# Structural phase transitions in the system $Dy_xTb_{1-x}VO_4$ involving Jahn-Teller lattice distortions of various symmetries

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In the temperature interval 1.6 K to 100 K we have measured the Young's modulus ($E$), the coefficient of internal friction ($Q^{-1}$), the magnetic susceptibility, and the crystal lattice parameters of the zircon-structure compounds $Dy_xTb_{1-x}VO_4$. We have determined the concentration dependence of the temperature $T_c$ at which the structural phase transition arising from the cooperative Jahn-Teller (JT) effect occurs. We show that in these systems there is a concentration region in which the crystal phase is characterized by an order parameter with two components, corresponding to two different types of JT distortions—$B_{1g}$ and $B_{2g}$. We study the effect of JT domains in determining the crystal's acoustic and magnetic characteristics for $T \leqslant T_c$, along with the effect of an external magnetic field on the functions $E(T)$ and $Q^{-1}(T)$, and discuss our results within the standard picture of the cooperative JT effect as it is manifested in the rare-earth zircon-structure compounds.

## 1. INTRODUCTION

In the rare-earth compounds $RXO_4$ with zircon structure (R = Tb, Dy, Tm; X = P, As, V) the strong electron-phonon interaction causes structural phase transitions (SPT); this phenomenon is called the cooperative Jahn-Teller effect (CJTE). Because of the CJTE, at the SPT temperature $T_c$ a rhombic distortion arises in the tetragonal lattice of $RXO_4$ along one of the crystallographic directions—[100] (type $B_{1g}$) or [110] (type $B_{2g}$). Since the JT ions interact essentially through long-wavelength acoustic phonons, i.e., the interaction is long-range, the basic physical properties of the rare-earth zircons are well described by molecular field theory. In particular, the characteristic dependence of $T_c$ on the concentration $x$ of JT ions and the low values of the critical concentration at which the CJTE first occurs are connected with this fact. The $T_c$–$x$ phase diagrams are different for different $RXO_4$, and are determined by the specific arrangements of low-lying electronic levels of the JT ions.

Up until now, only the disruption of the CJTE by concentrations of non-JT impurities has been investigated in detail, specifically for the dilute zircons $Dy_xY_{1-x}VO_4$ and $Tb_xGd_{1-x}VO_4$.[1,2] In these systems the JT ions Dy and Tb are replaced by Y and Gd ions, which are not JT ions. Considerably less data is available on compounds containing two kinds of JT ions.[3] We feel that the most interesting systems are those mixed ones in which the JT ions can cause different kinds of rhombic distortions. First of all, the following question remains unanswered: are such distortions truly competitive, or can they coexist? Secondly, because a crystal lattice instability generated by the CJTE is accompanied by softening (total or partial) of the elastic moduli and by significant reconstruction of the electronic spectrum, we may assume that unique SPTs (e.g., some form of elastic glass) will be observed in mixed systems with JT crystal lattice distortions of different symmetries, along with anomalous elastic, magnetic and other physical properties, which are different from the dilute JT systems. Our goal in this paper is to investigate the peculiarities of SPTs in systems with different JT interactions; to this end, we present here an experimental study of the elastic, structural and magnetic properties of the class of compounds $Dy_xTb_{1-x}VO_4$, in which the JT ions Dy and Tb cause rhombic distortions of the tetragonal structure of $B_{1g}$ and $B_{2g}$ types, respectively.

## 2. SAMPLES AND EXPERIMENTAL METHODS

Polycrystalline samples of $Dy_xTb_{1-x}VO_4$ ($0 \leqslant x \leqslant 1$, $\Delta x = 0.1$) were synthesized using a ceramic technology involving double firing, once at $T_1 = 900\,^\circ C$ and once at $T_2 = 1300\,^\circ C$. X-ray diffraction studies showed that the samples under study were single-phase (to an accuracy of $\sim 1\%$); the parameters of their tetragonal unit cells $a$ and $c$ were found to increase linearly from $a(1) = 7.147$ Å and $c(1) = 6.803$ Å for pure Dy to $a(0) = 7.176$ Å and $c(0) = 6.325$ Å for pure Tb. Because of the closeness of the ionic radii of Dy and Tb, the maximum variation of the parameters $a$ and $c$ in these systems does not exceed $\Delta a/a \sim 4 \cdot 10^{-3}$ and $\Delta c/c \sim 3 \cdot 10^{-3}$. This gives us grounds to suppose that the crystal field parameters and the energy spectra of the Dy and Tb ions in the tetragonal phase are the same for all $x$, while the magnitude of the JT interaction is proportional to the concentrations of Dy and Tb.

In this paper we studied the elastic and magnetic properties of $Dy_xTb_{1-x}VO_4$ in the temperature interval 1.6 K to 100 K. The Young's modulus $E$ and coefficient of internal friction $Q^{-1}$ were measured by the compound resonator method at frequencies 100 to 240 KHz. The construction of the apparatus allowed us to carry out measurements in magnetic fields up to 40 kOe.[4] For a number of samples with $x$ close to 0.5 we also carried out measurements of the magnetic susceptibility $\chi_M$ by the induction method (at a frequency of 64 Hz, and an amplitude of the AC field $H_{AC} = 50$ Oe) and carried out an x-ray diffraction study of the distortion of the crystal structure at low temperatures (a "Geigerflex" diffractometer with a circulating He cryostat was used; the temperature interval was 7 K to 300 K).

The essential results of this paper were obtained on polycrystalline samples, although we had single crystals of

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$Dy_xTb_{1-x}VO_4$ with various compositions at our disposal. Our choice of polycrystalline samples as the objects of study was dictated by two circumstances. In the first place, it is known that in single crystals, strong attenuation of sound along the "soft" direction interferes with acoustic measurements near $T_c$. In polycrystalline samples, because the number of crystallites for which sound propagates along a "soft" axis is small, the attenuation is not so great. This makes it possible to use the method of acoustic probing to determine $T_c$ more precisely and to carry out studies in the region $T \leqslant T_c$. Secondly, the ceramic technology allows us to obtain samples of a given composition within practically any concentration interval, which is important in studying the concentration phase diagram.

## 3. EXPERIMENTAL RESULTS

In our experiments we established that the elastic properties of polycrystalline samples of $DyVO_4$ and $TbVO_4$ have a number of anomalies which occur at temperatures which differ from the values of $T_c$ determined from acoustic measurements made on the corresponding single crystals.[5,6] In Fig. 1 we present as an example the temperature dependence of the relative values of the Young's moduli $\Delta E(T)/E$ [where $\Delta E(T) = E(T) - E$ and $E$ is defined as $E(T = 100\ \mathrm{K})$], and the coefficient of internal friction $Q^{-1}$ at $H = 0$ and $H = 40$ kOe for $DyVO_4$. It is clear that for $H = 0$ the minimum of $\Delta E(T)/E$ occurs at $T' = 10.5$ K, i.e., it is shifted to the temperature region below the value $T_{c1} = 13.5$ K determined from x-ray data[7]; at $T_{c1}$ we observed a point of inflection of $\Delta E(T)/E$. The coefficient of internal friction $Q^{-1}$ exhibits two absorption maxima; a weak one at $T_{c1}$ and a stronger one ($\approx 2 \cdot 10^{-2}$) at $T_{d1} = 7$ K.

A magnetic field significantly decreases these anomalies in $\Delta E(T)/E$ and $Q^{-1}$. Thus, in $DyVO_4$ near $T_{c1}$, the $\Delta E(H)$ effect (i.e., the variation of the modulus of elasticity with field) came to $2 \times 10^{-1}$ for $H = 40$ Oe. For $T > T_{c1}$, the $\Delta E(H)$ effect has a positive sign for all values of $H$, while for $T < T_{c1}$ the $\Delta E(H)$ effect exhibits a negative sign in weak fields. In a constant field $H = 40$ kOe the minimum value of $\Delta E(T)/E$ decreases in magnitude and shifts into the region of higher temperatures by roughly 5 K, while the maximum of $Q^{-1}$ decreases by a factor of three at $T_{d1}$.

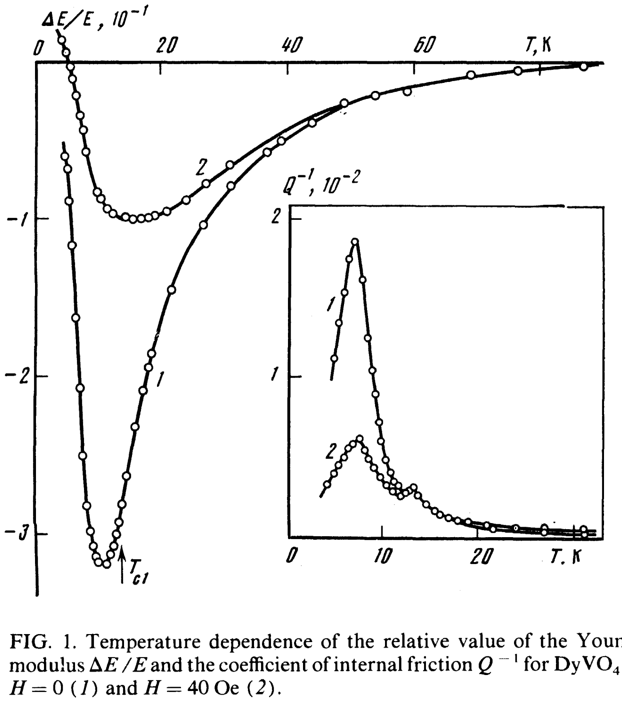

FIG. 1. Temperature dependence of the relative value of the Young's modulus $\Delta E/E$ and the coefficient of internal friction $Q^{-1}$ for $DyVO_4$ for $H = 0$ (1) and $H = 40$ Oe (2).

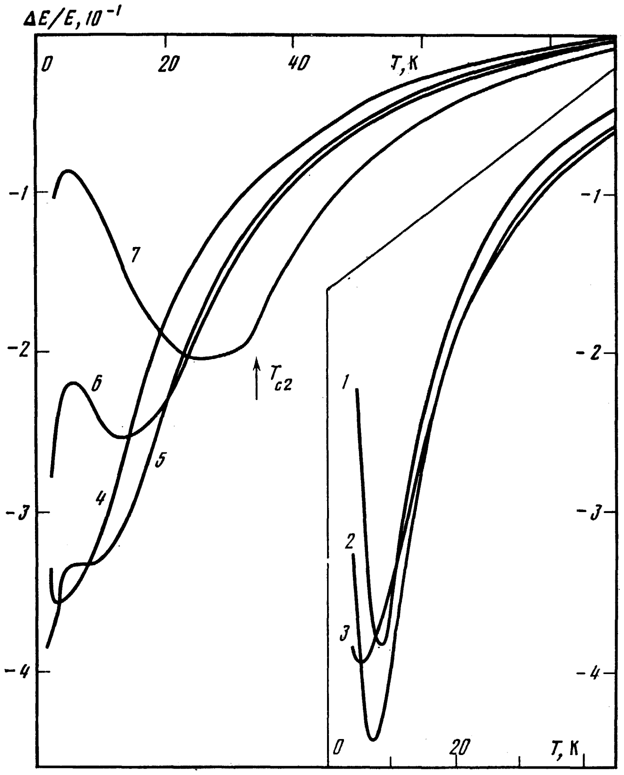

FIG. 2. Temperature dependence of the relative value of the Young's modulus $\Delta E/E$ for the compound $Dy_xTb_{1-x}VO_4$ for $x$: 1—0.8, 2—0.7, 3—0.6, 4—0.5, 5—0.4, 6—0.3, 7—0.

In $TbVO_4$ the functions $\Delta E(T)/E$ and $Q^{-1}(T)$ have the same features as $DyVO_4$ for $H = 0$. The minimum in $\Delta E(T)/E$ occurs at $T' = 26$ K ($T_{c2} = 34$ K), i.e., it is shifted by $\Delta T/T_c \approx 0.2$ toward the low-temperature region (Fig. 2, curve 7), while $T_{c2}$ coincides with the point of inflection of the function $\Delta E(T)/E$. The coefficient of internal friction $Q^{-1}$ for $TbVO_4$ exhibits a wide maximum at $T_{d2} = 10$ K, while at $T_{c2}$ no significant absorption is observed (Fig. 3, curve 7). Note also that the softening of $\Delta E(T)/E$ and $Q^{-1}(T)$ is twice as small for $TbVO_4$ as it is for $DyVO_4$.

The distinctive feature of $TbVO_4$ is the smaller effect of a magnetic field on $\Delta E(T)/E$ and $Q^{-1}$: the $\Delta E(H)$ effect in $TbVO_4$ is largest at low temperatures (4–6 K), and in a field of 40 Oe it has a value of $3 \cdot 10^{-2}$, i.e., an order of magnitude smaller than in $DyVO_4$. In weak fields the $\Delta E(H)$ effect is negative; the field interval where this negative $\Delta E(H)$ effect is observed grows as the temperature increases. The maximum in $Q^{-1}(T)$ at the same value of $H$ remains constant in magnitude and shifts by ~5 K toward the region of low temperatures.

The temperature dependence of $\Delta E(T)/E$ for all samples of the mixed compounds $Dy_xTb_{1-x}VO_4$ also exhibits a minimum (Fig. 2); the temperature of the SPT decreases with decreasing concentrations of both Dy and Tb. For convenience in comparison the functions $\Delta E(T)/E$ for all inves-

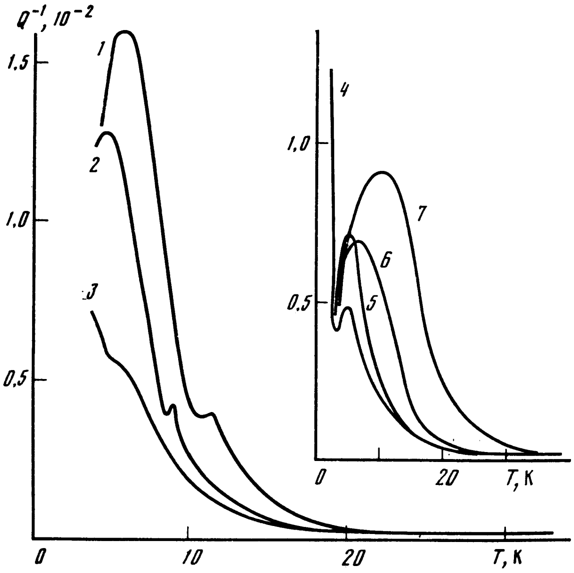

FIG. 3. Temperature dependence of the coefficient of internal friction for the $Dy_xTb_{1-x}VO_4$ system. Values of $x$: *1*—0.9, *2*—0.7, *3*—0.6, *4*—0.5, *5*—0.4, *6*—0.2, *7*—0.

tigated samples are normalized to the value $E$ at a temperature $T = 100$ K. It follows from Fig. 2 that the value of the softening of $\Delta E(T)/E$ depends nonmonotonically on concentration. As $x$ decreases the value of the softening first increase and reaches its largest value at $x = 0.7$ (curve *2*). As the Tb concentration decreases (i.e., $x$ goes to zero) the value of the softening also grows; this growth is particularly abrupt as the concentration varies from $x = 0.3$ to $x = 0.4$ (compare curves *6* and *5* in Fig. 2).

Figure 3 shows the temperature dependence of the internal friction for the system $Dy_xTb_{1-x}VO_4$. It is clear from this figure that for compositions close to $x = 1.0$ we observe a large narrow maximum in $Q^{-1}$ at the low temperature $T_{d1}$, just as for $DyVO_4$; this maximum decreases in height as the Dy concentration decreases and shifts to the low-temperature region. Analogously, for those compositions close to $TbVO_4$ the value of this maximum in the function $Q^{-1}(T)$, which occurs at a temperature $T_{d2}$, decreases with decreasing Tb concentration and shifts toward the low-temperature region (Fig. 3). For a sample with $x = 0.5$ (curve *4*) this maximum in $Q^{-1}(T)$ occurs at $T_{d2} = 5$ K and comes to $5 \cdot 10^{-3}$. For $T < 3$ K we observe an abrupt growth in the internal friction in this sample; this is characteristic of Dy-rich samples.

We carried out an x-ray investigation of the low-temperature unit cell parameters of samples with $x = 0.3$ and $x = 0.5$. In studying the powder-pattern x-ray photographs of a sample with $x = 0.3$ taken at $T = 7$ K, we observed a splitting of certain reflections which indicated a rhombic distortion of $B_{1g}$ type: $(hh0)$ reflections were split, while $(h00)$ reflections remain unchanged. The temperature dependences of the unit cell parameters $a'$, $b'$ of the rhombic phase, which are determined from the $(332) + (3\bar{3}2)$ and $(800)$ reflections ($a'$, $b'$ are unit-cell parameters in a crystallographic system of coordinates rotated by 45° around the $c$-axis; in the tetragonal phase $a' = b' = 2^{1/2}a$; the radiation used was Cu $K_\alpha$, and $2\theta$ 62°) are shown in Fig. 4b (curve *1*).

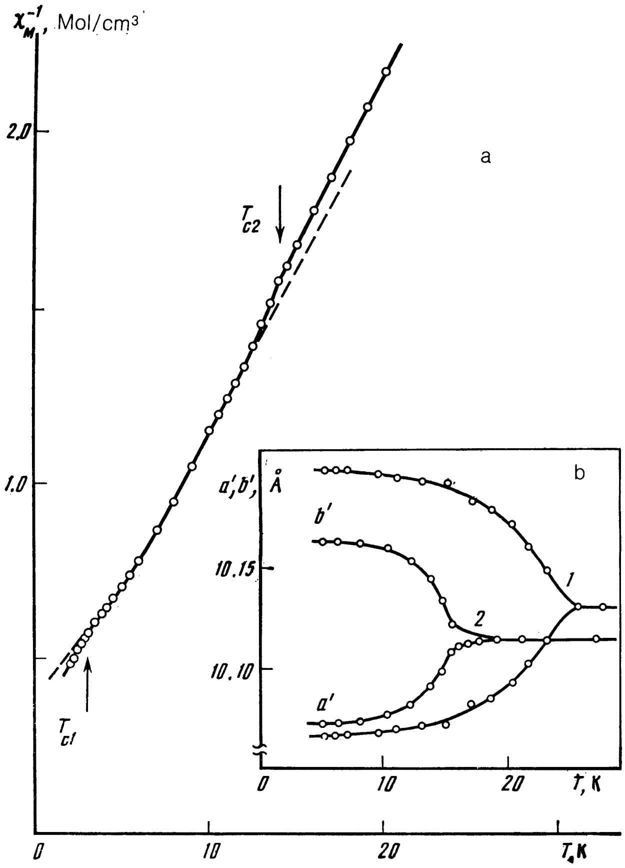

FIG. 4. Variation of the inverse molar susceptibility $\chi_M^{-1}$ for $Dy_{0.5}Tb_{0.5}VO_4$ (a) and the rhombic unit cell parameter (b) (*1*—$Dy_{0.3}Tb_{0.7}VO_4$; *2*—$Dy_{0.5}Tb_{0.5}VO_4$).

The value of the $B_{2g}$-type distortion in $Dy_xTb_{1-x}VO_4$ is $\varepsilon = (a' - b')/a' = 1.3 \cdot 10^{-2}$, i.e., it decreases almost twice as much as $TbVO_4$ ($\varepsilon = 2.3 \cdot 10^{-2}$), while the transition temperature is $T_{c2} = 25$ K.

In a sample with $x = 0.5$ at $T = 7$ K, we observed a broadening of the reflections, which also indicates a $B_{1g}$-type distortion that is preserved up to $T \sim 15$ K. The absence of intense isolated lines of type $(hh0)$ in the powder-pattern photos for the region of large angles $2\theta$ prevents us from reliably determining the value of the distortion and the transition temperatures at $x = 0.5$ for the polycrystalline samples. We therefore carried out an x-ray diffraction study of a single-crystal slice of $\langle 110 \rangle$ $Dy_{0.5}Tb_{0.5}VO_4$ (the radiation used was Cu $K_\alpha$, reflection (660), and $2\theta \approx 148°$). These data, presented in Fig. 4b, indicate the appearance of a distortion of $B_{2g}$-type with $\varepsilon = 9 \cdot 10^{-3}$ in the sample with $x = 0.5$ at a temperature $T_{c2} = 18$ K (curve *2*). Note the washed-out character of the functions $a'(T)$ and $b'(T)$ for samples of mixed composition (especially for $x = 0.5$) compared to pure $DyVO_4$ and $TbVO_4$, which hinders the determination of $T_c$ for the SPT from x-ray diffraction measurements.

For a polycrystalline sample with $x = 0.5$ we measured the differential magnetic susceptibility at low temperatures (Fig. 4a). The function $\chi_M^{-1}(T)$ of this sample exhibits two anomalies, both deviations from the Curie-Weiss law toward the abscissa axis, one at $T_{c1} = 3.0$ K and one at $T_{c2} = 14$ K. Similar anomalies in $\chi_M^{-1}(T)$ have been observed previously in the neighborhood of $T_c$ for unsubstituted $DyVO_4$ and $TbVO_4$.[8] The high-temperature anomaly in $\chi_M^{-1}(T)$ corresponds to the $B_{2g}$-transition; the value $T_{c2} = 14$ K coincides with the maximum coefficient of thermal broadening of the functions $a'(T)$ and $b'(T)$ obtained from x-ray diffraction data (curve *2* of Fig. 4). Note that the value of $\chi_M$ for $RVO_4$ compounds with JT ions depends on the domain state of the sample for $T < T_c$ (here we have in mind crystallographic domains, i.e., regions which differ in the directions of the lattice distortion axes). Our measurements of $\chi_M(T)$ were therefore carried out in a constant field $H = 4$ Oe, which stabilizes the domain structure with an easy magnetic axis parallel to $H$.

## 4. DISCUSSION OF RESULTS; PHASE DIAGRAM

**4.1. Unsubstituted $DyVO_4$ and $TbVO_4$.** The experimental data show that polycrystallinity significantly influences the acoustic characteristics of samples near $T_c$. In our view, this is connected with the appearance of structural (JT) domains below $T_c$. Under the action of mechanical stresses caused by the sound wave, reconstruction of the JT domain structure takes place (e.g., the long axes of the domains align along the stretching mechanical stress), which appears as an additional "softness" in the lattice. Consequently, we observe further softening of the modulus $\Delta E(T)/E$ for $T \lesssim T_c$, although the rate of softening, i.e., $d(\Delta E/E)/dT$, decreases.

This "domain" contribution to $\Delta E(T)/E$ for $T < T_c$ grows as the distortion of the lattice and the mobility of the domains increases, i.e., it has a nonmonotonic temperature dependence. Thus, for $T < T_c$ there are two contributions to the temperature dependence of $\Delta E(T)/E$ (Fig. 1): a negative contribution connected with the relaxation of the JT domains, and a positive contribution caused by the growth of the "pure" elastic modulus of a single-domain sample. The temperature $T'$ which minimizes $\Delta E(T)/E$ in this case is determined by the competition between these two contributions. We note that measurements of the magnetic[8] and magnetoelastic[9] properties of $TbVO_4$ made on single crystals attest to a change in the mobility of domain boundaries at $T' = 26$ K, which is where we observe a minimum in the Young's modulus $\Delta E(T)/E$.

The "domain" contribution apparently depends on the amplitude of the sound wave; however, in our experiments decreasing the amplitude by an order of magnitude does not significantly change the function $\Delta E(T)/E$. It should be noted that in measurements on single crystals the relaxation of JT domains causes strong attenuation of sound for $T \lesssim T_c$ and the existence of a "dead" zone where the system has no acoustic response. Obviously, the second, stronger maximum in $Q^{-1}$ for $T < T_d$ is connected with the relaxation of the domains. In measurements at the frequencies 110 and 230 kHz we observed a shift in this maximum in $Q^{-1}$ at a temperature of 1.5 K, which attests to its relaxational nature. We can assume that the internal friction attains its largest value when the frequency of domain boundary relaxation, which depends on temperature, coincides with the frequency of the sound.

As we might expect, a magnetic field significantly suppresses the value of the "domain" maximum of $Q^{-1}$, because it favors single-domain crystallites in which the axis of easy magnetization is oriented along the field; therefore these crystallites do not contribute to the relaxational absorption of sound. As for the decrease in the minimum of the curve $\Delta E(T)/E$ in a magnetic field, this behavior of the elastic modulus of $DyVO_4$ is predicted theoretically[10] and is related to the fact that the magnetic field splits the degeneracy of the $Dy^{3+}$ ion and through magnetostriction induces a $B_{1g}$ deformation, i.e., the order parameter for $T \gtrsim T_c$.

The weak influence of the magnetic field on the elastic modulus in $TbVO_4$ is most likely connected with the larger initial splitting of the levels of the $Tb^{3+}$ ion in the crystal field and with the weak influence of the field $H = 40$ Oe on the energy spectrum near $T_c$.[11] The negative $\Delta E(H)$ effect in $TbVO_4$ for $T < T_c$ is apparently caused by reorientation of the JT domains under the action of the magnetic field.

**4.2. The $Dy_xTb_{1-x}VO_4$ system.** The distinctive features of the behavior of $\Delta E(T)/E$ in samples of mixed composition are in our opinion due to the presence of two softened moduli. Whereas for $DyVO_4$ the modulus which softens is $C_{11}$–$C_{12}$ and for $TbVO_4$ it is $C_{66}$, in the samples of $Dy_xTb_{1-x}VO_4$ both of these moduli soften appreciably. The concentration dependence of the value of the softening allows us to estimate the critical concentration of Dy and Tb ions at which phase $B_{1g}$ and $B_{2g}$ transitions, respectively, appear in the $Dy_xTb_{1-x}VO_4$ system. The experimental data suggest that the largest value of softening $\Delta E(T)/E$ is observed in a sample with $x = 0.7$, for which both the $C_{11}$–$C_{12}$ and $C_{66}$ moduli vanish, while the values of $T_c$ for the two SPT are close. The concentration where these conditions are realized is near the critical concentration of Tb ions; therefore $1 - x_{c2} \lesssim 0.3$. The $B_{1g}$ transition apparently occurs at the point where the rapid increase in the softening $\Delta E(T)/E$ is observed; this occurs for $x = 0.4$, which is close to the critical concentration for the CJTE in the $Dy_xTb_{1-x}VO_4$ system, i.e., $x_{c1} = 0.35$.[1]

The variation in the character of the dependences $Q^{-1}(T)$ with concentration (Fig. 3) also suggests the appearance of a $B_{1g}$ SPT. In our opinion, the sharp growth in $Q^{-1}$ for $T < 3$ K in the sample with $x = 0.5$ is connected with the relaxation of $B_{1g}$ domains, i.e., in this sample $T_{c1} \approx 3$ K for the SPT of $B_{1g}$ type. Therefore, the variation in elastic properties of the $Dy_xTb_{1-x}VO_4$ system allows us to assert that for $0.4 \lesssim x \lesssim 0.7$ two SPT occur in the sample; in this case the resultant symmetry of the crystal lattice at low temperatures is monoclinic, with a monoclinic angle $\gamma \neq 90°$ in the *ab* plane.

Also unusual is an additional softening $\Delta E(T)/E$ in compositions near $x = 0$ for $T < 5$ K (a rather small softening $\approx 1.5\%$ is observed for $TbVO_4$ as well). This softening for $T < 5$ K may be due, e.g., to JT ions weakly coupled to the host matrix (due to inhomogeneities or defects), so that distortions around them are not stabilized by the CJTE. However, this implies the presence of defects in the unsubstituted $TbVO_4$ as well. Another more physical origin is also possible. It is known that the JTE for the Tb ion arises from an excited level; therefore, if no structural transition intervened, the JT interaction would decrease as the temperature and the occupancy of the excited level decreased. In dilute crystals of $Gd_xTb_{1-x}VO_4$ with $x = 0.65$ this effect is responsible for the existence of an inverse transition from the orthorhombic to the tetragonal phase ($O_2 \rightarrow T$) at low tem-

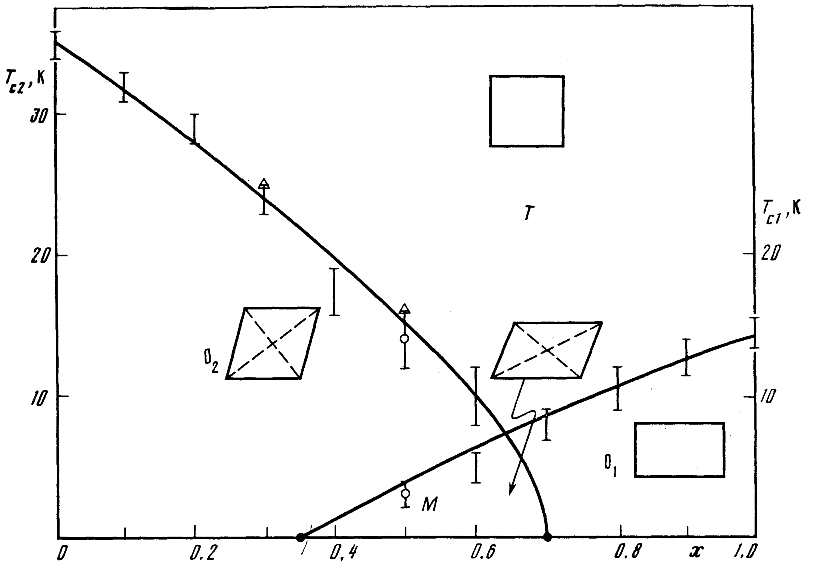

FIG. 5. Phase diagram of $Dy_xTb_{1-x}VO_4$ constructed according to the experimental data: *1*—measurements of elastic properties, Δ—x-ray diffraction measurements, O—magnetic susceptibility, ●—critical concentration (see text): *T*—tetragonal phase, $O_1$—rhombic phase of $B_{1g}$ symmetry, $O_2$—rhombic phase of $B_{2g}$ symmetry, *M*—monoclinic phase.

peratures, and to repeated vanishing of the modulus $C_{66}$. For $x<0.65$ there is no real $O_2 \rightarrow T$ transition; however, the mechanism for this transition remains in force and causes a rather small softening $\Delta E(T)/E$ for $T<5$ K. All of these arguments should also apply to the system $Dy_xTb_{1-x}VO_4$.

**4.3. Phase diagram.** The features in the behavior of the elastic, structural and magnetic characteristics of the $Dy_xTb_{1-x}VO_4$ system which we have observed in experiment allow us to construct the phase diagram (PD) of the system and to determine its special points, i.e., the critical (minimal) concentrations of Dy($x_{c1}$) and Tb($1-x_{c2}$) for the appearance of the $B_{1g}$ and $B_{2g}$ types of SPT respectively. Since the critical concentrations for each of the ions satisfy $x_{c1}$, $1-x_{c2}<0.5$, the phase boundaries corresponding to the $B_{1g}$ and $B_{2g}$ types of transitions intersect on the PD, i.e., there is a region of concentrations for which the two phases coexist in the sample. In particular, a detailed study of the sample with $x=0.5$ (Fig. 4) allows us to establish that $T_{c1}\approx 3.0$ K and $T_{c2}\approx 14$ K. In Fig. 5 we show the phase diagram for $Dy_xTb_{1-x}VO_4$ constructed on the basis of the data obtained from our experiments.

## 5. CONCLUSION

The studies we have carried out of the zircon-structure compounds $Dy_xTb_{1-x}VO_4$ have allowed us to construct the phase diagram of these compounds, from which two basic conclusions can be drawn. First of all, there is a region of concentration for which the system $Dy_xTb_{1-x}VO_4$ admits a phase with coexisting order parameters of differing symmetries. Secondly, the existence of two SPTs in a certain concentration region indicates that the JT distortions formed by the Dy and Tb ions inhibit each other only weakly in $Dy_xTb_{1-x}VO_4$, i.e., in this sense they are not competitive.

Let us note that for the unsubstituted $RVO_4$ compounds the interaction which lifts the degeneracy of the ground state is primarily with only one of the phonon types ($B_{1g}$ or $B_{2g}$); this leads to softening of only one component of the host matrix elastic moduli and gives rise to the rhombic distortion. The exception apparently is $TmVO_4$, in which both the $C_{66}$ and $C_{11}$–$C_{12}$ elastic moduli soften; however, the interaction with the $B_{2g}$ type phonon is dominant, so that only the modulus $C_{66}$ reduces to zero.[12] In this case, as a result of competition between the interactions which couple the electrons in the degenerate doublet of the $Tm^{3+}$ ion in $TmVO_4$ with the $B_{1g}$ and $B_{2g}$ types of phonons—which are comparable in magnitude—only one SPT is realized, the $B_{2g}$ type, at $T=2.15$ K. By combining different kinds of JT ions, we can obtain JT crystals in which there are two completely "soft" components of the host elastic moduli, and the resulting symmetry of the crystal will be less than rhombic.

The study of the properties of the $Dy_xTb_{1-x}VO_4$ system, which contains different types of JT ions, is also of interest in connection with the question of whether a JT glass is possible. In analogy with the magnetic glasses, in these systems we may perhaps expect that in the region of equal concentrations of JT components a state can occur with frozen-in (non-fluctuating) local deformations, but without good long-range order, analogus to the spin-glass state. However, our investigations of $Dy_xTb_{1-x}VO_4$ point to the existence in these systems of an ordered state with long-range order. In connection with this it would be interesting to investigate further the peculiarities in the physical properties of JT compounds with two phase transitions, and above all to experiment with single crystals of the corresponding compositions.

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