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Reentrant structural phase transitions induced by external magnetic fields in $Tm_xLu_{1-x}PO_4$ and $Tb_xY_{1-x}VO_4$ crystals

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In the framework of microscopic theory of structural phase transitions on the basis of the cooperative Jahn-Teller effect, the phase diagrams of the $Tm_xLu_{1-x}PO_4$ and $Tb_xY_{1-x}VO_4$ crystals under external magnetic fields are calculated. It is shown that depending upon the concentration of the Jahn-Teller ions and the value of the magnetic field one, two, or none of the phase transitions take place. The results are in agreement with the earlier suggested theory of the stimulated cooperative Jahn-Teller effect and the experimental data on the giant magnetostriction and Raman scattering.

The cooperative Jahn-Teller effect is one of the very few microscopic theories of structural phase transitions in condensed matter mostly developed for dielectric materials. Recently, a new impulse of interest to this approach has emerged in connection with microscopic mechanisms of phase transitions in high-temperature superconductors,[1,2] buckminsterfullerenes,[3,4] ferroelectrics,[5] and polymers.[6] In this situation, further development of the understanding of the phonon-mediated electron-electron correlations and of their unusual manifestations in the Jahn-Teller model systems is of general interest.

Some years ago the phenomenon of the stimulated cooperative Jahn-Teller effect was suggested and analyzed for pure and diluted crystals[7] and for mixed crystals.[8] On the basis of this phenomenon the magnetic-field-induced structural phase transitions were predicted. The mechanism of these transitions is connected with the reconstruction of the electronic spectrum by the external magnetic field. As a result of that the virtul phonon exchange between the Jahn-Teller ions becomes strong enough in comparison with the effective energy gap between the ground and the excited electronic states, so that structural phase transitions take place.

Such a structural phase transition, which was predicted, in part, for the $TmPO_4$ crystal in a magnetic field along the [100] axis ([100]$\|a$ axis) was recently observed in experiments on a giant magnetostriction[9] and Raman spectra.[10]

While much attention was paid in Refs. 7–11 to the discussion of the phase diagrams of the systems under consideration, no direct calculations of the critical temperature dependences upon the value of the external magnetic field were performed. However, it is clear that it is one of the most important questions for experimental observations of the phenomenon and for possible practical applications.

In this paper we discuss the results of such calculations for two groups of crystals, $Tm_xLu_{1-x}PO_4$ and $Tb_xY_{1-x}VO_4$. By diluting the Jahn-Teller $TmPO_4$ and $TbVO_4$ crystals with the non-Jahn-Teller Lu^{3+} and Y^{3+} ions we are able to change the ratio of the energy gap Δ between vibronically mixed electron states and the intersite electron-electron interaction parameter A for a wide range of values from $\Delta/A \gg 1$ (the $Tm_xLu_{1-x}PO_4$ crystal case at $x=0.1$) to $\Delta/A < 1$ (the $TbVO_4$ crystal case where the structural phase transition occurs even without the magnetic field). As a consequence of this, as shown below, a variety of phase diagram are possible for systems with the magnetic-field-induced structural transitions.

Taking into account the singlet-doublet-singlet structure of the lowest electronic states (which is qualitatively the same for the Tb^{3+} and Tm^{3+} ions in the zircon structure crystals), the Hamiltonian of the system under con-

sideration could be presented as

$$H=\Sigma A_{mn}s_z^m s_z^n-\Delta\Sigma\tau^m-g\beta H\Sigma(S_x^m+S_y^m)\ , \qquad (1)$$

where

$$A_{mn}=N^{-1}g_0^2\delta_{mn}+\Sigma(V_{m\kappa}^* V_{n\kappa}/h\omega_\kappa)\ ,$$

$$\sigma_z=\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{bmatrix},\quad \tau=\begin{bmatrix}0&0&1&0\\0&0&0&0\\1&0&0&0\\0&0&0&0\end{bmatrix},$$

$$S_x=\begin{bmatrix}0&1&0&0\\1&0&0&0\\0&0&0&0\\0&0&0&0\end{bmatrix},\quad S_y=\begin{bmatrix}0&0&0&0\\0&0&0&0\\0&0&0&1\\0&0&1&0\end{bmatrix}.$$

Here the constant of the molecular field

$$A=A(0)=g_0^2+2\Sigma V_{mk}^* V_{nk}(h\omega_k)^{-1}$$

caused by the electron-phonon (V) and electron-strain (g_0) interactions, the parameters Δ determine the gap between the doublet and the singlets [30 cm^{-1} for Tm^{3+} in $TmPO_4$ (Ref. 12) and 9 cm^{-1} for Tb^{3+} in $TbVO_4$ (Ref. 13)]. We would like to remind the reader that the systems under consideration are characterized by a very large correlation radius, which is why the molecular field approximation is good for both qualitative and quantitative analysis. Due to the small enough value of the vibronic constants, the vibronic reduction effects [14,5] are neglected. The magnetic field H is parallel to the [100] axis, so that the ordinary magnetostriction (proportional to H^2) is absent. (It is easy to show, using the symmetry group arguments, that the strain $U\sim\sigma_z\sim H^2$ if $H\|[110]$ only).

For the systems described by the Hamiltonian (1) the critical temperature of the possible structure phase transitions at $H=0$ is determined by the equation

$$A_0^{-1}=\{R_1^{-1}[1+h^2(1+h^2)^{-1/2}]\sinh(R_1/T_{c0})$$
$$+R_2^{-1}[1-h^2(1+h^2)^{-1/2}]\sinh(R_1/T_{c0})\}/\{\cosh(R_1/T_{c0})+\cosh(R_2/T_{c0})\} \qquad (2)$$
$$R_{1,2}=[1/2+1/4h^2\pm 1/2(1+h^2)^{1/2}]^{1/2}\ .$$

In the Eq. (2) all parameters are dimensionless

$$A_0=A/\Delta,\quad h=2^{1/2}h_0/\Delta,\quad T_{c0}=kT_c/\Delta\ , \qquad (3)$$
$$h_0=g\beta H,\quad H_x=H_y=H/2^{1/2}\ .$$

It is easy to show that at the absence of the magnetic field the critical temperature is determined by the equation

$$\Delta/A=[\sinh(\Delta/T_c)+\Delta/T_c]/[\cosh(\Delta/T_c)+1] \qquad (4)$$

discussed earlier.[15,16] As was shown in Ref. 15 using (4), at $\Delta/A<1$ the critical temperature $T_{c0}>0$ and the structural phase transition takes place as it is in the $TbVO_4$ crystal. At $1<\Delta/A<1.2$, two structural transitions (reentrant transitions) occur. Finally, when $\Delta/A>1.2$, no transitions are possible.

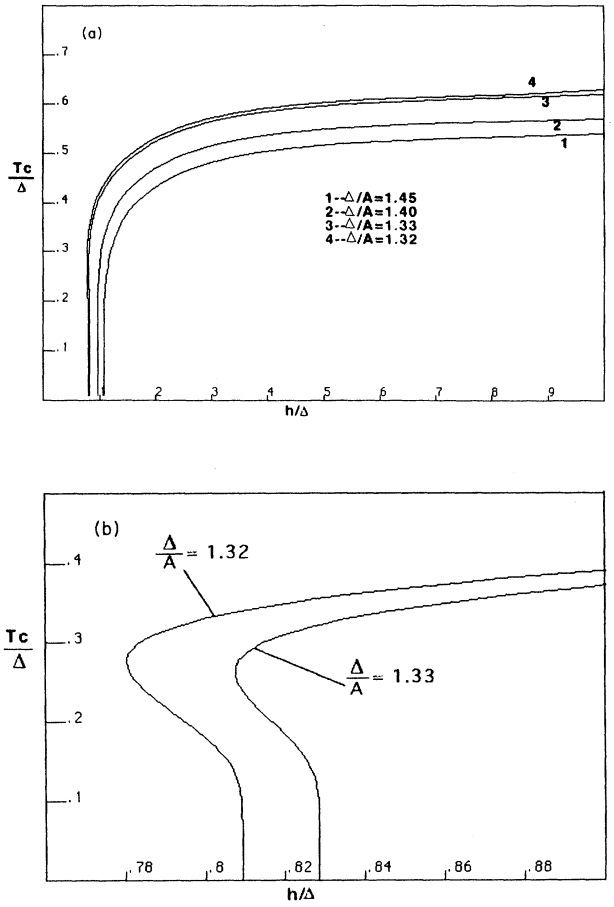

FIG. 1. (a) The dependence of the critical temperature of the structural phase transitions upon external magnetic field at different values of the Δ/A ratio. (b) The same for curves 3 and 4 at a smaller magnetic field scale.

The external magnetic field may drastically change the phase diagrams of the singlet-doublet-singlet systems as is found from Eq. (2). The results of numerical calculations are shown in Figs. 1 and 2.

One of the most important results of the influence of the magnetic field is that at some critical values it will induce the structural phase transition. The dependences of the critical temperatures upon the field for the different values of Δ/A are shown in Fig. 1. For the paraelastic systems ($\Delta/A>1$) T_c of the induced transitions increases mostly with the magnetic field value and is saturating at big fields. It can be shown from Eq. (2) that

$$T_c(h=\infty)=A\ .$$

This result is understandable as at very high magnetic

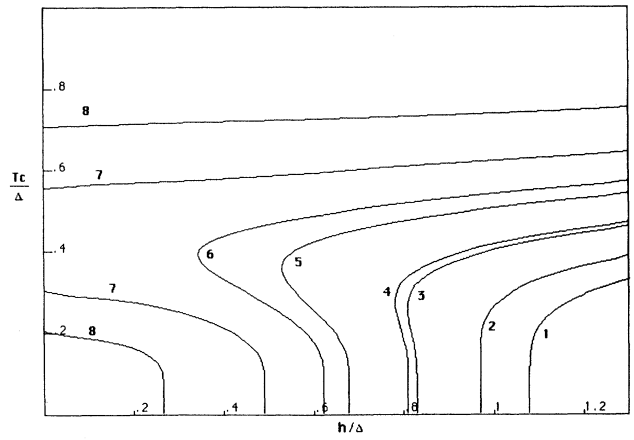

FIG. 2. Phase diagrams for the $Tm_xLu_{1-x}PO_4$ and $Tb_xY_{1-x}VO_4$ systems. Curves 1–7 correspond to $\Delta/A=1.45$; 1.40, 1.33; 1.32; 1.25; 1.22; 1.15; and 1.05.

fields the ground state of the Jahn-Teller ion becomes similar to an orbitally double degenerate state with vibronically mixed components. It is well known from the theory of the cooperative Jahn-Teller effect that the structure transition in such a system occurs at $T_c=A$.[13,17]

The most intriguing result of the magnetic field influence on the phase diagram of the crystals under consideration is shown in Fig. 2. Analysis of the Eq. (2) leads to the conclusion that for some range of Δ/A values the magnetic field induces a reentrant phase transition (a second transition from the low symmetrical to the high symmetrical phase at lowering the temperature). The $T_c(h)$ dependences have a "beak" that becomes sharp with the decrease of the energy gap to the electron-electron interaction ratio. When the Δ/A is smaller than 1.2 the "beak" becomes opened. That corresponds to a reentrant phase transition for this Δ/A value even at $H=0$, as is shown in Ref. 14.

It is necessary to note that the question about the number of possible structural phase transitions in the $TmPO_4$ type systems under magnetic field was discussed in Ref. 7. The results of our phase diagram calculations are in complete agreement with Ref. 7 on this point.

As was mentioned at the beginning of this paper, the magnetic-field induced structural transition in the $TmPO_4$ crystal at $H\|[100]$ was experimentally observed recently.[9,10] The experiments on giant magnetostriction were done at $T=4.2$ K, and the Raman scattering was observed at $T=13$, 15, and 19 K. While the data obtained in these experiments are not sufficient for detailed comparison with the $T_{c0}(h)$ theoretical dependences, they are in qualitative agreement with the theory.

The calculations of the "open beak" diagrams are of special interest. They show the difference between the ways the two critical temperatures change in the systems with the reentrant phase transition. The low-temperature structural transition is quickly reduced to zero with the increase of the magnetic field. But the critical temperature of the second (at higher temperatures) phase transition is slightly increased with H and is saturated at high magnetic fields.

In conclusion, we would like to note that all the diagrams discussed here should be experimentally observable in the diluted $Tm_xLu_{1-x}PO_4$ and $Tb_xY_{1-x}VO_4$ crystals. Both systems have a large radius of correlations. The molecular field parameter A can be changed under controlled conditions using different concentrations x of the Lu^{3+} and Y^{3+} ions. For example, curve 3 of Fig. 2 could be observed for the $TmPO_4$-based crystals and curve 1 of Fig. 1 could be observed for the $TbVO_4$ based systems. We expect that the "beak" behavior of $T_{c0}(h)$ dependence is easily observable in experiment. In fact, the anomalous increase of the critical temperature with a lowering of the magnetic field, for example, for $\Delta/A=1.32$, takes place at the change of $h/\Delta=0.04$. At $\Delta=30$ cm^{-1} it means that the change of the Zeeman energy is 1.2 cm^{-1} and correspondingly the change in the external field is approximately 2.5 kG ($H_0=4.5$ T). In this interval of 2.5 kG change in the magnetic field, the critical temperature will change from zero to 8 K.

Thus, in the framework of microscopic theory of structural phase transitions the influence of the external magnetic field on the phase diagrams is calculated. It is found that all varieties of the calculated diagrams may be experimentally observed for the $TmPO_4$ and $TbVO_4$ crystals under moderate magnetic fields.

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