}$ for most of the vanadates are comparable in magnitude and have opposite signs. Values of $B^{\alpha 1}$ and $B^{\alpha 2}$ of analogous sign and similar magnitude were obtained from the thermal-expansion anomalies for rare-earth phosphates with a zircon structure.[29]

The signs of the magnetoelastic contributions to the thermal expansion in the rare-earth vanadates RVO_4 are directly opposite those previously found in the rare-earth phosphates RPO_4. In our opinion, this is attributable to the different crystal fields and primarily to the different signs of the second-order parameter B_2^0 (Ref. 29). The role of B_2^0 becomes clearer from a comparison of the tetragonal and cubic symmetries. When the symmetry is lowered from cubic to tetragonal, a nonzero value of B_2^0 appears, and the ratio between the higher-order diagonal and off-diagonal parameters determined for cubic symmetry changes. A nonzero quadrupole moment and anisotropy of the magnetic properties along and perpendicularly to the tetragonal axis then appear in the rare-earth ion. Numerical calculations show that the spectrum and wave functions of the rare-earth ion (and, therefore, its quadrupole moment) are altered when the sign of this parameter changes: the splitting of the levels which are degenerate under cubic symmetry is characterized by reverse sequences of doublets and singlets for $B_2^0>0$ and $B_2^0<0$. Thus, the crystal-field term $\alpha_J B_2^0 O_2^0$ stabilizes as a ground state with a positive quadrupole moment $Q_{20}=\alpha_J\langle O_2^0\rangle$ for $B_2^0<0$ (vanadates) and with a negative quadrupole moment for $B_2^0>0$ (phosphates).

7. CONCLUSIONS

Experimental and theoretical investigation of the thermal expansion of the rare-earth vanadates RVO_4 with a zircon structure have been performed, and the adequacy of the quadrupole approximation for describing the totally symmetric magnetoelastic modes has been analyzed.

Considerable magnetoelastic thermal-expansion anomalies have been detected in the vanadates of Pr, Nd, Tb–Ho, and Tm, and the magnetoelastic contributions to the thermal expansion $\Delta c_{\mathrm{me}}/c$ and $\Delta a_{\mathrm{me}}/a$ have been isolated with consideration of the corrections for the variation of the phonon contribution along the series of rare-earth ions in the Debye model of thermal expansion. The conditions for applicability of the quadrupole approximation to the description of the totally symmetric magnetoelastic modes have been discussed on the basis of a comparison of the calculated quadrupole and multipole moments of different rare-earth ions in the vanadate structure with the experimental magnetoelastic contribution to the thermal expansion of RVO_4. It has been shown that the multipole moments make an insignificant contribution to the thermal expansion and that the magnetoelastic thermal-expansion anomalies of rare-earth vanadates are faithfully described by the temperature dependences of the quadrupole moments of the rare-earth ions calculated on the basis of known or slightly modified crystal-field parameters. It has been concluded that the quadrupole approximation is applicable to the description of the totally symmetric magnetoelastic modes even when the fourth- (Q_{40}) and sixth-order (Q_{60}) multipole moments significantly exceed the quadrupole moments Q_{20} and that the quadrupole magnetoelastic coefficients are probably considerably greater than the fourth- and sixth-order multipole coefficients.

Experimental values of the magnetoelastic contributions $\Delta c_{\mathrm{me}}/c$ and $\Delta a_{\mathrm{me}}/a$ have been used to determine the totally symmetric quadrupole magnetoelastic coefficients $B^{\alpha 1}$ and $B^{\alpha 2}$, which are comparable in magnitude and have opposite signs for all the rare-earth ions investigated in the vanadate structure. It has been noted that due to the different signs of the second-order crystal-field parameter B_2^0, the magnetoelastic contributions to the thermal expansion along the a and c axes for rare-earth vanadates and phosphates have opposite signs, while the magnetoelastic coefficients $B^{\alpha 1}$ and $\beta^{\alpha 2}$ are comparable in magnitude and have the same signs for the two isomorphous structures.

In conclusion, we note that only the totally symmetric magnetoelastic modes in rare-earth oxide compounds with a zircon structure were investigated in this work. Magnetoelastic effects which are described by low-symmetry magnetoelastic modes, such as elastic-constant anomalies, magnetostriction, etc., were not considered in the present work. The contribution of the multipole moments to such effects in this case requires special treatment. Just as for cubic crystals, the decisive role is probably played here by the corresponding quadrupole moments, which appear under the conditions of an external symmetry-lowering force. In our opinion, it would also be interesting to compare the contributions of the multipole moments to the corresponding magnetoelastic effects in different crystal structures of both oxide and intermetallic compounds. These questions are certainly of interest and merit further theoretical and experimental study.

This work was supported by the Russian Fund for Fundamental Research (Grant No. 94-02-05231).

[1] E. Callen and H. Callen, Phys. Rev. B **129**, 578 (1963).

[2] B. Luthi, in *Dynamical Properties of Solids*, G. K. Horton and A. A. Maradudin (eds.), North-Holland, Amsterdam (1980), Vol. 3, p. 245.

[3] A. K. Zvezdin, V. M. Matveev, A. A. Mukhin, and A. I. Popov, *Rare-Earth Ions in Magnetically Ordered Crystals* [in Russian], Nauka, Moscow (1985).

[4] P. Morin and D. Schmitt, in *Handbook on Ferromagnetic Materials*, E. P. Wohlfarth and K. H. J. Buschow (eds.), North-Holland, Amsterdam (1990), Vol. 5, p. 30.

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

[6] P. M. Levy and A. Chen, AIP Conf. Proc. **5**, 373 (1972).

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

[8] V. I. Sokolov, Z. A. Kazeĭ, N. P. Kolmakova, and T. V. Solov'yanova, Zh. Éksp. Teor. Fiz. **99**, 945 (1991) [Sov. Phys. JETP **72**, 524 (1991)].

[9] Z. A. Kazeĭ and N. P. Kolmakova, Zh. Éksp. Teor. Fiz. **103**, 316 (1993) [JETP **76**, 172 (1993)].

[10] B. Z. Malkin, in *Spectroscopy of Solids Containing Rare-Earth Ions*, A. A. Kaplyanskii and R. M. Macfarlane (eds.), North-Holland, Amsterdam (1987), p. 13.

[11] H. Gobel and G. Will, Phys. Status Solidi B **50**, 147 (1972).

[12] G. A. Slack and D. W. Oliver, Phys. Rev. B **4**, 592 (1971).

[13] E. de Lacheisserie, Ann. Phys. (Paris) **5**, 267 (1970).

[14] P. Morin, J. Rouchy, and Z. Kazei, Phys. Rev. B **50**, 12 625 (1994).

[15] C.-K. Loong, L. Soderholm, M. M. Abraham *et al.*, J. Chem. Phys. **98**, 4214 (1993).

[16] C.-K. Loong, L. Soderholm, J. P. Hammonds *et al.*, J. Phys. C **5**, 5121 (1993).

[17] B. Bleaney, J. F. Gregg, P. Hansen *et al.*, Proc. R. Soc. London A **416**, 63 (1988).

[18] H. Bischoff, B. Pilawa, A. Kasten, and H. J. Kahle, J. Phys. C **3**, 10 057 (1993).

[19] N. Karayianis, C. A. Morrison, D. E. Wortman, J. Chem. Phys. **62**, 4125 (1975).

[20] D. Kuse, Z. Phys. **203**, 49 (1967).

[21] K. D. Knoll, Phys. Status Solidi B **45**, 553 (1971).

[22] D. E. Wortman, R. P. Leavitt, and C. A. Morrison, J. Phys. Chem. Solids **35**, 591 (1974).

[23] M. D. Guo, A. T. Aldred, and S. K. Chan, J. Phys. Chem. Solids **48**, 229 (1987).

[24] C. A. Morrison and R. P. Leavitt, J. Phys. Chem. Solids **71**, 2366 (1979).

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

[26] Z. A. Kazeĭ and N. P. Kolmakova, Fiz. Tverd. Tela (St. Petersburg) **37**, 1063 (1995) [Phys. Solid State **37**, 577 (1995)].

[27] P. Morin, J. Rouchy, and Z. Kazei, Phys. Rev. B **51**, 15 103 (1995).

[28] T. Goto, A. Tamaki, T. Fujimura, and H. Unoki, J. Phys. Soc. Jpn. **55**, 1613 (1986).

[29] V. I. Sokolov, Z. A. Kazei, and N. P. Kolmakova, Physica B (Amsterdam) **176**, 101 (1992).

Translated by P. Shelnitz