Connection between the anomalies of the elastic and dielectric characteristics of the Jahn-Teller crystal DyVO$_4$

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The nature of the anomalies of the temperature dependence of the dielectric susceptibility χ of the Jahn-Teller crystal DyVO$_4$ is investigated, and their connection with the anomalies of the elastic modulus C is studied. This relation is due to the fact that a distortion phase transition of the ferro-para type, due to the cooperative Jahn-Teller effect, is at the same time an antiferroelectric–paraelectric transition. The influence of the electric field on C and χ is investigated. It is shown that the crystal undergoes in the field a metaelectric antiferroelectric–paraelectric transition accompanied by a distortion ferro–antiferro transition. The microscopic parameters that characterize the contributions of the various phonon modes to the intra- and interlattice interactions are determined. It is shown that at certain values of the parameters a ferridistortion polar phase is produced in the crystal in a narrow temperature interval, at the limits of which the anomalies of C and of χ are particularly strongly pronounced. The influence of the electric field on the spectrum of the elementary excitations is considered, and the elastic and dielectric anomalies are explained on the basis of an analysis of the temperature dependence of the modes that are active in the phase transition. It is shown that the phase transition is connected with a complete (down to zero) softening of the quasi-acoustic mode, accompanied by partial softening of the quasioptical branch that transforms in accordance with the same representation as the spontaneous deformation of the crystal.

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Much research is presently carried out on ferroelastics, which are crystals that undergo phase transitions in which the order parameter is the strain. In these compounds, the elastic susceptibility, the temperature dependence of which has traditionally received special attention, becomes infinite at the phase-transition point. At the same time, interest is increasing in substances in which susceptibilities other than the elastic susceptibility have considerable anomalies at the structural-phase transition point. Thus, a substantial anomaly of the dielectric susceptibility was observed in structural transitions in rare-earth vanadates[1], double tungstates,[2] and other compounds. In the present paper we investigate the connection between the elastic and dielectric anomalies in structural transitions, using the crystal DyVO$_4$ as an example. Dysporium orthovanadate is the first known ferrodistortion antiferroelectric. In this substance the structural phase transition due to the "ferro-ordering" of the local Jahn–Teller distortions is, from the point of view of the dielectric properties, a transition into a phase with antiparallel orientation of the dipole moments produced in the unit cell at $T < T_c$.[3]

The interrelated anomalies of both the elastic and dielectric characteristics at the transition point give rise to a number of most peculiar singularities in the behavior of such crystals. In particular, the elastic modulus and the dielectric susceptibility of such compounds should depend strongly on the electric and magnetic fields, and also on the pressure, since their action, influencing the structure of the electronic levels of the Jahn–Teller ions, change the characteristics of the phase transitions. Principal attention will be paid

below to a theoretical investigation of the properties of the Jahn–Teller ferrodistortion antiferroelectric DyVO$_4$ in an electric field.[1]

Analysis shows that in an electric field the crystal undergoes a metaelectric antiferroelectric–paraelectric transition accompanied by a distortion ferre–antiferrotransition. At definite values of the field, a ferridistortion phase is realized in the crystal in a narrow temperature interval, at the limits of which the anomalies of the elastic modulus C and of the dielectric susceptibility χ are particularly strongly pronounced.

1. At high temperatures the DyVO$_4$ crystal belongs to the crystallographic class D_{4h}^{19}—the tetragonal structure of zircon. The unit cell contains two equivalent Dy^{3+} ions coupled by an inversion operation; the local symmetry D_{2d} of the Dy^{3+} ions have no symmetry center (Fig. 1). The ground state of the rare-earth ion is a
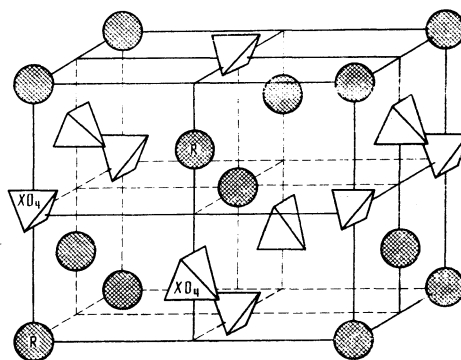

FIG. 1. Tetragonal (D_{4h}^{19}) structure of DyVO$_4$ with two formula units per unit cell (R = Dy^{3+}, Tm^{3+},...; X = V, As, P).

Kramers doublet E' at a distance $2\Delta = 9$ cm^{-1} above which is located a term E''. Their vibronic mixing leads to a structural phase transition from the tetragonal to the orthorhombic phase, due to the cooperative Jahn–Teller effect: at $T < T_c = 11.2$ K a spontaneous strain of the B_{1g} type is produced in the crystal.[5,6] In the vibronic mixing of the states E' and E'' of the Dy^{3+} ion, an active role is played by displacements that transform in accordance with the representations A_1, B_1, B_2, and E of the local group D_{2d}. The realization of B_{1g} strain in DyVO$_4$ at $T < T_c$ indicates that the largest contribution to the vibronic mixing is made by the interaction with the B_2-local displacements, inasmuch, as follows from the correspondence between the local group D_{2d} and the symmetry group D_{4h} of the unit cell, the representation $B_{1g}(D_{4h})$ goes over into the representation $B_2(D_{2d})$. Since the representation $A_{2u}(D_{4h})$ also goes over into $B_2(D_{2d})$, it follows from the foregoing that the local distortions of the representations B_2 are generated by the phonon modes of the representations B_{1g} and A_{2u} of the group D_{4h}.

In a lattice with zircon structure, the phonon branches are transformed at $q = 0$ in accordance with the following representations: the acoustic modes in accordance with $(A_{2u} + E_u)$, and the optical modes in accordance with $(A_{2u} + B_{1u} + 2E_u)$, $(A_{2g} + 2B_{1g} + 3E_g)$. The foregoing optical modes describe translations and rotations of the VO$_4$ groups relative to the rare-earth ions; the modes that describe oscillations within these groups are not active in the vibronic mixing and are therefore not cited.

From the point of view of the soft-mode concept, the instability of the high-temperature tetragonal structure of the lattice corresponds to a softening (with decreasing temperature) of the corresponding acoustic branch, which describes in the long-wave limit $q \to 0$ a homogeneous B_{1g} strain. Since among the optical branches there exists a mode that transforms in accordance with the same representation B_{1g}, its coupling with the electronic subsystem causes anomalies to be observed at the point of the structural phase transitions not only in the elastic modulus, but also in the dielectric susceptibility. In fact, it is easily seen that under B_{1g} strain of the unit cell the tetrahedral component of the surrounding of the two Dy^{3+} ions is distorted in such a way that the tetrahedra assume oppositely directed dipole moments (Fig. 2).

2. On the basis of the orbital states of the two lowest Kramers doublets of the Dy^{3+} ion, the Hamiltonian of the DyVO$_4$ crystal in an electric field takes the form

$$
\begin{aligned}
H = & \sum_q \hbar \omega_q \left(b_q^+ b_q + \frac{1}{2} \right) + \frac{1}{2} C_0 \Omega U^2 + \frac{\varepsilon_0^2}{8\pi\chi_0^2} \mathscr{P}^2 \\
& - g_0 \left(\frac{C_0 \Omega}{N} \right)^{1/2} U \sum_{m\alpha} \sigma_z^{m\alpha} + \mathscr{P}f \sum_m (\sigma_z^{mI} - \sigma_z^{mII}) \\
& - \sum_{mq\alpha} V_{mq}^\alpha (b_q^+ + b_q) \sigma_z^{m\alpha} + \Delta \sum_{m\alpha} \sigma_x^{m\alpha} - \frac{\varepsilon_0}{4\pi\chi_0} \mathscr{E} \mathscr{P},
\end{aligned}
\tag{1}
$$

where the first three terms are the energies of the phonons, of the elastic deformation, and of the polarized crystal. The next three terms describe the interaction

of the electrons with the deformation, polarization and the phonons, while the last term corresponds to the interaction of the polarization with the electric field $\mathscr{E} \| z$. Here $C_0 = (C_{11} - C_{12})/2$, x_0 and ε_0 are respectively the bare elastic moduli, the parallel dielectric susceptibility, and the dielectric constant, Ω is the volume of the crystal, N is the number of unit cells, and the indices $\alpha = I$ and II number the sublattices of the Dy^{3+} ions.

In (1) we have taken into account, as is customary, the interaction only with the B_2-local displacements, and also of the fact that the z component of the polarization $\mathscr{P}$ transforms in accordance with the representation A_{2u}.

A shift transformation in the Hamiltonian $H' = e^{iR} H e^{-iR}$, where

$$
R = \sum_{m\alpha} g_m^\alpha \sigma_z^{m\alpha}, \quad g_m^\alpha = i \sum_q V_{mq}^\alpha (b_q^+ - b_q)(\hbar\omega_q)^{-1},
\tag{2}
$$

gives rise to a term

$$
\sum_{mn} \sum_{\alpha\alpha'} \sum_q V_{mq}^\alpha V_{nq}^{\alpha'} \sigma_z^{m\alpha} \sigma_z^{n\alpha'} (\hbar\omega_q)^{-1},
$$

that describes the interaction of the electronic states via the phonon field. The equilibrium deformation and the polarization of the crystal are given in accord with (1) by the relations

$$
U = g_0 \left(\frac{\Omega}{C_0 N} \right)^{1/2} \sum_{m\alpha} \overline{\sigma_z^{m\alpha}}, \quad \mathscr{P} = \chi_0 \mathscr{E} + \frac{4\pi\chi_0^2}{\varepsilon_0} f \sum_m (\overline{\sigma_z^{mI}} - \overline{\sigma_z^{mII}}).
\tag{3}
$$

The sublattice order parameter σ_α that determine U and $\mathscr{P}$ can be obtained when account is taken of the electronic correlations in the molecular-field approximation. This approximation describes well phase transitions in rare-earth orthovanadates because of the considerable contribution made to the molecular field by the electron-strain coupling that leads to an infinite interaction radius. Substituting (3) in H' we obtain the single-mode Hamiltonian h_α, in which the electron and phonon systems are coupled only because the initial splitting Δ differs from zero.

We consider first the phase transitions, neglecting the dynamic interaction of the subsystems, i.e., under the assumption that

$$
f(\sigma)\varphi(b_q^+, b_q) = f(\sigma)\overline{\varphi(b_q^+, b_q)}.
$$

In this approximation[3]

$$
h_\alpha = (A\sigma_x + B\sigma_{\alpha'} \pm f\chi_0 \mathscr{E})\sigma_z^\alpha + \Delta\gamma\sigma_x^\alpha,
\tag{4}
$$

where $\gamma = \overline{\cos 2g_m}$ is the vibronic reduction factor, and the signs + or – correspond respectively to $\alpha = I$ and $\alpha = II$. The constants of the intrasublattice (A) and the
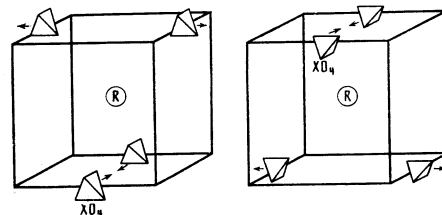

FIG. 2. Distortion of noncentrosymmetric component of the nearest surrounding of two R ions in a unit cell during the phase transition.

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intersublattice (B) molecular fields are determined by the relations

$$A=g_0^2+\lambda^{\alpha\alpha}+4\pi f^2\chi_0^2\varepsilon_0^{-1}, \quad B=g_0^2+\lambda^{\alpha\alpha'}-4\pi f^2\chi_0^2\varepsilon_0^{-1}. \tag{5}$$

The first term corresponds here to the electron-strain coupling, which makes equal contributions to the intra- and intersublattice interactions. The third term is due to the interaction of the electrons with an odd optical modes that makes contributions of opposite signs to A and B. The quantities $\lambda^{\alpha\alpha}$ and $\lambda^{\alpha\alpha'}$ are given by

$$\lambda^{\alpha\alpha}=K_{oe}-\nu/2, \quad \lambda^{\alpha\alpha'}=K_{oe}, \tag{6}$$

where K_{oe} is the contribution of the coupling with the even optical phonons and ν is the energy of the Jahn–Teller stabilization on the site, which is subtracted only from the intrasublattice interaction.[7] The eigenvalues of h_α are given by

$$E_\alpha=[\Delta^2\gamma^2+(A\sigma_\alpha+B\sigma_{\alpha'}\pm f\chi_0\mathscr{E})^2]^{1/2}. \tag{7}$$

The equilibrium values of σ_α are determined from the condition $\partial F/\partial\sigma_\alpha=0$, where the free energy F of the electron subsystem of the crystal is given by the formula ($\beta=1/kT$):

$$F=\tfrac{1}{2}A(\sigma_I^2+\sigma_{II}^2)+B\sigma_I\sigma_{II}-\beta^{-1}\ln(4\operatorname{ch}\beta E_I\operatorname{ch}\beta E_{II}). \tag{8}$$

This condition leads to the system of equations

$$\sigma_\alpha=E_\alpha^{-1}(A\sigma_\alpha+B\sigma_{\alpha'}\pm f\chi_0\mathscr{E})\operatorname{th}\beta E_\alpha. \tag{9}$$

It is convenient to change over from the quantities σ_α to $S=\sigma_I+\sigma_{II}$ and $Q=\sigma_I-\sigma_{II}$. The value of S, to which the total deformation of the crystal is proportional is the order parameter of the phase transitions; Q determines the dipole moment of the cell and the polarization of the entire crystal. The equations for these quantities are of the form [$a=(A+B)/2, b=(B-A)/2$]

$$S=\frac{aS-bQ-f\chi_0\mathscr{E}}{E_I}\operatorname{th}\beta E_I+\frac{aS+bQ-f\chi_0\mathscr{E}}{E_{II}}\operatorname{th}\beta E_{II}, \tag{10a}$$

$$Q=\frac{aS-bQ-f\chi_0\mathscr{E}}{E_I}\operatorname{th}\beta E_I-\frac{aS+bQ-f\chi_0\mathscr{E}}{E_{II}}\operatorname{th}\beta E_{II}, \tag{10b}$$

and the free energy is expressed in terms of S and Q in the following manner:

$$F=\tfrac{1}{2}aS^2-\tfrac{1}{2}bQ^2-\beta^{-1}\ln(4\operatorname{ch}\beta E_I\operatorname{ch}\beta E_{II}). \tag{11}$$

3. Equation (10a) always has a solution $S=0$ that corresponds to the undistorted crystal. It is clear that at high temperatures $\beta^{-1}>A+B$ the system will be in this phase. At low temperatures, however, there can exist one other phase, whose free energy is lower. This is easiest to see for the case $\Delta=0$. When $T\to0$, the system (10) has two solutions, $\sigma_I=1$ and $\sigma_{II}=\pm1$, and the free energy takes the form

$$F=A+B\sigma_{II}-|A+B\sigma_{II}+f\chi_0\mathscr{E}|-|A\sigma_{II}+B-f\chi_0\mathscr{E}|.$$

The phase with $S\ne0$ corresponds to $\sigma_{II}=1$, and its free energy is $F=-(A+B)$ in fields $f\chi_0\mathscr{E}<(A+B)$. The phase with $S=0$, corresponding to the solution $\sigma_{II}=-1$, has a free energy $F=2f\chi_0\mathscr{E}-3(B-A)$ at $f\chi_0\mathscr{E}<(B-A)$ and $F=(B-A)-2f\chi_0\mathscr{E}$ at $f\chi_0\mathscr{E}>(B-A)$. A comparison of the free energies shows that up to fields $f\chi_0\mathscr{E}_{cr}=B$ at $T=0$ the phase with $S\ne0$, which describes the deformed crystal (a deviation of Δ from zero does not change as a result and causes only a decrease of $\mathscr{E}_{cr}$). An increase in the temperature leads to a transition into a phase with $S=0, Q\ne0$.

Expanding the right-side of Eq. (10a) in powers of the parameter S, which vanishes at zero at $T=T_e$, we get the relation

$$\frac{\Delta^2\gamma^2}{E_0^2}\operatorname{th}\beta_c E_c-\beta_c\frac{E_0^2-\Delta^2\gamma^2}{E_0^2}\operatorname{sech}^2\beta_c E_c=(A+B)^{-1} \tag{12a}$$

$[E_0^2=\Delta^2\gamma^2+(f\chi_0\mathscr{E}-bQ)^2]$, which describes together with the equation that follows from (10b),

$$Q_c=2\frac{f\chi_0\mathscr{E}-bQ_c}{E_0}\operatorname{th}\beta_c E_0, \tag{12b}$$

the polarization of the undeformed lattice at $T>T_c$ a system from which we obtain the critical temperature T_c and the polarization T_c at this point. At $\mathscr{E}=0$ there is no polarization and the transition temperature is determined by the known relation

$$kT_c^0=\Delta\gamma[\operatorname{arcth}(\Delta\gamma/(A+B))]^{-1}. \tag{13}$$

It is easy to investigate also the case of weak fields, when $kT_c=kT_c^0(1-\xi^2\mathscr{E}^2)$, where

$$\xi^2=\frac{3}{2}\frac{f^2\chi_0^2}{\Delta^2\gamma^2}\left(1-\frac{2b}{\Delta\gamma}\operatorname{th}\beta_c\Delta\gamma\right)\left(\frac{\operatorname{sh}2\beta_c^0\Delta\gamma}{2\beta_c^0\Delta\gamma}-1\right).$$

Thus, the electric field lowers the temperature of the structural phase transition ($T_c\to0$) as $\mathscr{E}\to\mathscr{E}_{cr}$, since it tends to transform the crystal into a dipole-ordered antiferrodistortion phase.

Before we proceed to describe the results of the numerical solution of the systems (9) and (12), let us investigate the character of the phase transition, using the Landau expansion of the free energy in terms of the order parameter. In our case it takes the form

$$F=\bar{F}_0+\bar{a}_1S^2+\bar{a}_2S^4+\ldots, \tag{14}$$

where

$$\bar{a}_1=a(1-aZ_0^{-1}), \tag{15a}$$

$$\bar{a}_2=-a^4\left[3\frac{\Delta^2\gamma^2}{E_0^2}\left(1-5\frac{E_0^2-\Delta^2\gamma^2}{E_0^2}\right)\left(\beta\operatorname{sech}^2\beta E_0-\frac{1}{E_0}\operatorname{th}\beta E_0\right)\right.$$
$$-12\beta^2\Delta^2\gamma^2(E_0^2-\Delta^2\gamma^2)E_0^{-3}\operatorname{sech}^2\beta E_0\operatorname{th}\beta E_0+$$
$$\left.+2\beta^3(E_0^2-\Delta^2\gamma^2)E_0^{-1}\operatorname{sech}^2\beta E_0(2\operatorname{th}^2\beta E_0-\operatorname{sech}^2\beta E_0)\right), \tag{15b}$$

$$Z_\alpha^{-1}=(E_\alpha^2-\Delta^2\gamma^2)E_\alpha^{-2}\beta\operatorname{sech}^2\beta E_\alpha+\Delta^2\gamma^2E_\alpha^{-3}\operatorname{th}\beta E_\alpha. \tag{16}$$

If $\bar{\alpha}_2>0$ at the phase-transition point, then the critical temperature is determined from the condition $\bar{\alpha}_4(T_c)=0$, which coincides with (12a). The sign of $\bar{\alpha}_2(T_c)=0$. determines the order of the phase transition. At $\mathscr{E}=0$, the phase transition in DyVO$_4$ is of second order. In fact, in this case

$$\bar{a}_2(T_c)=a^4\frac{3}{\Delta^3\gamma^3}(\operatorname{th}\beta_c E_0-\beta_c\Delta\gamma\operatorname{sech}^2\beta_c E_0)\approx\frac{a}{4}>0.$$

The positiveness of $\bar{\alpha}_2(T_c)$ is preserved also in weak electric fields. The changes of the type of the phase transition takes place in the tricritical point of the phase diagram $(T,\mathscr{E})$ in the region of $\mathscr{E}$ close to $\mathscr{E}_{cr}$. For the case $\Delta=0$ the quantity

$$\bar{a}_2=2a^4\beta^3(1-3\operatorname{th}^2\beta E_0)\operatorname{sech}^2\beta E_0$$

becomes negative at the phase-transition point only at $\tanh\beta_c E_0>1/\sqrt{3}$. This inequality is satisfied in sufficiently strong electric fields, which cause an appreciable decrease of T_c. Estimates show that the transition temperature T_c begins to depend substantially on the electric field only when $\mathscr{E}$ is close to $\mathscr{E}_{cr}$. Thus, the transition

from the ferrodistortion in the antiferrodistortion ferroelectric phase of $DyVO_4$ in an electric field, is of second order in practically the entire field interval $\mathscr{E} < \mathscr{E}_{cr}$.

Knowing the free energy given by Eqs. (8) and (11), we can investigate the interrelated anomalies of the of the elastic and dielectric properties of the crystal. Thus, using the known relation $C = (\partial^2 F/\partial S^2)_{S=0}$ for the elastic modulus, it is easy to see that $C = \bar{\alpha}_1$ and vanishes at $T = T_c$.

To investigate the dielectric susceptibility it is convenient to expand the free energy both in terms of the parameter S that determines the deformation, and in the parameter Q that is connected with the polarization. This expansion, which takes the form

$$F = F_0 + \alpha_1 S^2 + \alpha_2 S^4 + \beta_1 Q^2 + \beta_2 Q^4 + \gamma_1 S^2 Q^2 + \ldots, \tag{17}$$

is valid, naturally, only at small Q, i.e., for not too strong electric fields. In the expansion (17), the coefficients at $\Delta = 0$ take the form

$$\begin{aligned}
\alpha_1 &= a(1 - 2\beta a \ \text{sech}^2 \ \beta f\chi_0\mathscr{E}), \\
\alpha_2 &= 4\beta^3 a^4 \ \text{sech}^2 \ \beta f\chi_0\mathscr{E} (1 - 3\text{th}^2 \beta f\chi_0\mathscr{E}), \\
\beta_1 &= b(1 - 2\beta b \ \text{sech}^2 \ \beta f\chi_0\mathscr{E}), \\
\beta_2 &= 4\beta^3 b^4 \ \text{sech}^2 \ \beta f\chi_0\mathscr{E} (1 - 3\text{th}^2 \ \beta f\chi_0\mathscr{E}), \\
\gamma_1 &= 4\beta^3 a^2 b^2 \ \text{sech}^2 \ \beta f\chi_0\mathscr{E} (1 - 3\text{th}^2 \ \beta f\chi_0\mathscr{E}).
\end{aligned} \tag{18}$$

From (17) we obtain for the dielectric susceptibility

$$\chi = \tfrac{1}{2}(\beta_1 + \gamma_1 S^2 + 6\beta_2 Q^2)^{-1},$$

from which it follows that at $\mathscr{E} = 0$, when

$$\chi = \tfrac{1}{2}(\beta_1 + \gamma_1 S^2)^{-1},$$

the dielectric susceptibility has a maximum at $T = T_c$, where the elastic modulus vanishes. In fact, at $T \to T_c - 0$ the increase of χ is due to the abrupt decrease of S ($\gamma_1 > 0$), and at $T \to T_c + 0$ the increase of χ is due to the decrease of $\beta_1 = b(1 - 2b/kT)$.

4. A quantitative analysis of the anomalies of C and χ is possible on the basis of a numerical solution of the system (9). The elastic modulus and the dielectric susceptibility are given by

$$\begin{aligned}
\frac{1}{C} &= \frac{\partial U}{\partial P} = \frac{1}{C_0} + g_0 \left(\frac{N}{C_0\Omega}\right)^{1/2} \left(\frac{\partial \sigma_I}{\partial P} + \frac{\partial \sigma_{II}}{\partial P}\right), \\
\chi &= \frac{\partial \mathscr{P}}{\partial \mathscr{E}} = \chi_0 + \frac{4\pi\chi_0}{\varepsilon_0}\left(\frac{\partial \sigma_I}{\partial \mathscr{E}} - \frac{\partial \sigma_{II}}{\partial \mathscr{E}}\right),
\end{aligned} \tag{19}$$

in which, in the calculation of the derivatives with respect to the field $\mathscr{E}$ and the pressure P it is necessary to make definite assumptions concerning the relaxation rates of the processes in the electron-phonon system. The isothermal elastic modulus and the static susceptibility correspond to a situation wherein the measurements are made at a frequency $\omega \to 0$, i.e., much lower than all the reciprocal relaxation times τ^{-1} of the system.

If $\omega \neq 0$, then one of the additional regimes considered in Refs. 5 and 6 can be realized: 1) an adiabatic regime sets in when ω^{-1} is less than the time τ_{el} of the electron-lattice relaxation, 2) an ideally isolated regime is realized if ω^{-1} is less than the electron relaxation time τ_{ee} and finally, 3) measurements at still higher frequencies, exceeding the vibronic frequency, yield bare values of C_0 and χ_0 which are not renormalized

by the electron-phonon coupling.

Determining in (19) the derivatives of the isothermal regime, we obtain

$$\frac{C}{C_0} = \left[1 - g_0^2 \frac{2(A - B) - Z_I - Z_{II}}{(A - Z_I)(A - Z_{II}) - B^2}\right]^{-1}, \tag{20}$$

$$\frac{\chi}{\chi_0} = 1 - \frac{2\pi\chi_0^2}{\varepsilon_0} f^2 \frac{2(A + B) - Z_I - Z_{II}}{(A - Z_I)(A - Z_{II}) - B^2}.$$

At $T \geqslant T_c$, when $Z_I = Z_{II} = Z_0$ because $S = 0$, Eqs. (20) assume the simpler form

$$\frac{C}{C_0} = \left[1 - \frac{2g_0^2}{A + B - Z_0}\right]^{-1}, \quad \frac{\chi}{\chi_0} = 1 - \frac{4\pi\chi_0^2}{\varepsilon_0} \frac{f^2}{A - B - Z_0}. \tag{21}$$

At the phase transition point, the elastic modulus redetermined by the vibronic coupling, should vanish, as is the case when the condition $A + B - Z_0 = 0$, which coincides with (12a), is satisfied. At $\mathscr{E} = 0$, the values of C and χ are determined by formulas of the type (21).

From the results of the numerical calculation of the temperature dependence of C and χ for different fields it follows that at $T < T_c$ the electric field increases χ and decreases C, while at $T > T_c$ the situation is reversed. The main singularity of the temperature dependence of χ in the electric field is that, in contrast to the elastic modulus at $\mathscr{E} \neq 0$, at the phase-transition point χ undergoes a jump that increases radidly with increasing field. Accordingly, the dependence of the polarization on the electric field is essentially nonlinear and is also characterized by a jump, thus attesting to a metaelectric-behavior of a Jahn–Teller crystal $DyVO_4$ (Fig. 3).

It is known that a meta-behavior is typical of strongly anisotropic systems, where the intersublattice interaction with the nearest neighbors has an antiferro-character, and the intrasublattice interaction with the nearest neighbors has a ferrocharacter.[8] Recognizing that the dipole moments of the sites are proportional to σ_z^α: $d_I \propto \sigma_z^I, d_{II} \propto -\sigma_z^{II}$ [see, e.g., Eq. (3)], as well as the values given below for the constant A and B, it is easy to verify that the meta-electric situation is indeed realized in $DyVO_4$. It follows also from the calculation that C and χ depend essentially on the crystal splitting Δ; this is of interest in connection with the possibility of modulating Δ by uniaxial pressure that transforms in accordance with the B_{2g} representation.

Figure 4 shows the temperature dependence of χ and C for the case $\Delta = 0, f\chi_0\mathscr{E} = 7.2$ cm^{-1}, when the sublat-
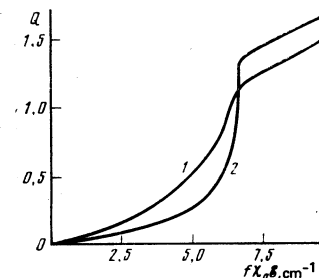
FIG. 3. Field dependence of the parameter Q that determines the polarization of the crystal, at different temperatures: 1—$kT = 6$ cm^{-1}, 2—$kT = 3$ cm^{-1}.

tices are oriented by the field already at $T = 0$ K. With increasing temperature, the parameters $\sigma_I = -\sigma_{II}$ decrease in absolute value. However, in the temperature interval (T_1, T_2), where $T_1 = 4.9$ K, $T_2 = 5.9$ K, there arises in addition to the indicated antiferrodistortion polar phase a ferrodistortion polar phase with $\sigma_I \neq |\sigma_{II}|$, having a smaller free energy. In this phase the macroscopic deformation of the crystal differs from zero in addition to the polarization; phase transitions accompanied by anomalies of C and χ take place at the limits of the temperature interval. The physical picture is similar here to the situation that takes place in Rochelle-salt where, in a definite temperature interval, a polarized state of the crystal is produced because of incomplete compensation of the antiparallel dipole moments of the sublattices.[9] We note that the entire region of existence of the ferri-phase the elastic modulus is anomalously small, and the dielectric susceptibility exceeds its value outside this phase by practically one order of magnitude. A similar behavior of C and χ in electric fields close to critical takes place not only in DyVO$_4$ under a uniaxial pressure that modulates Δ and transforms in accordance with the B_{2g}-representation, but also in the isomorphous DyAsO$_4$, where $\Delta = 0$.[5] The increase of Δ decreases the temperature interval of the existence of the ferri-phase, and at $\Delta = 4.5$ cm^{-1} (the case of DyVO$_4$ in the absence of uniaxial pressure) this phase is not realized. In this case, however, the elastic modulus assumes in the indicated interval anomalously small values ($C/C_0 \approx 0.05$), although the dielectric susceptibility has no noticeable anomalies.

The calculations whose results are shown in Figs. 3 and 4 were performed with the parameters determined in Ref. 3 from a comparison with experiment[1]: $A = 3.9$ cm^{-1}, $B = 7.2$ cm^{-1}, and $f^2 = 2.4$ cm^{-1}. Calculations were made also for other values of A and B (the sum $A + B$ remained equal to 11.2 cm^{-1}). The qualitative character of the field and temperature dependences of
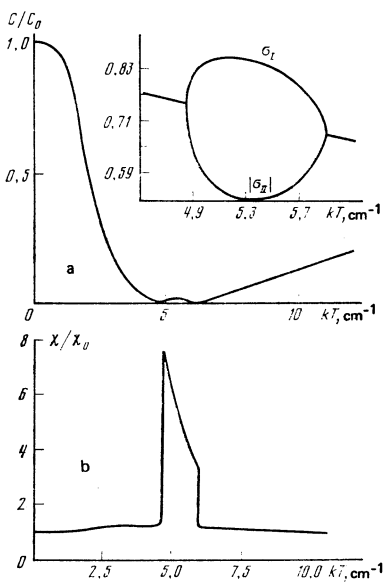

FIG. 4. Temperature dependence of the elastic modulus (a) and of the dielectric susceptibility (b) for $\Delta = 0$ and $f\chi_0\mathscr{E} = 7.2$ cm^{-1} (the inset shows the plots of the sublattice order parameters).

C and χ were kept the same, only the critical values of the field and of the transition temperature were altered.

The appreciable interest that attaches to the dielectric investigations in Jahn–Teller crystals is due to the possibility of their use for a detailed differentiation of the contributions of different interactions to the constants that characterize the investigated phase transition. In contrast to ultrasonic and piezospectroscopic experiments, where it is possible to determine the contribution of the electron-deformation interaction to the molecular-field constant, and analysis of the dielectric properties makes it possible to separate the intra- (8) and intersublattice (B) interactions.[3] Moreover, it turns out to be possible to determine the contributions made to the electron-phonon interaction by the even optical phonons (K_{oe}), the odd optical phonons (K_{oo}), as well as the value of the self-consistent dynamic correction ν, which constitutes the Jahn–Teller stabilization energy. In fact, using Eqs. (5) and (6) and the indicated values of A, B, and f^2, as well as the value $g_0^2 = 7.3$ cm^{-1}, we obtain $K_{oo} = 3.4$ cm^{-1}, $K_{oe} = 3.3$ cm^{-1}, and $\nu = 20.2$ cm^{-1}.

5. The foregoing results were obtained by studying only the electronic subsystem of the crystal, and neglecting its dynamic coupling with the phonons. As shown by a comparison with experiment, this analysis makes it possible to describe the properties of the Jahn–Teller crystals but, strictly speaking, is not quite consistent. In fact, the investigated phase transitions, while induced by the degeneracy of the electron subsystem, are structural, i.e., as already noted, they are due to the softening of the phonon modes. The latter can be obtained from a study of the spectrum of the coupled electron-phonon modes.

The spectrum of the elementary excitations of the system described by the transformed Hamiltonian H' will be calculated, after changing over to the operators $S_i = \sigma_i^I + \sigma_i^{II}$ and $Q_i = \sigma_i^I - \sigma_i^{II}$, with the aid of the equal-time Green's functions. Introducing Green's functions of the form $\langle\langle O(t)|Q_z^\eta(t')\rangle\rangle$, where $O(t)$ is one of the electrons (S_i, Q_i) or phonon ($b_q^+, b_i, \cos 2g_m, \sin 2g_m$) operators, and writing down the equations of motion for them, we can obtain a closed system of equations using splitting of the following type:

$$\langle\langle S_i^m S_j^{m'}|Q_z^n\rangle\rangle = \bar{S}_i\langle\langle S_j^{m'}|Q_z^n\rangle\rangle + \bar{S}_j\langle\langle S_i^m|Q_z^n\rangle\rangle, \tag{22}$$

$$\langle\langle S_i^m \cos 2g_m|Q_z^n\rangle\rangle = \bar{S}_i\langle\langle\cos 2g_m|Q_z^n\rangle\rangle + \overline{\cos 2g_m}\langle\langle S_i^m|Q_z^n\rangle\rangle, \tag{23}$$

$$\langle\langle\cos 2g_m b_q|Q_z^n\rangle\rangle = \overline{\cos 2g_m}\langle\langle b_q|Q_z^n\rangle\rangle. \tag{24}$$

The splittings (22) and (24) correspond to the self-consistent-field approximation in the electron and phonon subsystems, while the splittings (23) makes it possible to take into account the electron-phonon correlations under the assumption that $\Delta < \omega_D$ (ω_D is the Debye frequency). The spectrum obtained from the system of equations determined in this manner is in the general case quite complicated. We consider therefore here coupled electron-phonon modes only in the high-temperature phase of the crystal. The dispersion equations are then

$$E^2(E^2 - E_S^2 + a_1\bar{S}_x E_S^2)(E^2 - E_Q^2 + b_1\bar{S}_x E_Q^2) = 0, \tag{25}$$

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where

$$a_1 = - \left(E - \sum_e \frac{\Delta\gamma E \bar{S}_x}{E^2 - \hbar^2 \omega_{eq}^2} \right)^{-1} \sum_e \frac{\Delta\gamma E}{E^2 - \hbar^2 \omega_{eq}^2} \frac{|V_{eq}^+|^2}{\hbar\omega_{eq}}, \qquad (26)$$

$$b_1 = {}' E - \frac{\Delta\gamma E \bar{S}_x}{E^2 - \hbar^2 \omega_{o_{eq}}^2} \right)^{-1} \frac{\Delta\gamma E}{E^2 - \hbar^2 \omega_{o_{eq}}^2} \frac{|V_{oq}^-|^2}{\hbar\omega_{o_{eq}}}, \qquad (27)$$

$$E_S = 2[\Delta\gamma(\Delta\gamma - J(q)\bar{S}_x) + (f\chi_0\mathscr{E} - b\bar{Q}_z)^2]^{\frac{1}{2}}, \qquad (28)$$

$$E_Q = 2[\Delta\gamma(\Delta\gamma - H(q)\bar{S}_x) + (f\chi_0\mathscr{E} - b\bar{Q}_z)^2]^{\frac{1}{2}}. \qquad (29)$$

Here $|V_q^\pm|^2 = |V_{mq}^I \pm V_{mq}^{II}|^2$, while $J(q)$ and $H(q)$ are the Fourier transforms of the interactions of the local deformations.[2]

In Eqs. (26)–(27) the summation is carried out over the even (e) B_{1g} optical modes and the acoustic mode. Equation (25) takes into account the fact that at small values of q the main contribution to $|V_q^+|^2$ is made by the acoustic and optical modes, while the contribution to $|V_q^-|^2$ is made by the optical A_{1u} oscillation. As seen from (25), at $T \geqslant T_c$ the "strain" (S) and "polarization" (Q) electron-phonon modes differ from each other. This is a consequence of the fact that at $T \geqslant T_c$ the sublattices of the crystal are equivalent even at $\mathscr{E} \neq 0$. Equations (28) and (29) describe the spectrum of the electron subsystem neglecting the dynamic electron-phonon coupling. It follows from them that the frequency of the E_S mode vanishes at a temperature determined from the condition

$$\Delta\gamma(A+B)\bar{S}_x = \Delta^2\gamma^2 + (f\chi_0\mathscr{E} - b\bar{Q}_z)^2 \qquad (30)$$

[this temperature differs somewhat from that determined from the system (12), owing to the difference between the approximations used in the calculation]. The E_Q mode also softens, but does not vanish at $T = T_c$.

Allowance for the dynamic electron-phonon coupling leads to a redetermination of both the electron and phonon deformation modes. In particular, at small q, when $\hbar\omega_{ac} \ll E_S$, we obtain for the redetermined quasiacoustic $[\hbar\omega_{ac}'(q)]$ and quasielectronic $[E_S'(q)]$ branches

$$\hbar\omega_{ac}'(q) = \hbar\omega_{ac}(q) E_S(q)/E_S'(q), \qquad (31)$$

$$E_S'(q) = [E_S^2(q) + \Delta\gamma|V_{ac}^\pm(q)|^2 \bar{S}_x/\hbar\omega_{ac}(q)]^{\frac{1}{2}}. \qquad (32)$$

It is seen from (31) and (32) that, at the temperature of the structural phase transition induced by the electric field, the frequency of the electronic mode E_S'

is not equal to zero, and the frequency of the acoustic mode vanishes. It follows also from (25) that the frequencies of the optical modes also become temperature-dependent. It is easy to verify that this dependence is most significant for the even optical mode, the frequency has a minimum at $T = T_c$ (but does not vanish, in contrast to the acoustic mode).

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Note added in proof (20 *March* 1980). Recent investigations of the DyAsO$_4$ crystal (J. H. Page, S. R. P. Smith, D. R. Taylor, R. T. Harley, J. Phys. C: Solid State Phys., 12, L875, 1979) have shown that the anisotropy of its dielectric susceptibility is small. In similar systems, the influence of the electric field on the elastic and dielectric anomalies is more complicated than in the strongly anisotropic DyVO$_4$. In particular, one can expect in this case the electric field to produce in the dipole subsystem transitions of the "spin-flop" type in antiferromagnets.

[1]Some results were reported earlier in Ref. 4.

[1]H. Unoki and T. Sakudo, Phys. Rev. Lett. **38**, 137 (1977).
[2]L. N. Pelikh and A. A. Gurskas, Fiz. Tverd. Tela (Leningrad) **21**, 2136 (1979) [Sov. Phys. Solid State **21**, 1223 (1979)]. Ninth All-Union Conf. on Ferroelectricity, Abstracts of Paper Papers, Part. 1. Rostov-on-Don, 1979, pp. 154,155.
[3]V. G. Vekhter and M. D. Kaplan, Fiz. Tverd. Tela (Leningrad) **20**, 1433 (1978) [Sov. Phys. Solid State **20**, 824 (1978)].
[4]V. G. Vekhter and M. D. Kaplan, Pis'ma Zh. Eksp. Teor. Fiz. **29**, 173 (1979) [JETP Lett. **29**, 155 (1979)].
[5]R. J. Elliott, R. T. Harley, W. Heyes, and S. R. P. Smith, Proc. Roy. Soc. A328, **17** (1972).
[6]G. Gehring and K. A. Gehring, Rep. Prog. Phys. **38**, 1 (1975).
[7]H. B. Ergun, K. A. Gehring, and G. A. Gehring, J. Phys. C: Solid State Phys. **9**, 1101 (1976).
[8]E. Stryjewski and N. Giordano, Adv. Phys. **26**, 487 (1977).
[9]V. G. Vaks, Vvedenie v mikroskopicheskuyu teoriyu segnetoélektrikov (Introduction to the Microscopic Theory of Ferroelectrics), Nauka, 1973, Sec. 25.

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