A new type of structural Jahn-Teller phase transition in $DyVO_4$ induced by an electric field

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A structural transition from the ferro- to antiferro-distorted phase which also represents a transition from anti- to ferroelectric state is predicted for the $DyVO_4$ crystal in an electric field.

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Rare-earth vanadates, phosphates and arsenates—currently the subject of intensive investigation—undergo structural phase transitions (characterized by the ordering of local Jahn-Teller distortions) into the ferro-distorted state. The effect of the magnetic field and uniaxial pressure on the cooperative Jahn-Teller effect (CJTE)—the subject of several studies (see review[1])—was related to either the suppression of the structural phase transition (a decrease of the critical temperature, reduction of the order parameter, etc.) dependent on the stabilization of the para-phase or, on the contrary, to the maintenance of the ferro-state. It will be shown below that in contrast to such a situation the effect of the electric field on CJTE in the axisymmetric $DyVO_4$ crystal leads to a change in the type of phase transition: The crystal changes from an ordered ferro-phase to ordered antiferro-phase but not to a para-phase. Moreover, both modulus of elasticity C and dielectric susceptibility χ exhibit anomalous behavior. The latter does so because the structural transition of the ferro-antiferro-type in the dielectric sense turns out to be a transition from an anti- to a ferroelectric ordered state.

The study of the effect of the electric field on CJTE in $DyVO_4$ was stimulated by a reported observation of an anomaly in the dielectric constant ϵ in the course of the transition from tetragonal to orthorhombic phase.[2] The microscopic theory of this phenomenon was discussed by the authors elsewhere.[3] The phonon spectrum of $DyVO_4$ contains an optical branch that at $q = 0$ is transformed in the same manner as the spontaneous deformation. This vibration is associated with displacement in the two sublattices of the Jahn-Teller ions Dy^{3+} (the elementary cell contains two equivalent ions bound by the inversion operation) at which oppositely-directed polarizations occur. Thus, the ferro-distorted phase of a crystal is also the antiferroelectric phase, a fact which explains the anomaly in ϵ in the course of transition to the para-phase. The effect of the electric field on the properties of $DyVO_4$—a crystal evidently identified as the first ferro-distorted antiferroelectric—is considered below on the basis of concepts developed in Ref. 3.

As a result of displacement transformation on the Hamiltonian containing the electron-phonon interaction,

$$H \approx \sum_{a\,n\,\kappa} V^{a}_{n\kappa}\,(b^{+}_{\kappa} + b_{\kappa})\,\sigma^{z}_{na} + g_0\sqrt{\frac{C_0\Omega}{N}}\,u\sum_{na}\sigma^{z}_{na} + \mathcal{E}\sum_{na} f^{a}\sigma^{z}_{na} + \Delta\sum_{na}\sigma^{x}_{na},$$

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the deformation u, the polarization $\mathscr{P}$ and the crystal field Δ one can calculate the operator of effective interstitial interaction of the Ising type (σ—pseudo-spin operators, α—sublattice index). In terms of the molecular field approximation the sublattice order parameters $\overline{\sigma_a^z} = \sigma_a$ are determined from the following system

$$\sigma_a = E_a^{-1}(A\sigma_a + B\sigma_{a'} \pm f\chi_0\mathscr{E}) \text{ th } \beta E_a \ (\beta = 1/kT),$$

where the ($\pm$) signs correspond to $a = \text{I}$ and $a = \text{II}$, and the energies E_α are determined from the expression $E_\alpha = \{\Delta^2 + (A\sigma_\alpha + B\sigma_{\alpha'} \pm f\chi_0\mathscr{E})^2\}^{1/2}$. The "transverse" crystal field parameter $\Delta = 4.5$ cm^{-1}, values of constants of the intra-sublattice (A) and inter-sublattice (B) molecular fields, and the constants of the electron-polarization coupling f were all determined in Ref. 3: $A = 3.9$ cm^{-1}, $B = 7.2$ cm^{-1}, and $f^2 = 2.4$ cm^{-1}. In the case of the electric field $\mathscr{E} = 0$ the sublattice order parameters are identical ($\sigma_\text{I} = \sigma_\text{II}$) and at a temperature $kT_c = \Delta\,[\text{arc th}\Delta\,(A+B)^{-1}]^{-1}$ a phase transition of the second kind occurs in the crystal. The sublattice equivalence is impaired in the electric field and at critical fields $\mathscr{E}_{cr}$ that cause turnover of the sublattice dipole moments directed against the field, the parameters σ_α undergo sharp changes ($\sigma_\text{I} = -\sigma_\text{II}$ for $\mathscr{E} \geqslant \mathscr{E}_{cr}$).[1] Since the Jahn-Teller contribution to deformation and polarization are proportional to the parameters $S = (\sigma_\text{I} + \sigma_\text{II})$ and $T = (\sigma_\text{I}$

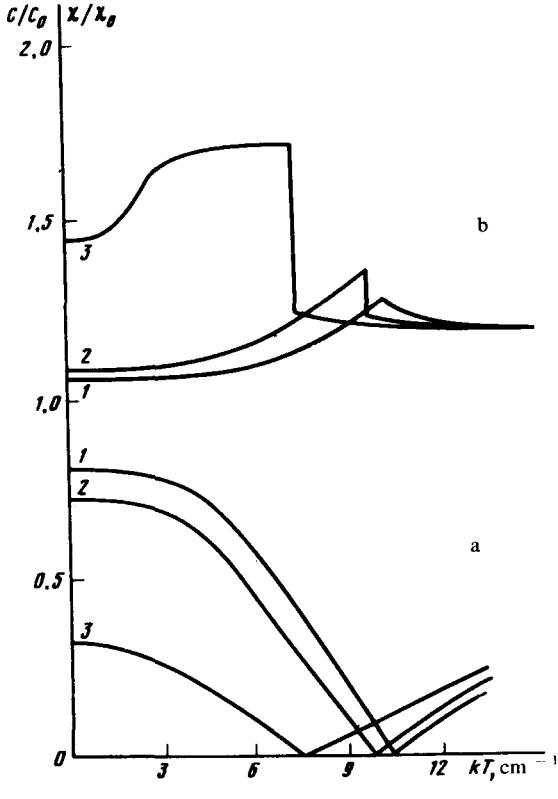

FIG. 1. Temperature dependence of the reduced modulus of elasticity (a) and dielectric susceptibility (b) in the electric field (curves 1–3 correspond to $f\chi_0\mathscr{E} = 0.3$ and 6 cm^{-1}, respectively).

$-\sigma_{II}$), respectively, the aforementioned behavior of the parameters σ_α indicates that there occurs in the $DyVO_4$ crystal in the electric field a sturctural phase transition of the ferro-antiferro type (as a result of which the spontaneous deformation vanishes) which also represents a transition from anti- to ferroelectric state. The moduli of elasticity C and dielectric susceptibility χ predetermined by the vibronic relationship are given by the following expressions:

$$\frac{C_0}{C} = 1 - g_0^2 \frac{2(A-B) - Z_I - Z_{II}}{(A - Z_I)(A - Z_{II}) - B^2},$$

$$\frac{\chi}{\chi_0} = 1 - \frac{4\pi\chi_0^2}{\epsilon_0} f^2 \frac{2(A+B) - Z_I - Z_{II}}{(A - Z_I)(A - Z_{II}) - B^2},$$

where

$$Z_a^{-1} = \Delta^2 E_a^{-3} \operatorname{th} \beta E_a + (E_a^2 - \Delta^2)\beta E_a^{-2} \operatorname{sech}^2 \beta E_a.$$

It follows from Fig. 1 that the electric field may differently affect the form of anomalies of C and χ. If the temperature dependence of C preserves its nature, χ takes on a jump at the transition point. This disparity may be understood from an analysis of the expansion of the free energy with respect to the order parameters S and T: at $\mathscr{E} \neq 0$, the series contains odd powers of T which cause a jump in χ. Consequently, the $DyVO_4$ crystal is a Jahn-Teller metaelectric: The dependence of its polarization on the field is essentially nonlinear and it exhibits a characteristic jump in the region of critical fields. Moreover, the metaelectric behavior of Jahn-Teller $DyVO_4$ is closely associated with anomalies of its elastic properties.

We should point out the following interesting feature of the thermodynamic behavior of $DyVO_4$ in the electric field. When the sublattices and field are aligned, $\sigma_I = -\sigma_{II}$ and both continuously decrease with increasing temperature. However, when certain relationships among $\mathscr{E}$, A, B and Δ hold, and in certain temperature intervals there occurs a state in which $|\sigma_{II}| \neq \sigma_I$ (similar behavior is exhibited by the sublattice polarization in potassium sodium tartrate[5]). States inside this region correspond to a ferroelectric spontaneously-deformed crystal while the modulus of elasticity and dielectric susceptibility exhibit anomalies at the boundaries.

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[1]Similar "meta-behavior" is characteristic of the Ising antiferromagnetics in the magnetic field.[4]

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