New effect of magnetic fields on structural phase transitions: stimulated cooperative Jahn-Teller effect

B. G. Vekhter, V. N. Golubev, and M. D. Kaplan
Institute of Chemistry, Academy of Sciences of the Moldavian SSR

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A new effect of a magnetic field on structural phase transitions is demonstrated in the particular cases of the Jahn-Teller crystals $Tb_xGd_{1-x}VO_4$ and $TmPO_4$. In particular, it is predicted that the field will raise the transition temperature, induce an internal phase, and give rise to an unusual magnetostriction.

The parameters of structural phase transitions which are caused by a cooperative Jahn-Teller effect may be significantly influenced by external fields because of an interaction of degenerate electron states of ions through the phonon field. The external fields will change the electron spectrum. Two types of manifestations of this influence are presently recognized. In case I (the suppression of a transition), the external fields

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split or shift electronic states in such a manner that local Jahn-Teller distortions are reduced. The consequence is a lowering of the transition temperature T_c, sometimes all the way to zero. This suppression of a structural transition by a magnetic field is seen in $TmVO_4$, for example.[1] In case II, the external field increases local distortions and causes a uniform deformation of the crystal, so that the phase transition becomes diffuse (the order parameter $\bar{\sigma}$ increases and becomes nonzero at all temperatures). This case of intensification occurs in $TbVO_4$, for example, at a magnetic field[2] $\vec{\mathscr{H}} \| [110]$.[2]

In the present letter we show that yet another situation is possible in Jahn-Teller crystals, a situation which is more complicated and more interesting. Specifically, the phase transition persists in an external field, but the temperature interval over which the ordered phase exists becomes wider (the field induces a structural phase transition). This case is illustrated in the example of the tetragonal dilute systems $Tb_x Gd_{1-x} VO_4$ and virtual elastics of the $TmPO_4$ type. In these compounds, a rare-earth ion has three lowest levels (a singlet, a doublet, and another singlet), which are well-separated from the other excited states.[1] Here cases I and II occur when magnetic fields are applied along the [001] and [110] directions, respectively. At first glance, it would appear that the effect of a field $\vec{\mathscr{H}} \| [100]$ would be analogous to that of $\mathscr{H}_z$: In each case, the first nonvanishing invariant of the magnetoelastic coupling is quadratic in both the magnetic field and the strain u, transforming in accordance with representation b_{2g} of the group D_{4h}. However, our analysis on the basis of an elementary theory reveals that in the case $\vec{\mathscr{H}} \| [100]$ the situation is different and considerably more complicated.

In the molecular-field approximation, the single-site Hamiltonian in the basis of the four lowest-lying states can be written[2]

$$H = \Delta\tau - A\bar{\sigma}\sigma_z - g_\perp \beta \mathscr{H} (S_x + S_y)/\sqrt{2},$$

$$\tau = \begin{pmatrix} 0&0&1&0 \\ 0&0&0&0 \\ 1&0&0&0 \\ 0&0&0&0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1&0&0&0 \\ 0&1&0&0 \\ 0&0&-1&0 \\ 0&0&0&-1 \end{pmatrix}, \quad S_x = \begin{pmatrix} 0&1&0&0 \\ 1&0&0&0 \\ 0&0&0&0 \\ 0&0&0&0 \end{pmatrix}, \quad S_y = \begin{pmatrix} 0&0&0&0 \\ 0&0&0&0 \\ 0&0&0&1 \\ 0&0&1&0 \end{pmatrix} \tag{1}$$

Here A is the constant of the molecular field which stems from the electron-phonon and electron-strain interactions; the parameters Δ determines the gap between the doublet and the singlets; $\vec{\mathscr{H}} \| [100]$; the x and y axis are rotated 45° from the a and b axes in the crystal; and the orthorhombic strain u is proportional to the order parameter $\bar{\sigma}$. The temperature dependence of $\bar{\sigma}$ has been calculated for various relations among Δ, A, and $\mathscr{H}$ (this point was first taken up in Ref. 3 for the case $\mathscr{H} = 0$). It turns out that the following situations are possible (Fig. 1). At $A/\Delta > 1$, there can be only a single phase transition in this system, regardless of the strength of the field. At $0.83 < A/\Delta < 1$, in fields $0 < \mathscr{H} < \mathscr{H}(AD)$ [$\mathscr{H}(AD)$ are the values of the fields on the curve AD], two phase transitions occur (an "internal" phase): As the temperature is lowered, the crystal initially (at T_{c2}) goes from a tetragonal phase to an orthorhombic phase. Later on (at T_{c1}) it returns to a tetragonal phase. At $0.73 < A/\Delta < 0.83$, in

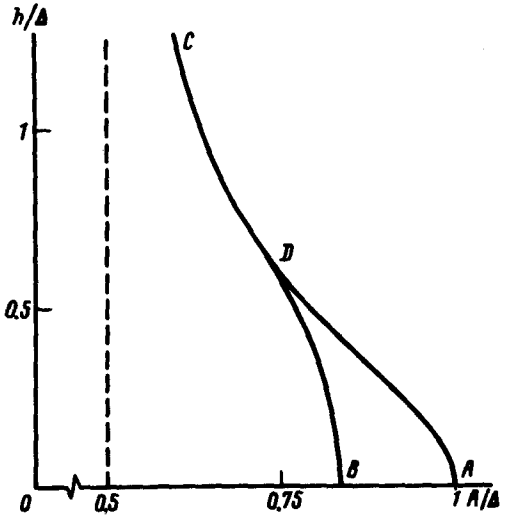

FIG. 1. Diagram of the various states in the plane of the magnetic field and the molecular field constant. $h = g_\perp \beta \mathscr{H}$; the vertical dashed line is the asymptote of curve *CD*.

fields $0 < \mathscr{H} < \mathscr{H}(BD)$, the crystal is in a tetragonal paraphase at all temperatures. At $\mathscr{H}(BD) < \mathscr{H} < \mathscr{H}(AD)$ there is an "internal" phase. Finally, at $\mathscr{H} > \mathscr{H}(AD)$, a single phase transition can occur in the system. In the case $0.5 < A/\Delta < 0.73$, curve *CD* separates regions with and without a single phase transition. Finally, at $A/\Delta < 0.5$ no phase transition occurs in any field. The calculations thus show that in the region $0.5 < A/\Delta < 1$ the magnetic field $\mathscr{H}$ can affect the electronic structure of the vibron levels. Depending on the strength of this field, the crystal may undergo a single phase transition, two phase transitions, or no phase transition. Such a radical effect of a magnetic field on the possible phase states should naturally lead to some specific anomalies in the field and temperature dependences of the properties of the crystals. The situation is seen most vividly in the magnetic-field dependence of the strain, for example, in the solution $Tb_{0.33}GD_{0.67}VO_4$, where $A/\Delta = 0.9$. This case corresponds to the presence of an internal phase (Fig. 2). The calculations show that with $\mathscr{H} = 0$ we

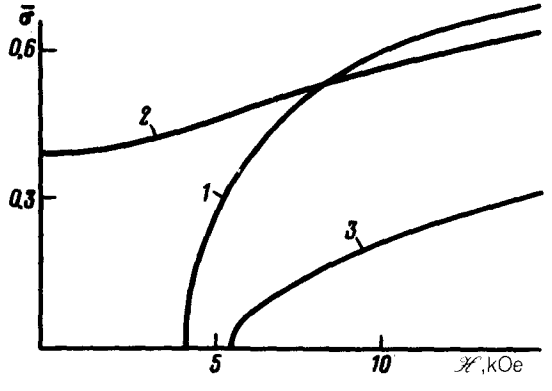

FIG. 2. Field dependence of the order parameter $\bar{\sigma}$. 1—2.1 K; 2—5.2 K; 3—8.3 K.

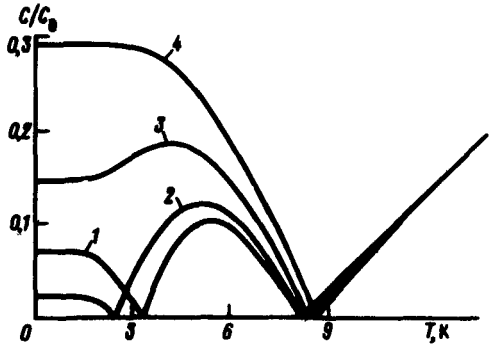

FIG. 3. Temperature dependence of the soft elastic modulus C_{66} ($C \equiv_{66}$; C_0 is the high-temperature value of C_{66}) in $Tb_{0.33}Gd_{0.67}VO_4$. Curves 1—4—fields $\mathscr{H} = 0$, 3.6, 7.1, and 10.7 kOe, respectively.

have $T_{c1} = 3.3$ K and $T_{c2} = 8.1$ K. As $\mathscr{H}$ is increased, the temperature interval in which this phase exists becomes wider: T_{c1} decreases, and T_{c2} increases. If we choose the temperature T outside this interval (curves 1 and 3), the strain appears in fields for which T is inside the interval $[T_{c1}(\mathscr{H}), T_{c2}(\mathscr{H})]$. Curve 2 corresponds to the case $T_{c1}(0) < T_2 < T_{2c2}(0)$. We wish to emphasize the fundamental distinction between ordinary magnetostriction, in which the field induces a strain directly, and the case at hand. In the case at hand, the role of the field is one of forming an electronic structure which is more favorable (than that with $\mathscr{H} = 0$) for the realization of a structural phase transition due to the cooperative Jahn-Teller effect. As a result, the behavior $u(\mathscr{H})$ is quite unusual (curves 1 and 3), as is the relative orientation of the field and the resulting strain [the axis of the strain (u) tensor makes an angle of 45° with the field].

In the course of structural transitions, the elastic modulus is known to have an anomalous temperature dependence, so that a change caused in the phase states of the crystal by a magnetic field should cause appreciable changes in this modulus. Curves 1–4 in Fig. 3 illustrate this change during the transition, during the imposition of a field, from a situation with an internal phase to the case of a single phase transition. If $A/\Delta < 0.73$, then no phase transition occurs at $\mathscr{H} = 0$, and the relation $C(T) > 0$ holds at all times. This is the situation in $TmPO_4$ ($A/\Delta = 0.67$), for example, where a phase transition is possible in sufficiently strong fields $\vec{\mathscr{H}} \| [100]$. This situation corresponds to the deepening, to $C = 0$, of the dip observed experimentally (at $\mathscr{H} = 0$)[4] on the $C(T)$ curve.

Numerical estimates show that the distinctive features in the field and temperature dependences of the properties of these systems occur in magnetic fields which are easily reached experimentally. For terbium vanadate solutions these fields are $\mathscr{H} \approx 10$ kOe; in thalium phosphate a phase transition occurs at stronger fields (~ 50 kOe); however, a significant effect of the field on the properties of $TmPO_4$ is seen even at $\mathscr{H} \approx 20$ kOe.

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