Magnetostriction of crystals exhibiting the cooperative Jahn-Teller effect

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A study is made of the anomalies in the magnetoelastic properties of Jahn-Teller crystals. It is shown that elastics, like magnets and ferroelectrics, can have anomalously large striction effects. The interplay of the distortional and magnetic correlations in the thermodynamic properties is examined, and it is shown that the correlation of the local Jahn-Teller distortions in magnets is basic to the underlying microscopic mechanism for the "compressible" Ising model.

1. Jahn-Teller crystals are of great interest as systems having a known microscopic mechanism for structural phase transitions (see, e.g., Ref. 1). This mechanism is the correlation of the local Jahn-Teller distortions due to the exchange of virtual phonons. However, these crystals are also of more general interest as compounds exhibiting a number of somewhat unusual properties, which are due to the strong coupling of the electrons with the lattice. A consequence of this coupling is that it is possible to effectively influence the lattice by acting on the electronic subsystem: In Jahn-Teller crystals the responses of the lattice to influence acting on the electrons are extremely strong. In other words, Jahn-Teller crystals are expected to exhibit strong striction effects.

The study of striction effects in solids and the search for materials having anomalously large striction coefficients is an important scientific and practical problem which has drawn many investigators (see, e.g., Ref. 2). Traditionally, the search for crystals exhibiting a large magnetostriction is focused on magnetically ordered systems, while large electrostriction effects are expected in crystals which lack a center of inversion, primarily in ferroelectrics. These systems are chosen because they can be influenced effectively by external fields, i.e., magnetic and electric fields acting on the magnetic and dipole subsystems of the crystal. It is quite clear, however, that in terms of striction effects a large elastic susceptibility is just as important as a large magnetic or dielectric susceptibility. From this standpoint elastics—compounds with structural phase transitions—are no less promising than magnets or ferroelectrics, particularly since for such substances one can have large magnetostriction and electrostriction interactions in the same compound.

Large striction effects should clearly be expected in crystals for which an external field acts effectively on the electronic subsystem, which, in turn, is strongly coupled to the lattice. Striction effects are due to the mixing of electronic states by the (magnetic or electric) field. The new electronic state dictates a new equilibrium configuration of the nuclei, and the crystal deforms as a result. It is clear that large striction coefficients are characteristic for systems with closely spaced (or degenerate) electronic levels (so that they are mixed significantly by the field), with large electron-vibrational coupling constants (so that the electroelastic and magnetoelastic forces are large), and with small elastic constants (so that the reconfiguration of the lattice is maximal). The first two of these conditions point to a Jahn-Teller situation, which would lead, through the cooperative Jahn-Teller effect, to (real or virtual) structural phase transitions. The softening of the elastic moduli, which is characteristic for structural phase transitions, indicates that the third condition for appreciable striction effects is also satisfied in Jahn-Teller crystals. If it is further considered that in a number of Jahn-Teller crystals there is evidence of a substantial influence of magnetic and electric fields on the electron-phonon states,[1] then it is obviously promising to search among Jahn-Teller compounds for crystals with anomalously large striction.

As we know, situations involving electronic degeneracy require special study, but there have been practically no studies of striction effects from this point of view (several particular cases have been studied in Refs. 3–8). In what follows we state the main features of striction effects in Jahn-Teller crystals and illustrate them with concrete examples.

2. Let us consider tetragonal crystals having a singlet-doublet-singlet scheme for the lowest levels. The choice of such a system is motivated, on the one hand, by the fact that a rather large number of crystals of this class have been investigated in detail.[1] It is also important that this level scheme admits various physical situations[9]: 1) for $\Delta > 1.2A$, as in $TmPO_4$, there is no structural phase transition; 2) for $\Delta < A$, as in $TbVO_4$, there is a single phase transition to an orthorhombic phase; 3) for $A < \Delta < 1.2A$, as in the solutions $Tb_{1-x}Gd_xVO_4$, there are two closely spaced phase transitions. In these relations we have used the standard notation in which A is a parameter characterizing the molecular field due to the correlation of the distortions and Δ is the energy gap between the doublet and singlet states of the rare earth ion. The Hamiltonian of our system is of the form[10,11]

$$H=-\sum_{mn}A_{mn}\sigma_z^n\sigma_z^m-\frac{\Delta}{2}\sum_m(1+\tau_z^m)\sigma_x^m-g_\perp\beta\sum_m(H_xS_x^m+H_yS_y^m), \quad (1)$$

where the first term describes the intersite interaction due to the exchange of virtual phonons and the electron-strain coupling, and the second and third term are, respectively, the crystalline field and the Zeeman interaction (with allowance for the fact that $g_\perp \gg g_\parallel \approx 0$ in the systems under study).

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In a singlet-doublet-singlet electronic basis the matrices for τ, S, and σ are of the form

$$\frac{1}{2}(1+\tau_z)\,\sigma_x=\begin{pmatrix}0&0&1&0\\0&0&0&0\\1&0&0&0\\0&0&0&0\end{pmatrix},\quad S_x=\begin{pmatrix}0&i&0&0\\-i&0&0&0\\0&0&0&0\\0&0&0&0\end{pmatrix},$$

$$S_y=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&0&-i\\0&0&i&0\end{pmatrix},\quad \sigma_z=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}. \qquad (2)$$

The strain U and magnetic moment M of the crystal are proportional to the mean values $\bar{\sigma}_z$ and $\bar{S}$, respectively. In the absence of magnetic field at temperatures above the temperature T_c of the Jahn-Teller phase transition, the strain U is zero. One can easily see that an applied magnetic field will make $U\neq 0$ at all temperatures. For $H_x=H_y=0$, however, there is no striction (see Part 4), and we shall therefore assume that $\mathbf{H}\|\mathbf{x}$.

a) Let us begin with the crystal $TmPO_4$, for which $\Delta=30\ \text{cm}^{-1}$, $A=20\ \text{cm}^{-1}$, and $g=10$ (Ref. 12, 13). For $H_\perp=0$ the crystal remains tetragonal all the way down to 0 K, but the dip (though not to zero) that has been observed[12] in the temperature dependence of the elastic modulus C_{66} indicates that correlations of the local Jahn-Teller distortions of symmetry b_1 are actually present. These correlations also explain the anomalies (noted in Ref. 13) in the magnetic properties of the $TmPO_4$ crystals.[10,11] Let us find out which particular anomalies in the magnetostriction effects are due to the indicated correlations. Figure 1 shows the behavior of the electronic levels in a magnetic field as obtained numerically from Eq. (1) in the molecular field approximation both with ($A\neq 0$) and without ($A=0$) allowance for correlations. It is seen that the correlations split levels 2 and 3 and decrease the energies of levels 1 and 4. Figures 2 and 3 show the field dependence of the strain and magnetic moment. It is seen that allowance for correlations leads to a significant enhancement of the striction (compare the curves for $A\neq 0$ and $A=0$ in Fig. 2). In the field dependence of the magnetic moment, allowance for correlations gives rise to inflection points on the $M(H)$ curve. This nonlinearity is due to the following magnetostriction mechanism. The magnetic field

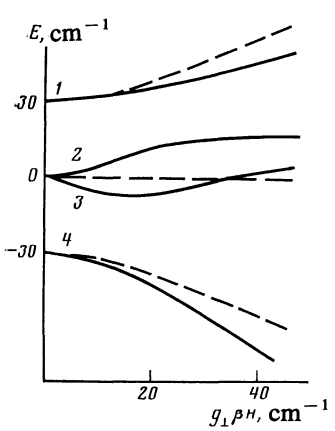

FIG. 1. Behavior, in a magnetic field, of the lowest levels of the Tm^{3+} ion in $TmPO_4$ (the dashed curves are for $A=0$, the solid for $A=20\ \text{cm}^{-1}$) at $kT=14\ \text{cm}^{-1}$.

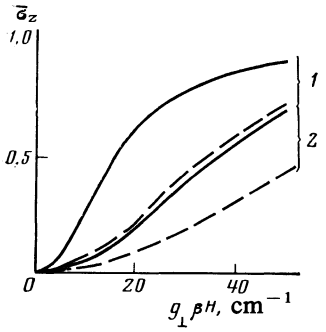

FIG. 2. Field dependence of the strain in $TmPO_4$: 1) $kT=14\ \text{cm}^{-1}$, 2) $kT=30\ \text{cm}^{-1}$. The dashed curves are for $A=0$, the solid for $A=20\ \text{cm}^{-1}$.

causes a strain which strengthens the correlation of the local distortions through the phonon field. This strengthening alters the electronic states of the site and the corresponding energies, increasing the resultant magnetic moment. It is seen from Figs. 2 and 3, which show this effect for two temperatures, that the influence of the correlations becomes weaker with increasing temperature. The influence of the correlations is maximum near $kT=14\ \text{cm}^{-1}$, i.e., in the region where the dip is observed on the temperature dependence of the elastic modulus C_{66}. It therefore seems worthwhile to ascertain whether the effect is anomalously large is crystals such as $TbVO_4$, which have a real structural phase transition (rather than a virtual transition, as in $TmPO_4$), at which the elastic modulus softens to zero. Let us now consider this new situation.

b) The $TbVO_4$ crystal ($\Delta=9\ \text{cm}^{-1}$, $A=25\ \text{cm}^{-1}$) undergoes a transition from the tetragonal phase to an orthorhombic phase at $T_c=34$ K.[9] The results of a numerical calculation of the field dependence of the strain show that the striction is small at both high and low temperatures. At $T\approx T_c$, however, the striction is large and correlation effects are appreciable. Near T_c there are anomalies (inflection points, etc.) in the magnetic moment which are analogous to those observed in $TmPO_4$.[13] Thus crystals of the $TbVO_4$ type, which have real phase transitions, are not as good strictors (except in a small region near T_c) as are virtual elastics such as $TmPO_4$. The reason for this is that a high temperature ($T>T_c$) the correlations are too weak, while at $T<T_c$

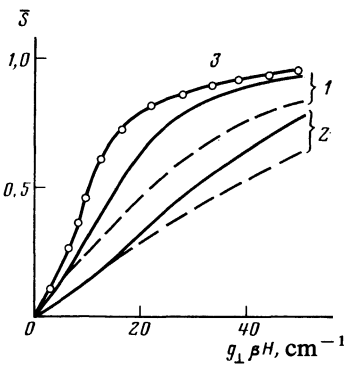

FIG. 3. Field dependence of the magnetic moment of $TmPO_4$: 2) $kT=14\ \text{cm}^{-1}$, 2) $kT=30\ \text{cm}^{-1}$, 3) $kT=3\ \text{cm}^{-1}$ (the points are experimental[13]).

they are too strong in comparison with the magnetic field. Large striction effects in comparatively weak fields at low temperatures, which do not smear out the correlations, should therefore be expected in Jahn-Teller crystals with values of A which are not too large. Of considerable interest in this regard are dilute crystals of terbium vanadate.

c) As we have said, crystals in which the ions of one of the sublattices have the singlet-doublet-singlet scheme for the lowest levels admit an interesting situation with two closely space phase transitions. If $A<\Delta<1.2A$, the crystal on cooling will, like $TbVO_4$, go first to an orthorhombic phase, but at low temperatures it will again be tetragonal. It has been shown[14] that the substitution of the non-Jahn-Teller ion Gd^{3+} for the Jahn-Teller ion Tb^{3+} in $TbVO_4$ leads to a weakening of the correlations and to a decrease in A, so that at Gd^{3+} concentrations $x\approx 0.6$ the above relation between A and Δ is satisfied. A calculation of the field dependence of $\bar{\sigma}_x$ and $\bar{S}$ for $A=8\ \mathrm{cm}^{-1}$ reveals the basic features of this situation: 1) the striction is considerably larger than in $TmPO_4$ and $TbVO_4$; 2) the temperature region ΔT in which the striction is anomalously large is rather wide ($\Delta T\sim T_c$).

There have been no direct measurements of the magnetostriction in the crystals considered above. It follows from our analysis, however, that the size of the striction is governed by the parameters of Hamiltonian (1), which have been reliably determined for these crystals from numerous ultrasound, optical, and magnetic experiments.[1] Therefore, our conclusions regarding the anomalously large magnetostriction, which were based on numerical calculations using these parameters, seem perfectly realistic. There is further support from the good quantitative agreement between theory and experiment (see Fig. 3) in the description of the nonlinear magnetic properties which stem from the magnetostriction in $TmPO_4$.[10]

Besides the crystals already considered, compounds with the singlet-doublet-singlet scheme for the lowest levels of the Jahn-Teller ion include $LiTmF_4$. This crystal does not have a structural phase transition, but the temperature curve of the elastic modulus does exhibit a dip due to the pronounced electron-phonon coupling.[15] Experiments[6] have actually detected an anomalously large ($\approx 10^{-4}$) magnetostriction. In $TmPO_4$ the experimentally observed[12] dip in $C_{66}(T)$ is considerably deeper than that observed in $LiTmF_4$, so vibronic effects and, consequently, the magnetostriction should be stronger in the thulium phosphate. The magnetostriction should be stronger still in $TbVO_4$ near T_c (see Part b) and in the mixed systems $Tb_{1-x}Gd_xVO_4$ (see Part c). Estimates show that in these crystals one can expect a giant magnetostriction $\sim 10^{-3}$–10^{-2} in saturating fields of the order of 50 kOe.

3. In Jahn-Teller crystals there is, in addition to the interaction through the phonon field, a direct magnetic interaction between ions, $J_{mn}S^mS^n$, with allowance for which Hamiltonian (1) becomes

$$H=-\sum_{mn}A_{mn}\sigma_z^n\sigma_z^m-\sum_{mn}J_{mn}(S_x^nS_x^m+S_y^nS_y^m)$$
$$-\frac{\Delta}{2}\sum_m(1+\tau_z^m)\sigma_x^m-g_\perp\beta\sum_m(H_xS_x^m+H_yS_y^m). \qquad (3)$$

In the rare earth compounds under study, the energy of the magnetic interaction is usually smaller than the quantity A which determines the correlation of the distortions. Nevertheless, for a quantitative comparison of theory and experiment, especially in the weak-field region, the magnetic interaction must be taken into account. For example, in a virtual elastic in a weak field the strain $U\sim\bar{\sigma}_z$, which is quadratic in the field, is small, and therefore the contributions of the terms JSS and $A\sigma\sigma$ can be of the same order for $J<A$ as well. A numerical calculation of the influence of magnetic correlations on the field dependence of the strain of a virtual elastic shows that the presence of magnetic correlations leads to appreciable changes in the magnetostriction: it increases for $J>0$ and decreases for $J<0$ on account of the strengthening (or weakening) of the correlations of the internal magnetic field.

The calculation also suggests a substantial influence of these correlations on the field dependence of the magnetic moment. For a ferromagnetic interaction ($J>0$) the inflection of the $S(H)$ curves[13] is much more pronounced than for $J=0$, while, on the other hand, antiferromagnetic interactions ($J<0$) decrease the inflection. These conclusions can also be reached on analytical grounds. In Refs. 10 and 11 an approximate formula was obtained for $\bar{S}(H)$ at $T=0$ K without allowance for magnetic correlations. An analogous treatment with allowance for magnetic correlations leads to the formula

$$\bar{S}=\frac{g_\perp\beta H+J\bar{S}}{[(g_\perp\beta H+J\bar{S})^2+\Delta^2]^{1/2}}+2A\frac{\Delta^2(g_\perp\beta H+J\bar{S})^3}{[(g_\perp\beta H+J\bar{S})^2+\Delta^2]^3}. \qquad (4)$$

The inflection of $\bar{S}(H)$ occurs at a positive coefficient K_3 of the H^3 terms in the expansion of $\bar{S}$ in powers of H. It is readily seen that a positive contribution to this coefficient can only come from the second term on the right-hand side of (4)—the term which arises when the correlation of the Jahn-Teller strains is taken into account. Allowance for magnetic correlations changes both the positive and negative contributions to K_3. This change is larger for the positive contribution and depends on the sign of J: for $J>0$ the positive contribution to K_3 increases (the inflection should consequently be more pronounced), while for $J<0$ the positive contribution decreases.

If the magnetic interactions are not small ($J>\Delta$), they themselves can cause a magnetic phase transition.[16] Because of the striction characteristic of Jahn-Teller crystals, the magnetic and structural ordering in them are coupled. Allowance for the intercoupling of the magnetic and distortional correlations, which are comparable in size, should therefore lead to distinctive features in the phase transitions which occur.

The magnetic interactions included in Hamiltonian (3) are isotropic in the xy plane. However, allowance for the electron-phonon interaction leads to an anisotropy which energetically favors an ordering of the magnetic moments along the x axis (see Part 2). Treating the intercenter interaction in the molecular field approximation, we rewrite Hamiltonian (3) for $H=0$ as

$$H=-A\bar{\sigma}_z\sigma_z-J\bar{S}_xS_x-{}^1/_2\Delta(1+\tau_z)\sigma_x. \qquad (5)$$

Let us begin our study of this Hamiltonian with the $\Delta = 0$ case, which admits an analytical treatment. We find from (5) that the energy levels in this case are described by the formulas

$$E_{1,2}=A\bar{\sigma}_z, \quad E_{3,4}=\pm J\bar{S}_x - A\bar{\sigma}_z,$$

from which we find the average values

$$\bar{\sigma}_z = \frac{\exp(A\bar{\sigma}_z/kT)\operatorname{ch}(J\bar{S}_x/kT) - \exp(-A\bar{\sigma}_z/kT)}{\exp(A\bar{\sigma}_z/kT)\operatorname{ch}(J\bar{S}_x/kT) + \exp(-A\bar{\sigma}_z/kT)},$$
$$\bar{S}_x = \operatorname{sh}\frac{J\bar{S}_x}{kT}\left[\operatorname{ch}\frac{J\bar{S}_x}{kT} + \exp\left(-\frac{2A\bar{\sigma}_z}{kT}\right)\right]^{-1}. \qquad (6)$$

Besides the trivial solution $\bar{\sigma}_z = \bar{S}_x = 0$, system (6) has a number of nonzero solutions depending on the relationship of the parameters A and J.

a) $A > J$, i.e., the interaction of the Jahn-Teller distortions is larger than the magnetic interaction. In this there can be two plase transitions in the crystal. The first, higher temperture, transition is a structural phase transition. Here the spontaneous strain of the crystal arises at a zero magnetic moment ($\bar{S}_x = 0$) and is determined by the equation

$$\bar{\sigma}_z = \operatorname{th}(A\bar{\sigma}_z/kT), \qquad (7)$$

which implies that $kT_c = A$. On further decrease in the temperature the strain is described, as before, by Eq. (7) until the magnetic phase transition occurs. The critical temperature of the magnetic transition is determined by the transcendental equation

$$kT_M = J\left[1+\exp\left(-\frac{2A\bar{\sigma}_z(T_M)}{kT_M}\right)\right]^{-1}. \qquad (8)$$

It can be seen from (8) that the correlations of the Jahn-Teller distortions have a substantial effect on the temperature of the magnetic transition-for $A \gg J$ we have $kT_M = J$, while for $A = 0$ (at which there is no structural transition) we have $kT_M = J/2$, i.e., structural correlations can double the temperature of the magnetic phase transition. System of equation (6) also implies that for $T \leqslant T_M$ the magnetic interaction increases the spontaneous strain. Thus, in the present case there can be two phase transitions; here correlations which lead to different phase states enhance each other, and the corresponding phases (for $T \leqslant T_M$) can coexist (see curves 1 and 2 in Figs. 4 and 5). Such a situation is realized in the crystals $TbVO_4$ and $TbAsO_4$.

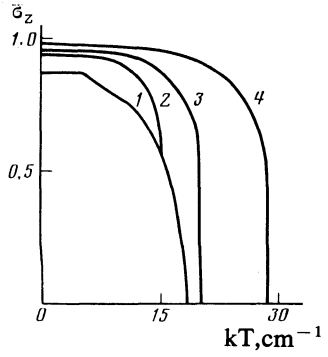

FIG. 4. Temperature dependence of the strain for $A = 20$ cm^{-1}, $\Delta = 15$ cm^{-1} (curves 1, 2, 3, 4 correspond to $j = 10, 20, 30, 50$ cm^{-1}).

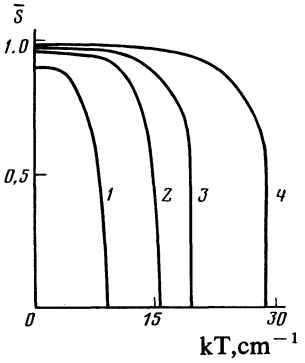

FIG. 5. Temperature dependence of the magnetic moment (the parameters are the same as in Fig. 4).

b) $J > A$, i.e., the magnetic interactions are stronger than the virtual-phonon exchange. In this case the mutual influence of the correlations under study is particularly clear. Analysis of system of equations (6) shows that only one phase transition can occur in the crystal. In fact, it follows from (6) that for $\bar{S}_x \neq 0$ we must have $\bar{\sigma}_z \neq 0$, i.e., spontaneous magnetization induces a homogenous strain regardless of the value of A. For example, $\bar{\sigma}_z$ is given for $A = 0$ by the relation

$$\bar{\sigma}_z = \left[\operatorname{ch}\frac{J\bar{S}_x}{kT} - 1\right]\left[\operatorname{ch}\frac{J\bar{S}_x}{kT} + 1\right]^{-1}, \qquad (9)$$

from which we see that $\bar{\sigma}_z \sim \bar{S}_x^2$ in weak molecular magnetic fields, i.e., the magnetic ordering "smears out" the possible structural phase transition. Using this result and the equation for $\bar{S}_x$ from system (6), one can show that at sufficiently high temperatures, allowance for the Jahn-Teller correlations leads to a renormalization of the magnetic interaction parameter J. Here it is easily found that the change in this parameter, $\Delta J \sim A\bar{S}_x^2$, is of the same form as in the "compressible" Ising model (which gives a first-order transition)[17] and is governed by the correlations of the Jahn-Teller distortions (see curves 3 and 4 in Figs. 4 and 5). The electron-phonon interaction thus underlies the microscopic mechanism which accounts for the possibility of first-order magnetic phase transitions. The causes of this effect are discussed in the review by Nagaev[18] on the basis of model Hamiltonians, but they can apparently also be based on a consistent incorporation of the electron-phonon coupling, in analogy with what we have just done.

The case $J > A$, Δ has not been realized in any of the crystals with the singlet-doublet-singlet level structure that have been studied to date. Significant magnetic and distortional correlations of comparable size are realized in DySb, TbP, and TmCu. For a quantitative comparison of theory and experiment in these cases it must be taken into account that the structure of the energy level of the rare earth ions differs from the singlet-doublet-singlet structure, but the phase-transition features observed[19] in these compounds agree qualitatively with those obtained above.

c) $J \approx A$. In this situation it must be kept in mind that the accuracy of the molecular field method is different for the cases of structural and magnetic ordering. For structural phase transitions accompanied by homogeneous deforma-

tion of the crystal, the main contribution to the interaction of the local distortions comes from long-wavelength acoustic phonons. This is due to the large correlation length, owing to which the molecular field approximation turns out to be quite accurate. In the case of magnetic interactions, on the other hand, a more adequate treatment than the molecular field approximation will be given by the various cluster approximations, which take better account of the short-range forces. Because of the differences in the correlations lengths, the magnetic order parameter falls off more rapidly with increasing temperature. For this reason, if J is slightly larger than A it is possible to have a transition of the crystal from a low-temperature magnetic phase to an energetically favored high-temperature distortional (magnetically disordered) phase. Further increase in temperature will lead to a structural-order–magnetic-disorder phase transition, since the short-range magnetic correlations are stronger than the distortional correlations near the temperature of the structural transition. Quantitative treatment of this situation requires a numerical calculation of the temperature dependence of the magnetic order parameter in some sufficiently accurate cluster approximation. For the singlet-doublet-singlet systems under discussion this is an extremely difficult problem which we shall not solve here, since we know of no real objects in which the indicated relationship between A and J holds.

4. It is appropriate here to compare the above microscopic description of the striction with the results of a phenomenological approach. For a phenomenological description of striction effects in elastics the expression for the free energy

$$\Phi=\frac{1}{2}c_0(T)U^2+\frac{1}{4}c_1U^4-UP+\frac{M^2}{2\chi_0}-MH+\sum_{mn}\lambda_{mn}M^mU^n \tag{10}$$

must include mixed terms M^mU^n containing both the strain U and the magnetic moment M. The remaining terms on the right-hand side of (10) describe the elastic energy of the strained elastic ($c_1=\text{const}>0$, $c_0\sim T-T_c$), the interaction of the strain with the pressure P, the energy of the magnetized crystal, and the interaction of the magnetized crystal with the magnetic field. In paramagnets the exponent m should be even, i.e., the expansion should begin with $m=2$. The minimum value of n is determined by whether the square of the representation Γ_M according to which $\mathbf{M}$ transforms contains the representation Γ_U (in which case $n=1$) or Γ_U^2 ($n=2$). In the tetragonal crystals under consideration the components M_x and M_y transform according to the E representation, while the component M_z corresponds to the representation A_2 of the point group D_{4h} of the unit cell. Because $[E^2]=A_1+B_1+B_2$ and $A_2^2=A_1$, while the spontaneous strain U transforms according to the representation B_1, the free energy expansion is of the form

$$\Phi={}^1/_2c_0(T)U^2+{}^1/_4c_1U^4-UP$$
$$+M^2/2\chi_0-MH+\lambda_\perp U(M_x^2-M_y^2)+\lambda_\parallel U^2M_z^2. \tag{11}$$

The equilibrium values $\bar{M}$ and $\bar{U}$ of the magnetization and strain are determined from the conditions $\partial\Phi/\partial U=\partial\gamma/\partial M=0$. Replacing M by $M_0=\chi_0H$ and U by $U_0=(-c_0c_1^{-1})^{1/2}$ in the terms proportional to λ_{mn}, we obtain the following expressions for $\bar{U}$ and for the dynamic striction coefficients $D=\partial U/\partial H$ in the case $H\|z$:

$$\bar{U}=[(-c_0-2\lambda_\parallel\chi_0^2H^2)c_1^{-1}]^{1/2},\quad D=-4\lambda_\parallel\chi_0^2c_{ef}^{-1}H\bar{U}, \tag{12}$$

where the effective elastic modulus is given by

$$c_{ef}=(\partial U/\partial P)^{-1}=2c_1\bar{U}^2. \tag{13}$$

In fields $H\|x$ we obtain the stiction coefficient as

$$D=2\lambda_\perp\chi_0^2H(c_0+3c_1\bar{U}^2)^{-1} \tag{14}$$

It follows from (12) and (14) that the striction coefficients have a characteristic temperature dependence which is due to the temperature dependence of the spontaneous strain $\bar{U}$. In both cases ($H\|z$ and $H\perp z$) in the ordered phase of the crystal the striction increases on approach to T_c. For $H\|z$ the coefficient D is proportional to $(T-T_c')^{-1/2}$, where $T_c'=T_c-2\lambda_\parallel\chi_0^2H^2$, i.e., it diverges at $T\to T_c'$. For $H\perp z$ the maximum value of this coefficient is reached at $T\approx T_c$, and in weak magnetic fields this coefficient becomes anomalously large. The reason for the different behavior of the striction for $H\|z$ and $H\perp z$ is that in the first case the phase transition remains present in the field (and so the elastic modulus goes to zero as $T\to T_c'$), while in the second case the field "smears" the transition ($\bar{U}\neq0$ at all temperatures if $H_\perp\neq0$). Accordingly, the striction coefficient can diverge in fields $H\|z$, but it remains finite for $H\perp z$ (in the latter case the striction coefficient is larger for smaller values of the magnetic field, since the elastic modulus increases in a magnetic field).

It is easy to see that these conclusions of the phenomenological treatment agree qualitatively with the results of the microscopic description (the behavior in $H\perp z$ was considered above (in Part 2b) for $TbVO_4$; the case $H\|z$ was studied in Ref. 3 for $TmVO_4$). However, an approach based only on group-theoretical and phenomenological treatments does not establish the relative sizes of the constants λ_i and, accordingly, gives the most general description. An adequate estimate of both the absolute and relative values of the coefficients λ_i can be given, as we have seen, in the framework of our microscopic theory based on the cooperative Jahn-Teller effect. Importantly, the problem of the relationship between the constants λ_i can be solved without complicated computations, but only if one knows the response to a magnetic field of the lowest electronic levels which participate (through vibronic mixing) in the phase transition. For example, for the ion Tm^{3+} in tetragonal $TmVO_4$ it is known that its ground, non-Kramers doublet is not split in transverse fields ($g_\perp=0$). If follows immediately that in this compound $\lambda_\parallel\gg\lambda_\perp\approx0$. Conversely, in the singlet-doublet-singlet scheme of the Tb^{3+} ion in $TbVO_4$ we have $g_\perp\gg g_\parallel$, from which one can conclude that $\lambda_\perp\gg\lambda_\parallel$. In a number of cases the values of λ_i can be expressed analytically in terms of the constants of the microscopic theory. For example, writing the formula for the free energy for $\Delta=0$, in which case analytical expressions are known for the levels E_i (see Part 3), and expanding it in a series in the parameter σ, one easily finds that

$$\lambda_\perp=g_\perp^2\beta^2\chi_0^{-2}AK_0^{1/2}(g_0k^2T^2)^{-1}.$$

Here

$$c_0=A(1-A/kT)K_0g_0^{-2},\quad c_1=K_0^2A^4(4!k^3T^3g_0^4)^{-1},$$

where K_0 is the elastic modulus in the absence of electron-phonon coupling, and g_0 is the electron-strain coupling constant.

In an analogous way one can consider the features of magnetic transitions in elastics. Simultaneously incorporating both the magnetic correlations and the correlations of the local Jahn-Teller distortions, we obtain for the case $\Delta = 0$ the following free-energy expansion

$$\Phi=\frac{1}{2}J\left(1-\frac{J}{2kT}\right)S^2+\frac{J^4}{96k^3T^3}S^4+\frac{1}{2}A\left(1-\frac{A}{kT}\right)\sigma^2+\frac{A^4\sigma^4}{12k^3T^3}-\frac{AJ^2}{12k^2T^2}\sigma S^2. \quad (15)$$

It is easily shown that the last term in (15), by redefining the exchange integral ($J' - J \sim AS^2$), leads to the "compressible" Ising model, which for sufficiently large A (sufficiently strong electron-phonon interaction) gives a first-order phase transition.

5. In summary, on the basis of what we have said we can draw the following conclusions.

1) Jahn-Teller crystals, because of the substantial electron-phonon coupling and the anomalous "softening" of the lattice due to the correlation of the local distortions, are a class of compounds which can support a giant magnetostriction. The stated results of a numerical calculation imply that the coefficient of dynamic magnetostriction, which determines the effectiveness of the crystals for practical expoitation, can reach large values at comparatively low external magnetic fields.

2) The ranges of temperature and external magnetic field in which the anomalous striction occurs can be varied by changing the concentration of Jahn-Teller ions.

3) Of particular interest are the magnetoelastic properties of Jahn-Teller systems having substantial intercenter magnetic interactions. Such interactions can appreciably enhance the striction and the anomalies (due to the exchange of virtual phonons) in the nonlinear magnetic properties. These effects are manifested particularly clearly when the temperatures of the structural and magnetic phase transitions are close together.

4) We have shown that the correlations of the local Jahn-Teller distortions in magnets strengthen the "first-order" character of the anomalies at magnetic phase transitions and underlie the microscopic mechanism of the "compressible" Ising model.

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[1]T. Riste (ed.), Electron-Phonon Interactions and Phase Transitions, Plenum Press, New York (1977).
[2]K. P. Belov, G. I. Kataev, R. Z. Levitin, *et al.*, Usp. Fiz. Nauk **140,** 271 (1983) [Sov. Phys. Usp. **26,** 518 (1983)].
[3]B. G. Vekhter and M. D. Kaplan, Fiz. Tverd. Tela (Leningrad) **16,** 1630 (1974) [Sov. Phys. Solid State **16,** 1064 (1974)].
[4]P. J. Becker, Phys. Status Solidi B **74,** 285 (1976).
[5]S. I. Andronenko, A. N. Bazhan, I. A. Bondar', V. A. Ioffe, B. Z. Malkin, and L. P. Mezentseva, Fiz. Tverd. Tela (Leningrad) **25,** 423 (1983) [Sov. Phys. Solid State **25,** 239 (1983)].
[6]S. A. Al'tshuler, V. I. Krotov, and B. Z. Malkin, Pis'ma Zh. Eksp. Teor. Fiz. **32,** 232 (1980) [JETP Lett. **32,** 217 (1980)].
[7]B. G. Vekhter and M. D. Kaplan, in: Kooperativnye Yavleniya [Cooperative Phenomena], Valgus, Tallin (1983), p. 100.
[8]J. M. Bloch and D. Davidov, Phys. Rev. B **26,** 3631 (1982).
[9]R. J. Elliott, R. T. Harley, W. Hayes, and S. R. P. Smith, Proc. R. Soc. London Ser. A **238,** 217 (1972).
[10]M. D. Kaplan and V. G. Vekhter, J. Phys. C **21,** L197 (1983).
[11]V. A. Ioffe, S. N. Andronenko, A. N. Bazhan, *et al.*, Zh. Eksp. Teor. Fiz. **84,** 707 (1983) [Sov. Phys. JETP **57,** 408 (1983)].
[12]R. R. Harley and D. I. Manning, J. Phys. C **11,** L633 (1978).
[13]V. A. Ioffe, S. I. Andronenko, and I. A. Bondar', *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **34,** 586 (1981) [JETP Lett. **34,** 562 (1981)].
[14]R. T. Harley, W. Hayes, A. M. Perry, *et al.*, J. Phys. C **7,** 3145, (1974).
[15]F. L. Aukhadeev, R. Sh. Zhdanov, M. A. Teplov, and D. N. Terpilovskiĭ, Fiz. Tverd. Tela (Leningrad) **23,** 2225 (1981) [Sov. Phys. Solid State **23,** 1303 (1981)].
[16]V. I. Krotov, B. Z. Malkin, and A. A. Mitel'man, Fiz. Tverd. Tela (Leningrad) **24,** 542 (1982) [Sov. Phys. Solid State **24,** 305 (1982)].
[17]H. W. Capel, L. W. J. Den Ouden, and J. H. H. Perk, Physica A **95,** 371 (1979).
[18]E. L. Nagaev, Usp. Fiz. Nauk **136,** 61 (1982) [Sov. Phys. Usp. **25,** 31 (1982)].
[19]P. Morin and D. Schmitt, Phys. Rev. B **27,** 4412 (1983).

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