

Article

# Magnetolectricity in Jahn–Teller Elastics

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**Abstract:** The magnetolectric effects in Jahn–Teller crystals are discussed on the basis of phenomenology and microscopic theory. New magnetolectric effects—metamagnetolectricity—are analyzed. Formation of multiferroic crystal states as the consequence of the cooperative Jahn–Teller effect is discussed.

**Keywords:** magnetolectricity; elastics; cooperative Jahn–Teller effect

Around 25 years ago it was recognized that the electrons are able to transfer not only the electrical charge, but, additionally, spin. This was the beginning of spintronics [1]. In technology, the understanding of information transfer by electron spins led to the emergence of a new field, where a variety of materials and devices for different applications was developed. The modern state of the connection between chemistry, physics, materials science, and engineering in this field is analyzed in detail in [2]. Especial importance for spintronics is related to physics and chemistry of magnetic cluster compounds, where deep quantum-mechanical analysis allows for better understanding of the system spin states and more precise control of them at the measurements [3].

Several similar to spintronics fields of physics and technology were considered based on quantum chemistry of materials. As the electronic states are characterized by the orbital momentum and its projection that also could be transferred by the electrons, the orbitronics [4] field was suggested. In semiconducting materials, some electrons are characterized by pseudospin and its projection (index of the electronic band valley). Transfer of information by electron pseudospin led to pseudospintronics and valleytronics [5].

In this article, we would like to suggest a new field of research following the same logic. In crystals, with the cooperative Jahn–Teller effect, the elementary energy excitations of the crystal are dynamically coupled spins, orbital momentum (pseudospins describing the degeneracy of the electron states) and phonons. These elementary excitations are called vibrons (coming from vibronic interaction). It is clear that a new field of electronics could be created—vibronics. The Jahn–Teller crystals are the smart materials for the necessary devices. The magnetolectric properties of these materials [6] are of especial interest as they allow for both the traditional—electric—and magnetic channel of the information transfer. Evidently, the physics of magnetolectricity in Jahn–Teller elastics is of big interest for the spintronics field.

The phenomenon of magnetolectricity was at the center of attention a while ago, and about 15–20 years ago, it reappeared as a property of multiferroics [7]. The interest in this phenomenon continues nowadays. It is probably mostly connected to multiple applications of these materials. At the same time, new fundamental results are obtained and more could be expected in the future.

Nowadays, there are many very good reviews on magnetolectricity of multiferroics ([8] and references therein). Nevertheless it makes sense to return to this problem once again for the following reasons: (a) the Jahn–Teller elastics represent a new class of smart materials with magnetolectric effects; (b) the microscopic mechanism of the magnetolectricity is still under discussion; (c) the Jahn–Teller ferro- and antiferroelastics are of great interest since, in this class of materials, magnetolectric coefficients may be significant, and a microscopic mechanism can be developed.



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### 1. Phenomenology of Magnetoelectricity in Jahn–Teller Ferroelastics

The concept of multiferroicity was introduced in 1970 [9] and defined as a state of crystals with several simultaneously existing ferro-, antiferro-, or ferri-type orderings. From this point of view, multiferroic magnetoelectricity is a characteristic of materials with the ordering of magnetic and electric dipoles. In this article, we are going to discuss magnetoelectricity in elastics—crystals with structural phase transitions.

It was mentioned for the first time in [10] that the magnetoelectric effects exist in materials that are characterized by the simultaneous presence of magnetostriction and electrostriction. On the other hand, the Jahn–Teller crystals are typically materials with the giant magneto- and/or electrostriction [11]. This leads to the search of the magnetoelectric effects among the Jahn–Teller elastics.

The thermodynamic potential of a Jahn–Teller elastic (for simplicity, the tetragonal symmetry crystals will be considered) in the external electric and magnetic fields can be described as:

$$\Phi = \frac{1}{2}C_0U^2 + \frac{1}{4}C_1U^4 - UP + \frac{L^2}{2\chi_{0L}} - LF + \sum_{nm} \lambda_{nm}^L L^n U^m \quad (1)$$

In Equation (1), the first two terms describe the elastic energy ( $C_1$  and  $C_0$  are elastic constants,  $C_1 > 0$ ,  $C_0 \sim (T - T_s)$ ,  $T_s$ —critical temperature of the structural phase transition), the third one is the interaction of the strain  $U$  with the external pressure  $P$ , next is the energy of the magnetized ( $L = M$ , where  $M$  is magnetization of the system) and/or polarized ( $L = P$ ,  $P$  is the polarization of the system) crystal,  $\chi_{0L}$  is the corresponding susceptibility,  $F = H$  or  $E$ , and the last term is the interaction of the strain with the magnetization and/or polarization. In the lowest order in  $U$ , for nonpolar paramagnets and/or paraelectrics, we have  $n = 2$  and  $m = 1$  or  $2$ , depending on whether or not the representation  $\Gamma(U)$  is present in the square of representation  $\Gamma(L)$ .

Starting with the case  $n = 2$ ,  $m = 2$ , from the conditions  $\partial\Phi/\partial U = \partial\Phi/\partial L = 0$ , it is easy to find the equilibrium values of the magnetization (polarization):

$$\bar{L} = F \left( \frac{1}{\chi_{0L}^{-1}} + 2\lambda_{22}\bar{U}^2 \right)^{-1} \quad (2)$$

and the strain  $U$  (at  $P = 0$ ):

$$\bar{U} = \sqrt{(-C_0 - 2\lambda_{22}\bar{L}^2)C_1^{-1}} \quad (3)$$

Accepting that the corrections proportional to  $\lambda_{22}$  are small, we can replace  $\bar{L}$  by  $L_0 = \chi_{0L} F$  and replace  $\bar{U}$  by  $U_0 = \sqrt{-C_0/C_1}$  in the corresponding terms and obtain:

$$\bar{U} = \sqrt{(-C_0 - 2\lambda_{22}\chi_{0L}^2 F^2)/C_1} \quad (4)$$

It follows from Equation (4) that the dynamic direct magneto- or electrostriction coefficient is:

$$D_L \equiv \frac{\partial\bar{U}}{\partial F} = -\frac{2\lambda_{22}\chi_{0L}^2 F}{\sqrt{(-C_0 - 2\lambda_{22}\chi_{0L}^2 F^2)C_1}} = -\frac{2\lambda_{22}\chi_{0L}^2 F}{\bar{U}C_1} \quad (5)$$

From Equation (1), we obtain the effective elastic constant:

$$C_{\text{eff}} \equiv \left( \frac{\partial\bar{U}}{\partial P} \right)_{P=0}^{-1} = 2C_1\bar{U}^2, \quad (6)$$

which means that  $C_{\text{eff}} = 0$  at  $T = T_s$ . Using Equation (6), we can rewrite Expression (5) in the form where the effective elastic constant  $C_{\text{eff}}$  is in the denominator. From Equation (5) it is evident that  $D_L \rightarrow \infty$  near the structural phase transition temperature  $T = T_s$ .

Switching now to the case of  $m = 1$  in the thermodynamic potential Equation (1) for the crystals with linear in strain magneto-/electroelastic coupling, from the condition  $\partial\Phi/\partial U = \partial\Phi/\partial L = 0$ , we similarly obtain the direct dynamic magneto-/electrostriction coefficients in the form:

$$D_L = -2\lambda_{21}\chi_{0L}^2 F(C_0 + 3C_1\bar{U}^2)^{-1} \quad (7)$$

Note that this formula is obtained in the first approximation in  $\lambda_{21}$ . In this approximation, it is easy to show that the elastic constant  $C_{\text{eff}}$  remains unrenormalized by the external fields (the renormalization is proportional to  $\lambda_{21}^2$ ). Hence, Equation (7) can be written similarly to Equation (5) with the elastic constant in the denominator.

It follows from Equations (5)–(7) that the dynamic magneto- and electrostriction coefficients have a characteristic temperature dependence due to the temperature dependence of the spontaneous strain  $U$ . In both cases ( $m = 1$  and  $m = 2$ ) in the elastically ordered phase of the crystal, these coefficients increase as the temperature approaches  $T_s$ . For magneto- or electroelastic coupling, the coefficients that are quadratic in the order parameter ( $m = 2$ ) are proportional to  $(T - T_s^1)^{-1/2}$  with:

$$T_s^1 = T_s - 2\lambda_{22}\chi_0^2 F^2, \quad (8)$$

i.e., they diverge as  $T \rightarrow T_s^1$ . In the case of linear coupling, the phase transition does not occur in an external field  $F$ , because  $\bar{U} \neq 0$  at all temperatures. It is easy to show that for  $T > T_s$  and  $F \neq 0$ :

$$\bar{U} = \frac{\lambda_{21}L^2}{C_0} \quad (9)$$

In this case, the maximum value of the dynamic magneto-/electrostriction coefficient is reached at  $T = T_s$  and becomes anomalously large in weak external fields  $F$ . Note that the difference of the  $D_L$  coefficients for the cases of the linear and quadratic coupling is also manifested in the fact that in the first case  $\partial U/\partial F = 0$  in the paraelastic phase of the crystal.

From the previous discussion, it becomes clear that in the Jahn–Teller elastics, the magneto- and electrostriction coefficients could be large, even in the crystals that are not ferromagnetic or ferroelectric. This is a result of large forces applied to the crystal in the external fields  $F$ , of strong electron-lattice coupling, and of a large crystal strain under applied forces. The last is the result of lattice softness caused by structural phase transition.

So far, in this section, only monoferroic elastics have been discussed. However, there are crystals that exhibit more than one structural phase transition, i.e., in addition to the structural transition, the ferromagnetic and/or ferroelectric phase transitions take place. If the critical temperatures of these transitions are significantly different, their influence on each other is small, and the phenomenology of striction coefficients could be analyzed similarly to the way discussed above. But if the critical temperatures are close, their mutual influence cannot be ignored. For example, if two structural phase transitions occur (this happens in some virtual Jahn–Teller elastics), the thermodynamic potential is still described by Equation (1) and is different only in that:

$$C_0 \sim (T - T_{s1})(T - T_{s2}), \quad (10)$$

i.e., reverts to zero twice. The ordered phase is of internal type. It is not difficult to show that, in such crystals, the strain reaches a maximum at the temperature

$$T_{\text{max}} = \frac{2T_{s1}T_{s2}}{T_{s1} + T_{s2}}. \quad (11)$$

In the virtual Jahn–Teller elastics with  $m = 1$  and  $n = 2$  the dynamic striction coefficients are described by Equation (7), but the temperature dependence is determined by Equation (10). The temperature dependence of  $D_L$  has two peaks near  $T_{s1}$  and  $T_{s2}$  and a minimum at  $T \approx T_{\max}$ .

Similarly to Equation (2) in the case of  $m = 1$  the equilibrium polarization  $P$  can be obtained from the thermodynamic potential Equation (1):

$$P = E(P = E(\chi^{-1}_{0P} + 2\lambda_{21}^P U)^{-1}) \quad (12)$$

so that the magnetoelectric coefficient  $R = (\partial P / \partial H)_{E,H}$  is equal to:

$$R = -2 \lambda_{21}^P \epsilon_c (\chi^{-1}_{\text{op}} + 2 \lambda_{21}^P U)^{-2} \left( \frac{\partial U}{\partial H} \right)_{\epsilon_c, H_c} \quad (13)$$

Thus,  $R$  is proportional to the dynamic magnetostriction  $D$  and therefore has a maximum in the vicinity of the structural phase transition temperature. However, it is evident from the phenomenological theory and could be shown on the basis of microscopic calculations, that  $R$ , unlike  $D$ , does not become infinite at  $T \approx T_s$  in the limit of  $E, H \rightarrow 0$ .

Equation (13) generalizes the previously suggested idea of magnetoelectric coupling in materials with magnetostriction and electrostriction [10] for the case of crystals with structural phase transitions. In these materials, the magnetoelectric effects are rendered considerably larger as a result of anomalously large striction effects.

## 2. Microscopics of Magnetoelectricity in Crystals with Ferroelastic Ordering

Microscopics of magnetoelectricity in Jahn–Teller ferroelastics will be presented for two different crystals: monoferroic  $\text{TmAsO}_4$  and multiferroic  $\text{TbPO}_4$ .

In the  $\text{TmAsO}_4$  crystal, a structural transition from the tetragonal to the orthorhombic phase takes place at  $T = T_s = 6.1$  K with the spontaneous strain of  $B_{2g}(D_{4h})$  symmetry. The lowest electronic states of  $\text{Tm}^{3+}$  ion are the ground doublet and the excited singlet, separated by a small gap  $\Delta = 14 \text{ cm}^{-1}$ . An electric field oriented in the base crystal plane induces a polarization  $P_{x,y}$ , which transforms according to the  $E_u(D_{4h})$  representation. Since the spontaneous strain  $U$  transforms according to the  $B_{2g}$  representation of the crystal group, the case of linear strain electroelastic coupling ( $n = 2, m = 1$ ) clearly occurs in this situation (see Equation (1)). Similarly, a magnetic field  $H$  oriented in the same crystal plane, will induce  $M_{x,y}$  and the spontaneous strain  $U$  according to the magnetoelastic coupling.

The Hamiltonian of the electronic subsystem can be written in the following form (the dynamic electron-phonon interaction is neglected) [12]:

$$H = \sum_{m\alpha\alpha'} A_{mn}^{\alpha\alpha'} \sigma_z^{m\alpha} \sigma_z^{n\alpha'} + \Delta \sum_{m\alpha} \tau^{m\alpha} - f \gamma \epsilon_x \sum_{m\alpha} \tau_x^{m\alpha} - g \beta \gamma H_x \sum_{m\alpha} S_x^{m\alpha} \quad (14)$$

where  $f$  is the electron-polarization interaction constant,  $g$  is the  $g$ -value factor,  $\beta$  is the Bohr magneton,  $\gamma$  is the vibronic reduction factor,  $\alpha, \alpha' = I, II$  are the crystal sublattice indexes,  $A_{mn}^{\alpha\alpha'}$  is the interaction between electrons in  $m\alpha$  and  $n\alpha'$  sites caused by virtual phonon exchange and electron-strain interaction,

$$\sigma_z = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \tau = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \tau_x = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad S_x = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (15)$$

At  $T < T_s$   $\overline{\sigma_z^{mI}} = \overline{\sigma_z^{mII}} = \overline{\sigma_z} \neq 0$  and  $\overline{\tau_x^{m\alpha}} = 0$ ,  $\overline{\tau_x} = \overline{\tau_x^I} + \overline{\tau_x^{II}} = 0$ ,  $\overline{S_x^{m\alpha}} = 0 \overline{S_x} = \overline{S_x^I} + \overline{S_x^{II}} = 0$ , if  $H_{x,y} = E_{x,y} = 0$ ; however it could be shown that in the presence of the external electric and magnetic fields, structural transition does not take place (it is smeared out,  $\overline{\sigma_z} \neq 0$  at all temperatures) and the polarization (magnetization)  $P$  ( $M$ ) of the crystal is not zero ( $\overline{\tau_x} \neq 0, P \sim \overline{\tau_x}$ ).

The macroscopic crystal polarization  $P$  is defined by  $\bar{\tau}_x$

$$\bar{\tau}_x = \frac{2f\gamma}{E_0} \frac{1}{Z} e^{-(\Delta-W)/2kT} \sinh\left(\frac{E_0}{kT}\right) \bar{\epsilon}_x \quad (16)$$

where  $W = A\bar{\sigma}_z$ ,

$$E_0 = \left[ \left(\frac{\Delta+W}{2}\right)^2 + f^2\gamma^2\chi_0^2\bar{\epsilon}_z^2 + g^2\beta^2\gamma^2H_x^2 \right]^{1/2} \quad (17)$$

$$Z = e^{-W/kT} + 2e^{(W-\Delta)/2kT} \cosh(E_0/kT) \quad (18)$$

The magnetoelectric coefficient may be calculated by direct differentiation of polarization by magnetic field. The formula for this calculation (not shown here) contains two terms. One of them does not have anomalous temperature dependence at the critical temperature  $T = T_s$  ( $H_x, E_x = 0$ ) and corresponds to the  $P^2M^2$  term in phenomenology. The second term is proportional to the dynamic magnetostriction coefficient  $D$ , the anomalous behavior of which, at structural transition, has been discussed earlier. Coefficient  $D$  is described by the following expression:

$$D = g_0 \sqrt{\frac{N}{C_0\Omega}} \frac{g^2\beta^2\gamma^2 H_x F_1}{C/C_0 [kTZ - (A - g_0^2)F]} \quad (19)$$

where  $A$  is the molecular field constant,  $g_0$  is the electron-strain interaction constant:

$$F_1 = \exp\left(-\frac{\Delta - W}{kT}\right) \left[ \sinh\frac{E_0}{kT} \left( \frac{1 - \bar{\sigma}_z}{E_0} + \frac{kTW}{E_0^3} \right) + 2\frac{W}{E_0^2} \cosh\frac{E_0}{kT} \right] \quad (20)$$

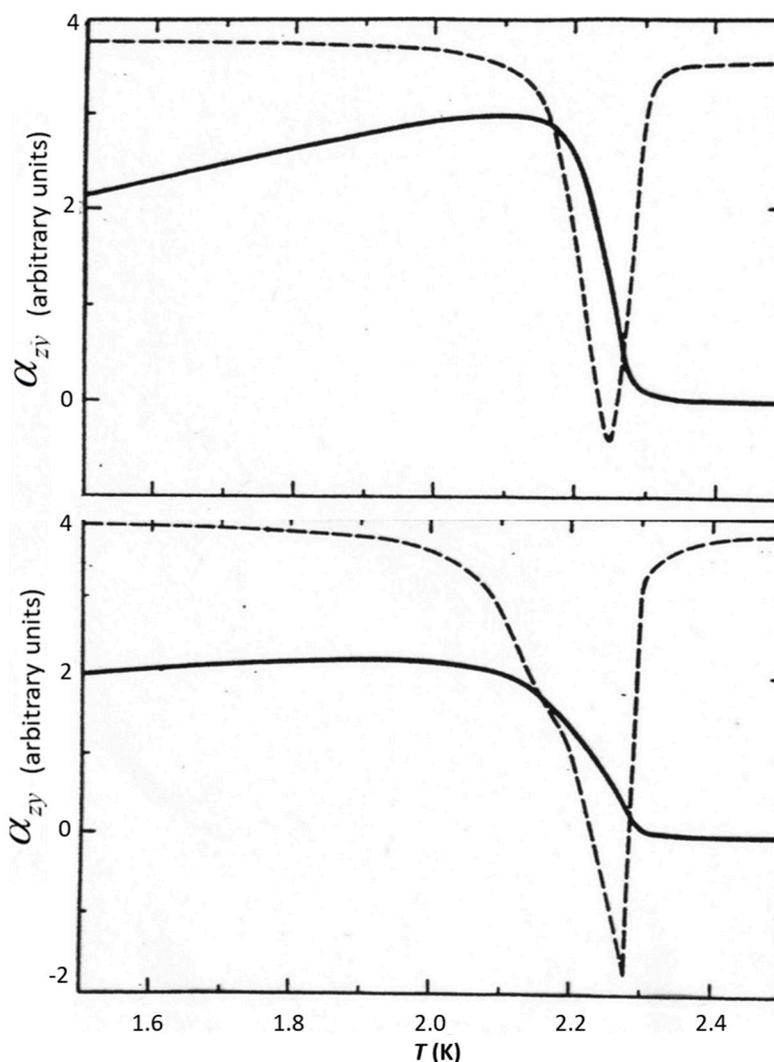
$$F = \exp\left(\frac{\Delta - W}{kT}\right) \left[ \cosh\frac{E_0}{kT} \left( 1 - 2\bar{\sigma}_z + \frac{W(\Delta + W)}{2E_0^2} \right) + \sinh\frac{E_0}{kT} \left( 2 + \frac{\Delta + W}{4E_0} - \bar{\sigma}_z \frac{\Delta + 4W}{2E_0} - 2\frac{E_0^2 + \frac{1}{4}W(\Delta + W)}{E_0^2} \right) \frac{kT}{E_0} \right] \quad (21)$$

So far, we have discussed the anomalous magnetoelectric effects in paramagnetic and paraelectric ferroelastics. On the other hand, anomalous striction is also possible in magnetic materials near the magnetic phase transition. Taking this into account, an especially large magnetoelectric effect could be expected in Jahn–Teller compounds with close or coinciding critical temperatures of structural and magnetic phase transitions. An example of such a ferroelastic is the  $\text{TbPO}_4$  crystal where a magnetoelectric effect of unusually large magnitude has been observed [13].

Terbium phosphate has a zircon crystal structure (group  $D_{4h}^{19}$ ). The unit cell contains two formula units, and the local symmetry  $D_{2d}$  of the  $\text{Tb}^{3+}$  ions has no inversion center [14]. At  $T_N = 2.28$  K, the magnetic phase transition to a collinear ( $\parallel$  to a four-fold C axis) double-sublattice antiferromagnetic structure takes place. A second phase transition occurs at  $T_s = 2.15$  K, where a monoclinic homogeneous strain occurs, and the magnetic moments deviate from the C axis [15–18]. As the local surrounding of  $\text{Tb}^{3+}$  ions has no inversion center, spontaneous monoclinic strain should produce an electric dipole—active distortion of this surrounding. The resulting dipole moments of different sublattices of ions lie in the base plane and are antiparallel, so that the ordered monoclinic phase is non-polar. Thus, the  $\text{TbPO}_4$  crystal is a Jahn–Teller multiferroic with coexisting elastic, magnetic and electric dipole orderings [19].

Using an approach typical for the theory of cooperative Jahn–Teller effect [11], the average polarization, the magnetic moment, and the magnetoelectric coefficients  $\alpha_{ij} = \partial M_i / \partial E_j$  were calculated. The calculation results for  $\alpha_{xy}$  and  $\alpha_{zy}$  were compared with the experimental data ([15,19] and Figure 1). It was shown that for all three temperature areas  $T < T_s$ ,  $T_s < T < T_N$ , and  $T > T_N$ , the theoretical and experimental results are in qualitative agreement. However, the agreement is not fully satisfactory. There are several possible reasons

for that. One of them may be related to an energy level structure of the  $\text{Tb}^{3+}$  ions that is more complicated than the one taken into account in the calculations (there are excited singlet levels that should be considered in addition to the lowest doublet-singlet states). The second reason is a quite complicated polydomain structure of the crystal samples used in the experiments.



**Figure 1.** Magnetolectric coefficient  $\alpha_{zy}$  (solid line) and its derivative (dashed line) dependence upon temperature  $T$  [15]: top—experimental; bottom—theoretical.

Thus, within the framework of the microscopic approach based on the cooperative Jahn–Teller effect, the anomalously large magnetolectric effect in terbium phosphate is caused by (a) strong coupling of electrons and phonons, resulting in formation of local dipole moments (elastic and electric); (b) closeness of the critical temperatures of structural (simultaneous ferroelastic and antiferroelectric) and antiferromagnetic transitions; (c) softness of the crystal lattice caused by the ferroelastic transition.

### 3. Metamagnetolectricity in Jahn–Teller Elastics

The well-known phenomenon of metamagnetism refers to a sharp increase in the crystal magnetic moment with the increase of the external magnetic field, parallel to the easy magnetic axis of the crystal. This phenomenon is typical for antiferromagnets of the Ising type. In the framework of the cooperative Jahn–Teller effect, as the microscopic theory of structural phase transitions, those transitions are caused by the intersite interaction of

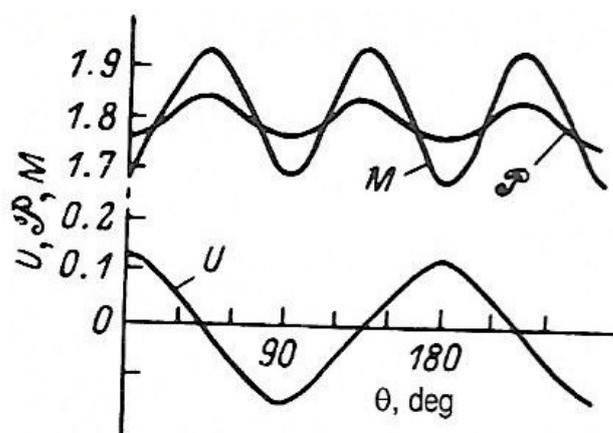
the Ising type between the local pseudo-spins. Since the average local pseudo-spin defines the local elastic dipole, it is expected that in antiferroelastics, a metaelasticity phenomenon similar to metamagnetism takes place. In other words, in antiferroelastics (this type of ordering is typical, for example, for some crystals with zircon or sheelite structure), the strain exhibits a strong nonlinear behavior as a function of external uniaxial pressure.

On the other hand, as it was mentioned above, the external magnetic field and external electric field can, at some orientation, create crystal (or crystal sublattice) strain with the same symmetry as that of the spontaneous strain. That means that this nonlinear dependence of the homogeneous strain (for antiferroelastics) or homogeneous polarization (for antiferroelectrics) could be induced by external magnetic or electric field. These phenomena may be called metamagnetoelasticity and metaelectroelasticity (for antiferroelastics) or metamagnetoelasticity (for antiferroelectrics) correspondingly.

It is clear that the variety of physics phenomena related to the overturn of a crystal sublattice dipoles is much richer for elastics than for magnets. This is connected not only to the variety of the external fields—uniaxial pressure, magnetic, electric. It is also due to the possibility of a sharp decrease (not only of an increase) of the average moment caused by the change of the corresponding external field.

In order to illustrate the metamagnetoelastic phenomena, we will discuss the dependence of electric polarization upon orientation of the external magnetic field in the base crystal plane. As an example, we will analyze antiferroelastics with a zircon structure where a Jahn–Teller ion is characterized by two Kramers doublets, separated by a small gap. We assume that the intersite interactions support a two-sublattice antiferrodistortive structure at  $T < T_s$ . Since the crystals under discussion are centrosymmetric at  $T > T_s$ , the ordered phase is ferroelectric. This means that, in these crystals, the interaction of electrons with polarization  $P$  is bigger than with the homogeneous strain  $U$ . In the real, not hypothetical,  $\text{DyVO}_4$  crystal with the same structure that is described above, the ferroelastic antiferroelectric ordering takes place at  $T < T_s$ . However, in the large enough external electric field, the ferroelectric antiferroelastic phase can be induced [11].

The external magnetic field oriented perpendicularly to the  $C_4$  crystal axis ( $H \parallel [100]$  or  $[010]$ ) creates spontaneous strain (magnetostriction), and at some critical value, overturns the sublattice of the electric dipoles transferring crystal into the ferroelastic antiferroelectric phase. This is what is suggested to call metamagnetoelasticity. If the angle  $\theta$  is the angle between the magnetic field  $H$  and the crystal  $[100]$  axis in the crystal base plane, the dependence of the electric polarization (together with the induced magnetic moment and the homogeneous strain) upon the angle  $\theta$  is shown in Figure 2 for antiferroelastic ferroelectric crystal.



**Figure 2.** Dependence of the uniform polarization  $P$ , strain  $U$ , and magnetic moment  $M$  upon the angle between the external magnetic field and the crystal axis  $[100]$  in the antiferroelastic phase [20,21].

It is clear from Figure 2 that the electric polarization is linearly proportional to the magnetic field, while the homogeneous strain is quadratic in  $H$  according to the magnetostriction of the nonmagnetic materials. Changing the angle  $\theta$  from  $90^\circ$  to  $180^\circ$  changes the sign of the orthorhombic strain as the stabilized and inverted sublattices exchange places.

Another example of metamagnetolectricity is related to reorientational structural phase transitions. It is known that in Jahn–Teller elastics, several (two or more) crystal states with different orientation of the order parameter—homogeneous strain—are possible. This happens in polydomain samples or in single domain crystal when uniaxial pressure and external magnetic or electric fields stabilize states with different (e.g., of opposite sign) order parameters. Monodomenization of Jahn–Teller crystals at  $T < T_s$  by external magnetic field was studied in [14,22]. The overturn of the elastic domain happens due to magnetostriction at large enough magnetic fields.

Sometimes, the reorientational phase transition occurs in single domain crystal that is not only a ferroelastic, but also an antiferroelectric (such as the  $\text{DyVO}_4$  crystal discussed above) or a ferroelectric. Accordingly, unique dielectric anomalies should be experimentally observed at a reorientational transition induced by external magnetic field.

In the presence of a pressure  $P$  of  $B_{1g}(\text{D}_{4h})$  symmetry, a magnetic field  $H$ , and an electric field  $E \parallel 0Z$ , the free energy of the  $\text{DyVO}_4$  crystal can be written as:

$$F = \frac{1}{2}A(\overline{\sigma_z^I}^2 + \overline{\sigma_z^{II}}^2) + B\overline{\sigma_z^I}\overline{\sigma_z^{II}} - kT \ln(Z_I Z_{II}), \quad (22)$$

where  $A$  and  $B$  are the molecular field constants of the intersite electron interactions inside the crystal sublattices I and II and between them:

$$Z_\alpha = 2[\exp(-\frac{h}{2kT}f_1) \cosh \frac{E_\alpha^-}{kT} + \exp(\frac{h}{2kT}) \cosh \frac{E_\alpha^+}{kT}], \quad (23)$$

$$E_\alpha^\pm = 2[(H_{mol}^\alpha \pm \frac{h}{2}f_2)^2 + \Delta^2\gamma^2]^{1/2}, \quad h \equiv g\beta H, \quad (24)$$

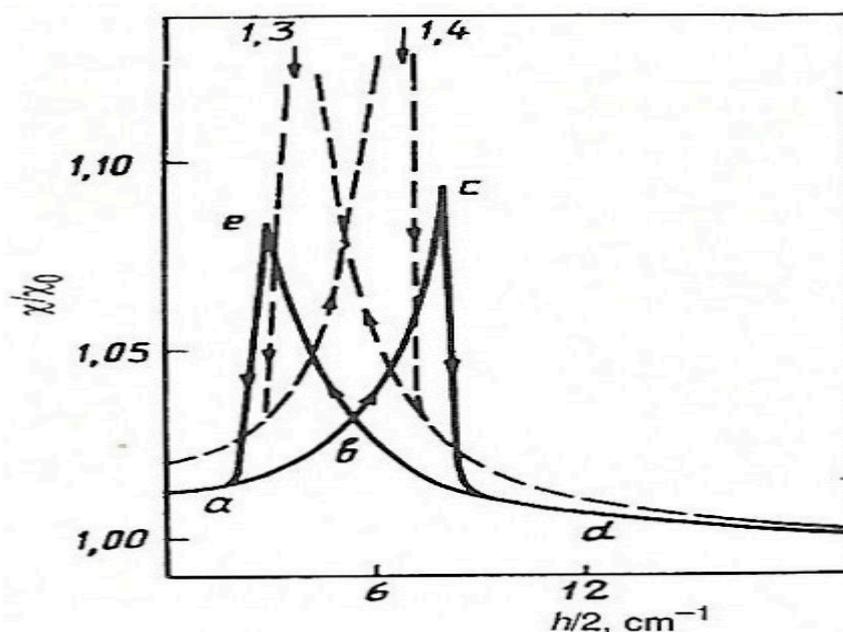
$$H_{mol}^\alpha = A\overline{\sigma_z^\alpha} + B\overline{\sigma_z^\alpha} \pm f\chi_0\epsilon_z + g_0P(C_0\Omega N)^{-1/2} \quad (25)$$

$$f_{1,2} \equiv f_{1,2}(\theta, \varphi) = \sin\theta(\cos\varphi \pm \sin\varphi). \quad (26)$$

Angles  $\theta$  and  $\varphi$  define the orientation of the magnetic field; I and II are indexes of the crystal sublattice.

In the ordered state of the  $\text{DyVO}_4$  crystal, each unit cell has two antiparallel electric dipole moments  $d_I \sim \overline{\sigma_z^I}$  and  $d_{II} \sim -\overline{\sigma_z^{II}}$  oriented along the crystal  $c$ -axis. Clearly, if the magnetic field changes the sign of the crystal strain, the field-induced inversion of the elastic dipoles is, at the same time, the inversion of the electric dipole moments of both sublattices. Thus, a phase transition of the antiferroelectric-type takes place [23]. The influence of the magnetic field on the dielectric susceptibility at such a transition is shown in Figure 3. The variation of  $\chi$  corresponds to curve abcd in an increasing magnetic field and to curve dbea in a decreasing field. If the field varies sufficiently slowly, hysteresis does not occur, and the behavior of  $\chi(H)$  is described by curve abcd. It should be noted that, in this case, the magnitude of the anomaly is smaller than in transitions from metastable states, but still noticeable ( $\approx 8\%$ ).

Figure 3 also shows a similar magnetolectric effect in the presence of the external electric field (dashed lines). In this case, the anomaly magnitude is much larger, which could be expected. In the presence of the external electric field  $E(A_{2u}(\text{D}_{4h}))$ , the ferroelastic antiferroelectric  $\text{DyVO}_4$  crystal transfers to antiferroelastic ferroelectric state. Naturally, the magnetolectric anomalies in ferroelectrics are much more significant than in the antiferroelectric crystals.



**Figure 3.** The dependence of the dielectric susceptibility of a  $\text{DyVO}_4$  crystal upon the external magnetic field at the reorientation transitions for electric field  $E_z = 0$  (solid curves) and  $f\chi_0 E_z = 4 \text{ cm}^{-1}$  (dashed lines),  $f^2 = 2.1 \text{ cm}^{-1}$ ,  $A = 3.9 \text{ cm}^{-1}$ ,  $B = 7.2 \text{ cm}^{-1}$ .

#### 4. Formation of Jahn–Teller Multiferroics

The Jahn–Teller crystals are compounds that contain at least one sublattice of ions, molecules, or structural units with orbitally degenerate or pseudodegenerate electronic states. The interaction of electrons with local vibrations of their surrounding leads to the formation of local elastic dipoles. These elastic dipoles become ordered at some temperature  $T$  below critical temperature  $T_s$ . In other words, due to the virtual phonon exchange, a structural phase transition takes place—cooperative Jahn–Teller effect. In structural units with a center of inversion, the odd vibrations could create an elastic dipole that is, at the same time, an electric dipole, if the electron pseudo-degeneracy takes place [24]. If the center of inversion is absent in the local symmetry of the crystal, the vibrations could still form an electric dipole moment, even in the case of degenerate electronic state due to piezoelectric effect [25]. This means that in Jahn–Teller crystals, the state with the ordered elastic dipoles could be, at the same time, a state with the ordered electric dipoles. Examples of such a system were discussed above. On the other hand, as it was shown in [26], if the local crystal site is characterized by the absence of time inversion symmetry and center of inversion, local distortion could create a vibronic magnetic moment due to piezomagnetic effect. (More accurately speaking, the vibronic interaction forms a new component of the magnetic moment [26]).

In connection with that, other local moments that could be ordered at a phase transition, should be mentioned—these are toroidal moments. One of the possible definitions of a toroidal moment through the electrical dipole  $\vec{d}$  and magnetic dipole  $\vec{M}$  is:

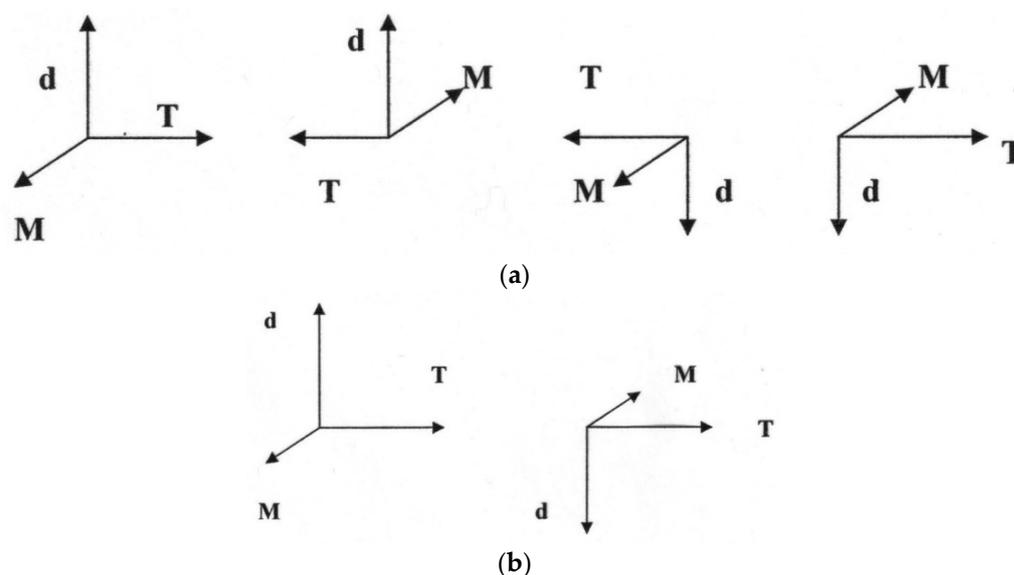
$$\vec{T} = \vec{d} \times \vec{M}. \quad (27)$$

As it was shown earlier, the coexistence of elastic and electric dipole orderings in Jahn–Teller crystals with the center of space inversion requires the presence of at least two sublattices. In the ferroelastic crystal state, the two sublattices differ by the orientation of the electric dipole moments so that the total crystal polarization is zero. For the antiferroelastics, the same two sublattices are characterized by different orientation of the elastic dipole moments ( $U_{\text{tot}} = 0$ ) and not-zero total crystal polarization  $P$ . If, in addition to the elastic

and electric dipoles, the magnetic moments are ordered, the crystal lattice could be divided in two or four sublattices.

Correspondingly, the toroidal moments in each of the sublattices could be oriented differently [6].

In Figure 4a, each of the electric dipole sublattices is divided in two others with antiparallel toroidal moments. At the same time, in Figure 4b, a ferrotoroidal ordering with antiparallel dipole moments ordering is shown.



**Figure 4.** (a) Antiferrotoroidal ordering in a four sublattice crystal; (b) Ferrotoroidal ordering in a two sublattice crystal.

As a rule, the toroidality of crystals is connected with their chirality—a property extremely important for many applications in physics, chemistry, and biology.

In conclusion, the Jahn–Teller elastics represent a class of materials promising for research of multiferroics. In Jahn–Teller multiferroics, the magnetoelectric effects are large because of strong electron-phonon interaction and soft crystal lattice. The microscopic theory of magnetoelectricity in these materials is described in the framework of the cooperative Jahn–Teller effect theory.

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