Phase diagram of $Dy_xTb_{1-x}VO_4$ crystals with competing Jahn-Teller lattice distortions

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A theoretical and experimental study has been made of structural phase transitions in $Dy_xTb_{1-x}VO_4$ crystals, in which the Jahn-Teller ions Dy^{3+} and Tb^{3+} cause competing spontaneous lattice deformations. In the system studied, structural phase transitions with a long-range order exist throughout the concentration interval, and a phase with two order parameters exists at $x \sim 0.5$.

Most of the experimental and theoretical studies of the Jahn-Teller interactions in crystals containing ions with an orbital degeneracy have dealt with compounds in which local distortions of the crystal lattice of a single symmetry occur around Jahn-Teller ions at the temperature of the structural phase transition, T_c (Ref. 1). In tetragonal crystals with the zircon structure RVO_4 (R = Tb, Dy, Tm), for example, orthorhombic lattice distortions are observed below T_c either along the [100] direction (B_{1g} type, $DyVO_4$, $T_{c1} = 13.5$ K) (Ref. 2) or along the [100] direction (B_{2g} type, $TbVO_4$, $T_{c2} = 34$ K) (Ref. 3).

A question of fundamental importance is the nature of a structural phase transition in a system with competing Jahn-Teller distortions of the crystal lattice. The concentration phase diagram of such a system is not clear: Are structural phase transitions observed over the entire concentration interval, and if so then what is their symmetry? According to Refs. 4 and 5, a state of a "Jahn-Teller glass" can exist in such systems. In that glass state, the directions of the local lattice distortions near the Jahn-Teller ions are oriented randomly, by analogy with spin glasses.

Rare-earth zircons of mixed composition $Dy_xTb_{1-x}VO_4$ with $x \sim 0.5$ fall in the category of systems with competing Jahn-Teller lattice distortions. These zircons were the subject of the present study. Crystals of $Dy_xTb_{1-x}VO_4$ ($x = 1.0$, 0.8, 0.65, 0.6, 0.5, 0.4, 0.2, 0.0) were grown by spontaneous crystallization from the melt in a molten PbO-PbF_2-B_2O-V_2O_5-R_2O_3 system. The test samples had average dimensions of $1 \times 1 \times 1.5$ mm. To determine the temperature and type of distortion at the structural phase transition, we measured the magnetic susceptibility χ_M (by an induction method at a frequency of 64 Hz; the amplitude of the alternating field was $H_{\sim} = 50$ Oe). We also measured the elastic modulus (by the compound-resonator method, at a frequency of 200 kHz), and we carried out low-temperature x-ray diffraction studies (using a Geigerflex diffractometer with a flow-through helium cryostat, over the temperature range 7–300 K).

Figure 1 illustrates the results in the particular case of a $Dy_{0.6}Tb_{0.4}VO_4$ crystal. The x-ray diffraction measurements, carried out on a ⟨110⟩ thin section [Co $K\beta$

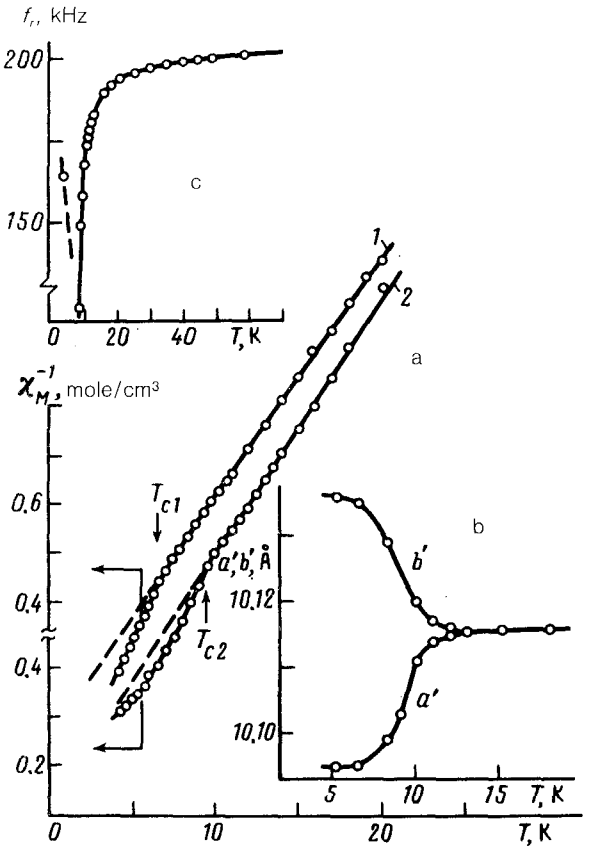

FIG. 1. a: Temperature dependence of the reciprocal magnetic susceptibility χ_M^{-1} for (1) $\mathbf{H}\|[100]$ and (2) $\mathbf{H}\|[110]$. b: Parameters of the orthorhombic cell, a' and b'. c: The resonant frequency f_r of the compound quartz-sample resonator for longitudinal acoustic waves along the [100] direction in the $Dy_{0.6}Tb_{0.4}VO_4$ crystal.

radiation, (660), $2\theta \approx 148°$], reveal an orthorhombic distortion of the structure, of the B_{2g} type at $T_{c2} \approx 10$–12 K. The magnitude of the distorion, $\varepsilon = (a' - b')/a' = 4 \times 10^{-3}$, is one-sixth that in $TbVO_4$ ($\varepsilon = 2.3 \times 10^{-2}$) (Fig. 1b).

Because of the low value $T_{c1} \approx 7$ K, we were not able to study the B_{1g} transition in this crystal by the x-ray method. We accordingly measured the propagation velocity of longitudinal sound waves along the [100] direction. Figure 1c reveals a sharp decrease ($\sim 50\%$) in the resonant frequency f_r of the compound quartz-sample resonator at $T_{c1} \approx 7.5$ K; at $T \lesssim T_{c1}$, we do not observe a resonance in the quartz-sample system down to 4.5 K, apparently because of a relaxation of structural domains and a strong attenuation of the sound. This behavior is characteristic of the B_{1g} structural phase transition. Note that we have $f_r \sim \sqrt{E_{100}}$, where the Young's modulus $E_{100} = 1/S_{11} \sim (C_{11} - C_{12})$ vanishes at $T = T_{c1}$ because of a softening of the elastic modulus

$(C_{11} - C_{12})$. In our experiments, the crystal (~ 1.7 mm long) was not matched with the quartz, and in the limit $E_{100} \to 0$ we had $f_r \to f_{qu}/2$.

The magnetic susceptibility of the $Dy_{0.6}Tb_{0.4}VO_4$ crystal exhibits two anomalies: deviations from a Curie-Weiss law toward the abscissa, at $T_{c2} = 10$ K for $\mathbf{H} \| [110]$ and at $T_{c1} = 7.0$ K for $\mathbf{H} \| [100]$ (Fig. 1a). Anomalies of this sort in χ_M have been observed previously[6] in $DyVO_4$ and $TbVO_4$ upon a structural phase transition and have been linked with a splitting of a degenerate ground state of a rare-earth ion at $T < T_{c1}, T_{c2}$. The temperatures of the anomalies in χ_M coincide with the values of T_{c1} and T_{c2} found from the x-ray and acoustic measurements; the temperature T_{c2} coincides with a maximum of the thermal-expansion coefficient of the crystal along the orthorhombic axes $a'(T)$ and $b'(T)$ (Fig. 1b).

We carried out similar studies of $Dy_xTb_{1-x}VO_4$ crystals with various values of x. On the basis of the experimental results, we constructed the phase diagram in Fig. 2.

In the theoretical analysis of the $Dy_xTb_{1-x}VO_4$ system, we took into account the interaction of each of the Jahn-Teller ions (Dy and Tb) with both of the orthorhombic vibrational modes, b_1 and b_2, which lift the degeneracy of the ground state. The presence of Jahn-Teller ions with competing local distortions implies that the crystal has degenerate levels with two different vibrational modes which lift the degeneracy and which are comparable in terms of the strength of the electron interactions. The Hamiltonian of the system is

$$H = H_{cryst} + H_{ph} + H_{str} + H_{el\text{-}str} + H_{el\text{-}ph} \,.$$

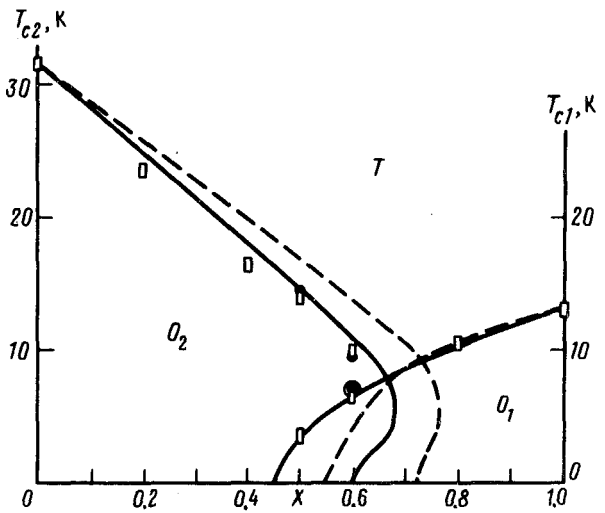

FIG. 2. Experimental and theoretical phase diagrams of the $Dy_xTb_{1-x}VO_4$ system. □—Magnetic susceptibility; ○—x-ray diffraction; ●—acoustic measurements; solid line—calculated for $B^{zz} = 2.2$ cm^{-1} and $B^{xx} = 3.2$ cm^{-1}; dashed lines—calculated for $B^{zz} = 5.4$ cm^{-1} and $B^{xx} = 8.2$ cm^{-1} (see the discussion in the text proper). T) Tetragonal phase; O_1) orthorhombic phase of B_{1g} symmetry; O_2) orthorhombic phase of B_{2g} symmetry.

The first three terms of the Hamiltonian describe the splitting of the energy levels of the Dy^{3+} and Tb^{3+} ions by the crystal fields, the free phonons of the crystal lattice, and the energy of the elastic deformation which arises upon the structural phase transition. The last two terms characterize the coupling of the electrons with the deformations and with the phonons of two symmetry types.

Using the molecular-field method, and ignoring the dynamic electron-phonon coupling, we derived a system of equations for the order parameters $\sigma_{z,x}^{(1),(2)}$ which contain the parameters of the molecular fields produced by the interactions between identical ions (A^{zz},A^{xx}) and between different ions (B^{zz},B^{xx}).

On the basis of the calculations we constructed a phase diagram of the $Dy_xTb_{1-x}VO_4$ system, which is shown in Fig. 2 for two pairs of the values of the parameters B^{zz} and B^{xx} (in the calculations, we used the values $A^{zz} = 9.8$ cm^{-1} and $A^{xx} = 22.5$ cm^{-1}, which we took from the literature). A composition of the phase diagrams for the various values of the parameters B^{zz} and B^{xx} shows that the interaction between the Dy and Tb ions shifts the phase boundaries and alters the critical concentrations of Dy and Tb ions for the occurrence of the structural phase transitions of types B_{1g} and B_{2g}. Since the literature reveals no data on the interaction of Dy ions with the b_1 orthorhombic vibrational mode or of the Tb ion with the b_2 orthorhombic vibrational mode, we estimated the parameters B^{zz} and B^{xx} from the experimental phase diagram. The best fit of the theoretical and experimental results was found with the values $B^{zz} = 2.2$ cm^{-1} and $B^{xx} = 3.2$ cm^{-1}.

In summary, this theoretical and experimental study leads to two basic conclusions. 1. In the $Dy_xTb_{1-x}VO_4$ system there is a concentration region in which there is a phase with coexisting order parameters of different symmetries. 2. The existence of two structural phase transitions in certain concentration interval suggests that the different types of Jahn-Teller distortions do not compete in a system for which interactions with b_1 and b_2 orthorhombic vibrational modes, comparable in magnitude, occur for ions in different lattice sites. This circumstance distinguishes these $Dy_xTb_{1-x}VO_4$ crystals from $TmVo_4$, in which a competition between interactions of Tm^{3+} ions with b_1 and b_2 orthorhombic vibrational modes (these interactions are comparable in strength) leads to only a single structural phase transition, of the B_{2g} type at $T_{c2} = 2.15$ K (Ref. 7).

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