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A GENERALIZED JAHN-TELLER STRUCTURAL PHASE TRANSITION DESCRIBED BY THE THOMAS-MÜLLER MODEL

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Consider a lattice of ions the three lowest states of which, a doublet and a singlet, are well separated from higher excited states. For the description of such a system Thomas and Müller have proposed the following pseudospin (with $S = 1$) Hamiltonian /1/

$$H = \sum_{\ell} H_{\ell}^{JT} - \frac{1}{2} \sum_{\ell\ell'}{}' \frac{1}{4} V_{\ell-\ell'} Q_{\ell} Q_{\ell'} , \tag{1}$$

where the Jahn-Teller tunneling part is given by

$$H_{\ell}^{JT} = -\frac{1}{2} \Omega \left[\sqrt{2}\, S_{x\ell} - \left(S_{x\ell}^{2} - S_{y\ell}^{2} \right) \right] , \tag{2}$$

and

$$Q_{\ell} \equiv 3 S_{z\ell}^{2} - 2 . \tag{3}$$

As will be shown, systems described by the Hamiltonian (1) undergo a phase transition in which energy doublets split with decreasing temperature (see Fig. 1).

Generally, we are dealing with three different cases:
(a) $\Omega > 0$,
with the ground-state doublet in the disordered region (Fig. 1a). This model describes a typical Jahn-Teller structural phase transition and has been studied for $\Omega \ll V$ in /1/ (where additional references may be found).
(b) $\Omega = 0$,
with the triplet in the high-temperature region (it was discussed, e.g., by Chen and Levy /2/).
(c) $\Omega < 0$,
with the doublet lying above the ground-state singlet and, therefore, not satisfying the commonly used definition of the Jahn-Teller effect.

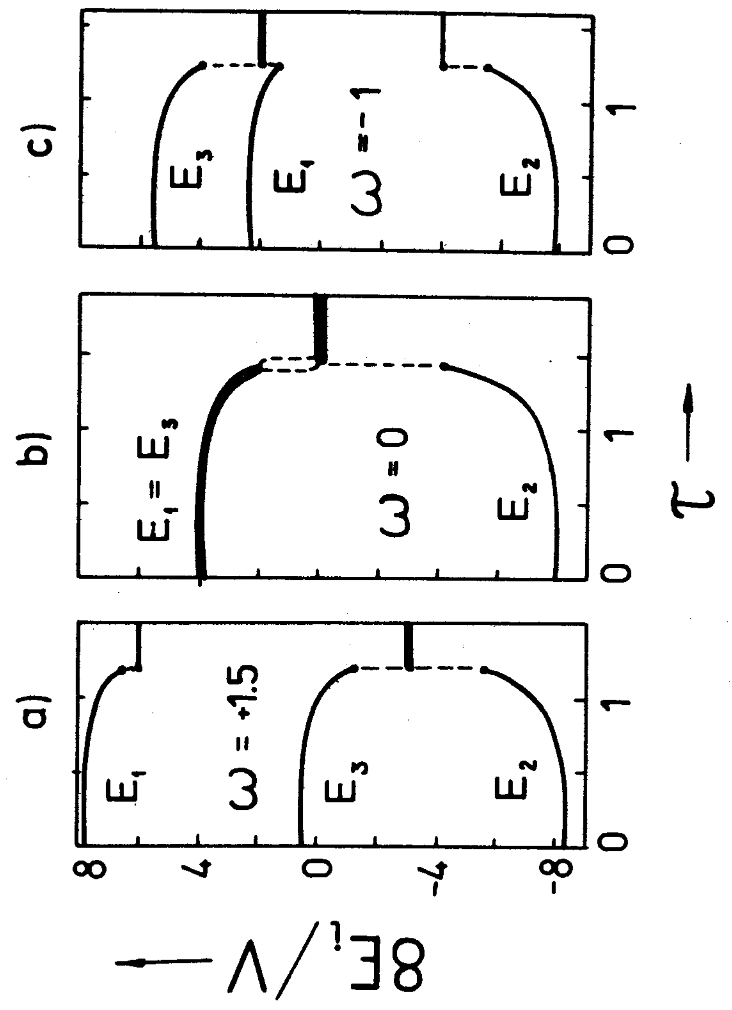

Fig. 1. The energy levels E_i vs temperature τ for three values of tunneling parameter: (a) $\omega = 1.5$, (b) $\omega = 0$, and (c) $\omega = -1$.

Nevertheless, because of the same physics (splitting of the energy terms which considerably contribute to the free energy of the system) we shall regard this case as a generalized Jahn-Teller structural phase transition.

The aim of the present work is to analyse all the cases, i.e., any sign and magnitude of Ω, and discuss the similarities and differences between them.

In this paper we confine ourselves to the zeroth approximation of the self-consistent method (the so-called mean field approximation). With that accuracy the energy levels of the Hamiltonian (1) are the following:

$$E_{1,2} = \frac{1}{8} V (\omega + Q \pm 3p) , \qquad E_3 = -\frac{1}{4} V (\omega + Q) \tag{4}$$

(see Fig. 1), where $V \equiv \sum_{\ell}' V_{\ell - \ell'}$ and, for abbreviation

$$p \equiv \sqrt{\omega^2 - \frac{2}{3} Q\omega + Q^2} .$$

In Eqs. (4) we introduced the order parameter

$$Q = \langle Q_\ell \rangle , \tag{5}$$

and the dimensionless tunneling parameter

$$\omega \equiv 2 \frac{\Omega}{V} . \tag{6}$$

In order to describe the thermodynamic properties of the system, one should calculate the free energy per particle, which for the investigated system is equal to $(\beta^{-1} = kT)$

$$F = \frac{1}{8} V Q^2 - \beta^{-1} \ln (e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3}) . \tag{7}$$

Rewritting it in the dimensionless form we obtain

$$\phi(Q,\tau;\omega) = Q^2 + Q + \omega - 3\tau\, \ell n\, [2\mathrm{ch}\, \frac{p}{\tau} + e^{\frac{\omega+Q}{\tau}}], \tag{8}$$

where the dimensionless free energy ϕ and temperature τ are defined as

$$\phi \equiv 8 \frac{F}{V}, \tag{9}$$

$$\tau \equiv \frac{8}{3} \frac{kT}{V}, \tag{10}$$

respectively.

The extremum condition, $(\partial F/\partial Q) = 0$, represents the equation describing the temperature dependence of the order parameter

$$Q = 1 - \frac{3\,\mathrm{ch}\,\frac{p}{\tau} + \frac{\omega - 3Q}{p}\,\mathrm{sh}\,\frac{p}{\tau}}{2\,\mathrm{ch}\,\frac{p}{\tau} + \exp\left(\frac{\omega+Q}{\tau}\right)}. \tag{11}$$

Figure 2 demonstrates this dependence for a set of different values of ω. The transition is of the first order as expected from symmetry. It is interesting that nontrivial solutions ($Q \neq 0$) of Eq. (11), describing the ordered phase, exist for all positive values of ω, while they disappear for negative ω less than $\omega_{ex} = -1.5225$.

For the fixed "material parameter" ω, the phase transition temperature τ_c is defined by the condition that the free energies in ordered and disordered phases become equal:

$$\phi(Q(\tau_c;\omega), \tau\ ;\omega) = \phi(0, \tau_c; \omega). \tag{12}$$

It is illustrated on Fig. (3a) for $\omega = 0$. The phase diagram calculated for the whole ω range is demonstrated on Fig. 4. It represents the curve given by Eq. (12) with the substituted Eq. (11). The limiting temperature τ_ℓ of the existence of the overcooled disordered phase is given by the simple equation (see the dashed line on) Fig. 4).

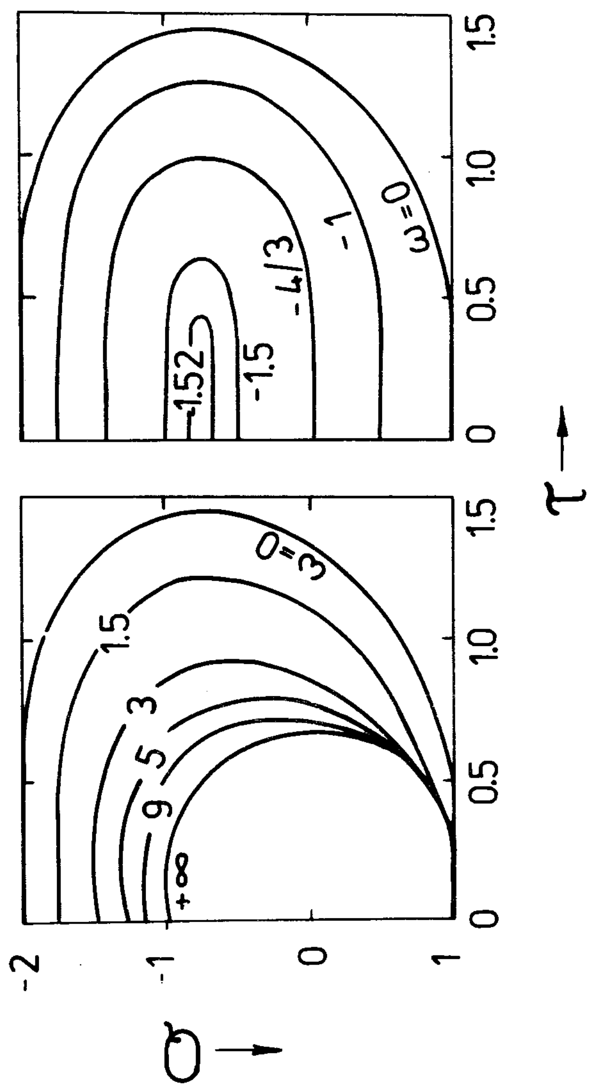

Fig. 2. Order parameter Q vs temperature τ for a set of values of tunneling parameter ω.

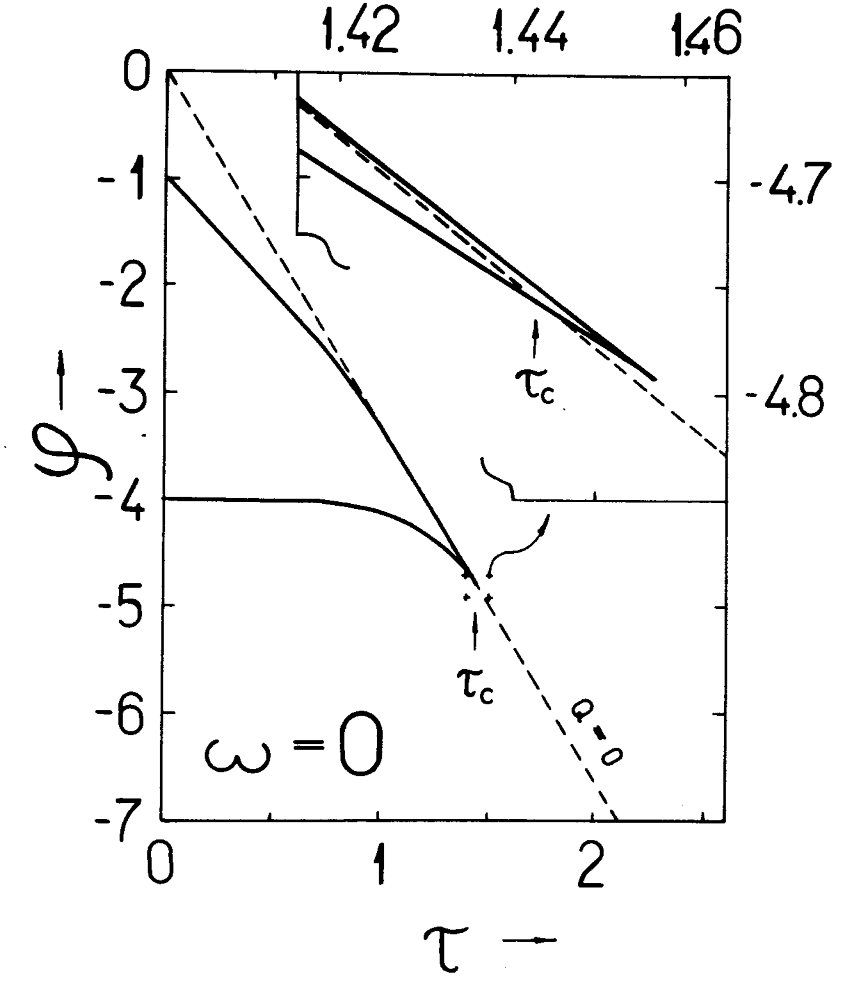

Fig. 3a. Free energies ϕ vs temperature τ for ordered (full line) and disordered (dashed line) phases at $\omega=0$. The lower point of intersection determines the critical temperature τ_c while the higher one - the stability limit of disordered phase (i.e., overcooling temperature); see also Fig. 4 and 5. The region close to τ_c is demonstrated on insert in magnification.

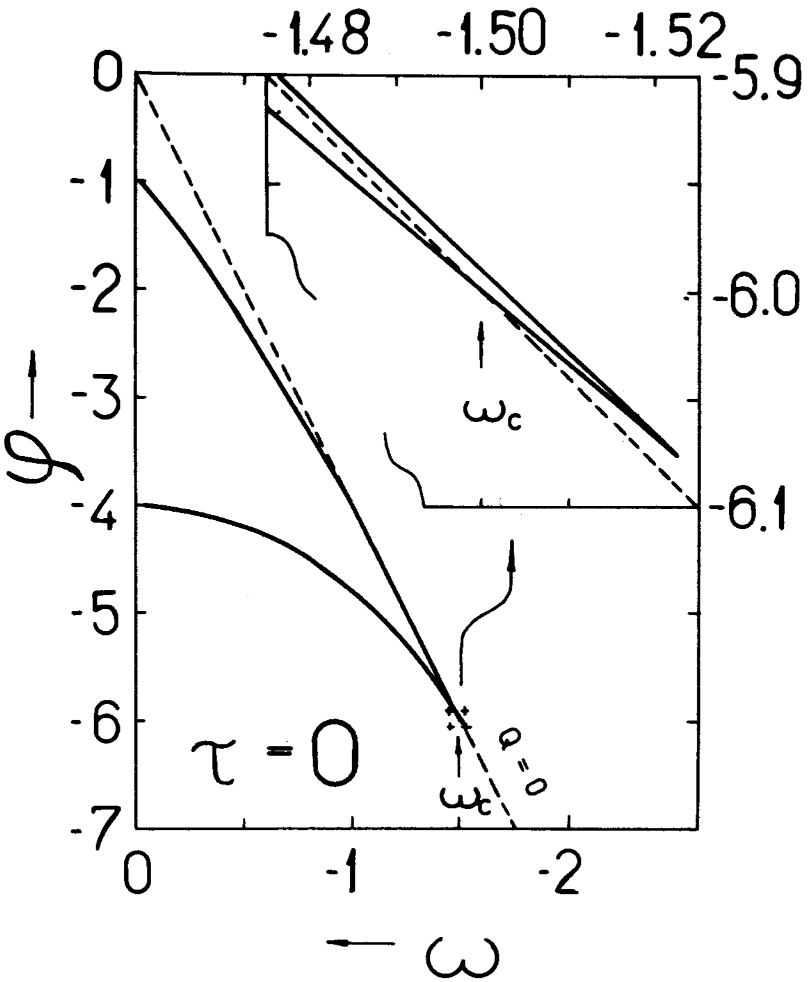

Fig. 3b. Free energies ϕ vs tunneling parameter ω for ordered (full line) and disordered (dashed line) phases at $\tau = 0$. The lower point of intersection determines the critical tunneling value ω_c. The region close to ω_c is demonstrated on insert in magnification.

$$\tau_\ell = \frac{4}{3}\,\frac{x^2(1+\ell n\ x)-1}{(2x^2+1)\ \ell n\ x}\ ,$$

$$x = \exp\left(\frac{\omega}{\tau_\ell}\right)\ ,$$

which gives the values $\tau_\ell = 2/3$ for $\omega \to \infty$, $\tau_\ell = 4/3$ for $\omega = 0$ and $\tau_\ell = 0$ for $\omega = \omega_\ell = -4/3$.

Figure 4 demonstrates an interesting feature of the discussed model; the region of the existence of the ordered phase is closed on the negative ω side ($\omega_c = -3/2$ for which $\tau_c = 0$), while it is opened for positive ω.

For the case (a) the phase transition can occur for any positive value of Ω, i.e., also for $\Omega \gg V$. The region $\Omega \gg V$ may be discussed in two ways. If the tunneling parameter Ω goes to infinity, for fixed value of interaction V, then there exists the temperature range $0 \leq T \leq T_c^\infty \equiv$ $\equiv V/4k$, where only ordered phase can exist. On the other hand, if interaction V goes to zero, when Ω is held fixed, then the critical temperature goes to zero proportionally to V, because according to (10)

$$T_c = \frac{3}{8k} V \tau_c\ .$$

In the opposite case (c) $\omega < 0$ there exists the critical value of the tunneling energy parameter $\omega_c = -3/2$. In the region $\omega_{ex} < \omega < \omega_c$ the metastable ordered phase can exist. For $\omega < \omega_{ex} = -1.5225$ the ordered phase cannot exist at all, by analogy with the two-valley model /3/.

We have noticed that thermodynamic properties of our system at constant temperature depend on tunneling parameter ω in an analogous way as they depend on temperature at constant ω. This full analogy is easy to observe, e.g., comparing Fig. 5a with 5b or Fig. 3a with 3b. (According to the above mentioned, in the case $\omega > 0$ this analogy holds only for temperatures $T > T_c^\infty$).

In conclusion we want to remark that for the full description of a wider class of structural phase tran-

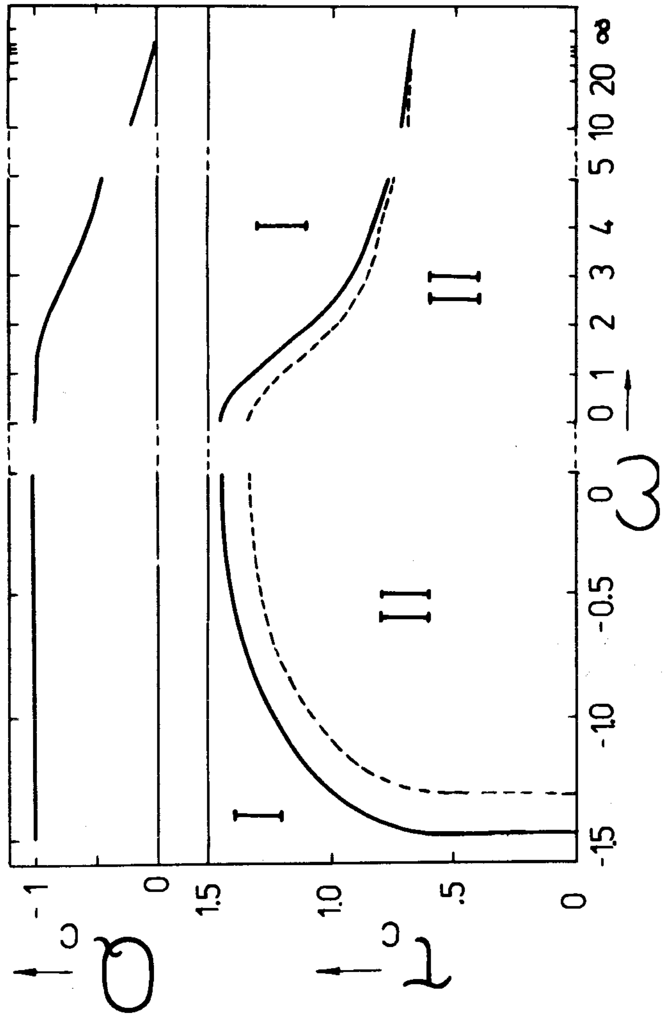

Fig. 4. The phase diagram. Down: The heavy line τ_c separates the region of stable ordered phase (II) from the region of disordered phase (I). The space between the heavy line τ_c and dashed line τ_ℓ corresponds to the overcooled disordered phase (Region of overheatted ordered phase is as narrow as linewidth on the figure). Top: Value of spontaneous order parameter Q_c at critical temperature vs ω.

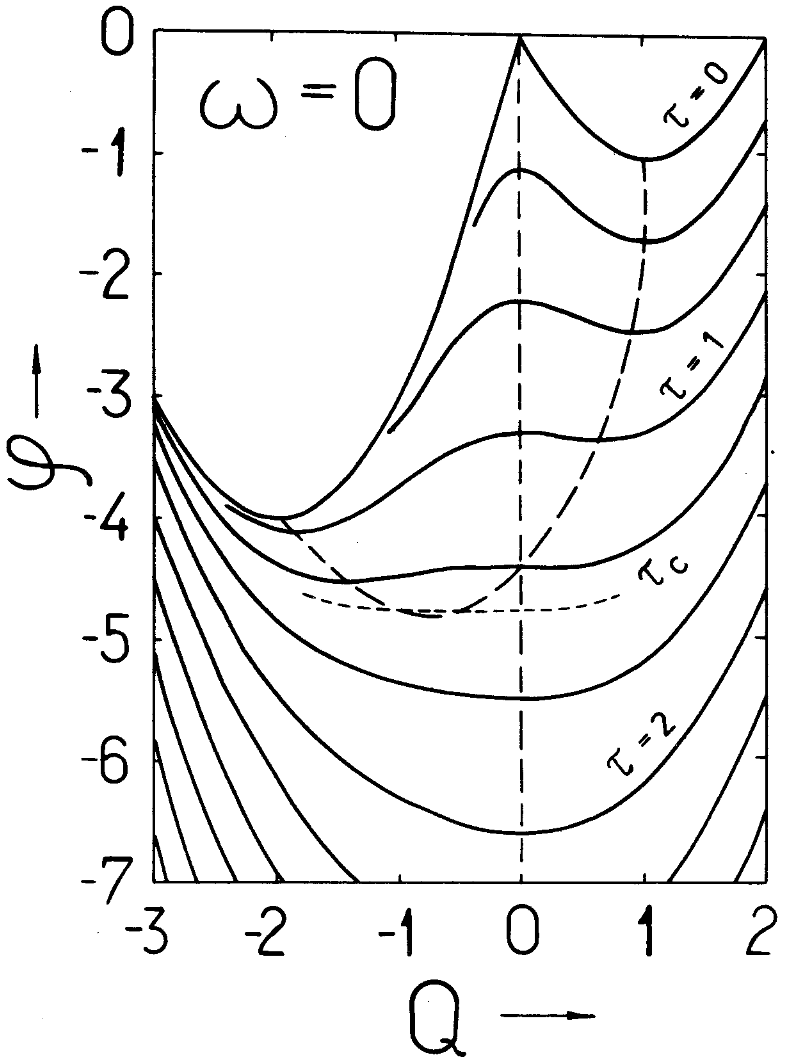

Fig. 5a. Free energy ϕ vs order parameter Q for a set values of temperature τ at constant $\omega = 0$. The critical isoterm ($\tau = \tau_c$) is distinguished by dotted line. The dashed lines show the extremum curves for ordered ($Q \neq 0$) and disordered ($Q \equiv 0$) phases.

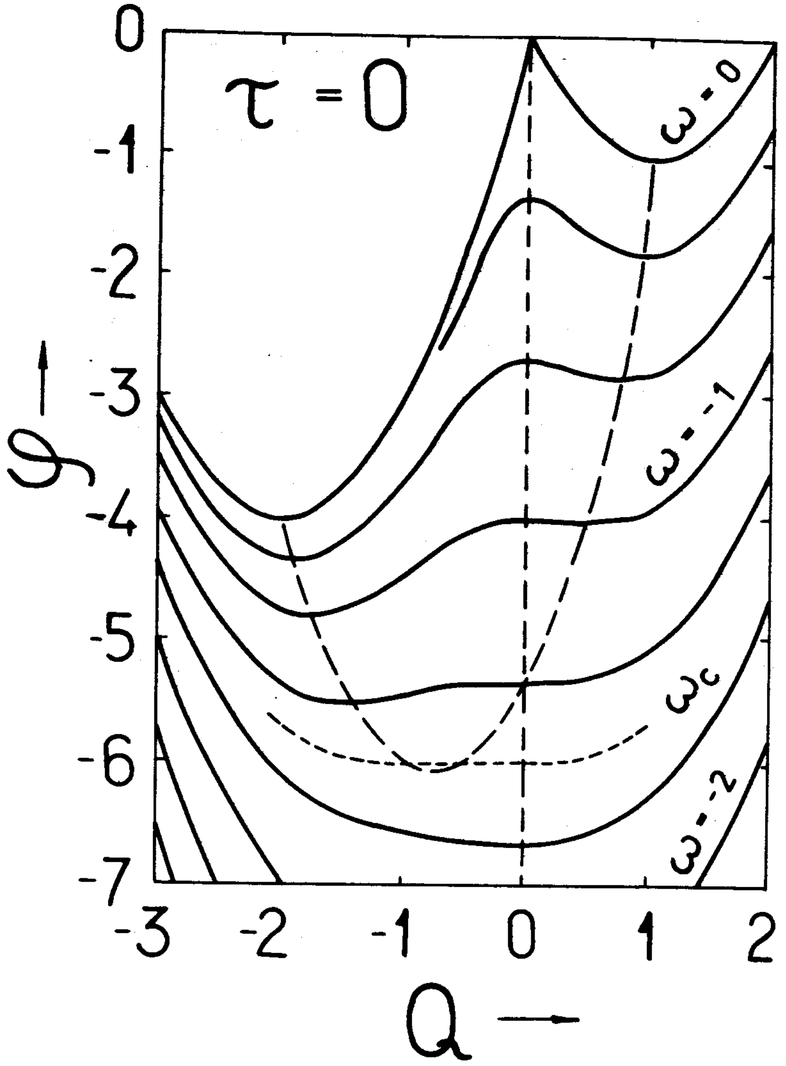

Fig. 5b. Free energy ϕ vs order parameter Q for a set of values of tunneling parameter ω at constant $\tau = 0$. The critical line ($\omega = \omega_c$) is distinguished by dotted line. The dashed lines show the extremum curves for ordered ($Q \neq 0$) and disordered ($Q \equiv 0$) phases.

sitions the present model has to be improved by taking into account the coupling with the elastic displacements /4/ and first of all, by taking into account the Ising part of the Hamiltonian, dropped by Thomas and Müller /1/. The latter leads however serious mathematical complications. On the other hand, the quadrupole type Hamiltonian (1) gives the simplest description of the first order phase transition for the nontrivial physical system. Some characteristic features of which we want to underline.

1°. Firstly, as one can find on Fig. 5a, the critical isoterm of the free energy curve for $\omega = 0$ is symmetric with respect to its maximum point, $Q_m = -1/2$ It can easily be checked that this symmetry is exactly fulfilled if we rewrite the free energy (8) substituting the value of critical temperature $\tau_c = 1/\ln 2$, $(q = Q - Q_m)$

$$\phi^\circ(q) = \phi(q + Q_m, \tau_c; 0) =$$

$$= (q + \frac{1}{2})(q - \frac{1}{2}) - \frac{3}{2} - \frac{3}{\ln 2}\ln(2^q + 2^{-q}) =$$

$$= \phi^\circ(-q).$$

Critical isoterm for $\omega = \omega_c$ ($\tau_c = 0$) is also exactly symmetric with respect to its maximum point $Q_m = -1/2$:

$$\phi^c(q) = \phi(q + Q_m, 0; \omega_c) =$$

$$= (q + \frac{1}{2})(q - \frac{1}{2}) - 3\sqrt{\frac{9}{4} + (q + \frac{1}{2})(q - \frac{1}{2})}.$$

In these two points, $\omega = 0$ and $\omega = \omega_c$, the critical order parameter is $Q_c = -1$ exactly, while for the intermediate points it is only slightly greater than -1 (with the difference not exceeding 1%), see Fig. 4 - Top. We observed that in this region the critical isoterm is practically symmetric (with deviations from the symmetry of the same order as the deviation of Q_c from -1). Such a symmetry was found by Strässler and Kittel /5/ for the combinatorical model. This however, is not a general feature. Really, in the region $\omega > 0$ the asymmetry of the critical isoterm increases with ω (together with increasing deviation of Q_c from -1, see Fig. 4 - Top).

2° The height of the barrier between the two minima on critical isoterm ($\Delta\phi = \phi_{max} - \phi_{min}$) is very small (e.g., $\Delta\phi = 0.005$ at $\omega = 0$, $\Delta\phi = 0.008$ at $\omega = \omega_c$) and is going to zero in the $\omega \to \infty$ limit. In this limit, the phase transition changes its character from the 1st to 2nd order. The dependence between the temperature τ and order parameter Q becomes a symmetrical function of Q, defined in the range $-1 \le Q \le 1$ as follows

$$\tau = \frac{2}{3}\,\frac{Q}{\mathrm{Arth}\,Q}.$$

3°. The simple rule according to which τ_c can be determined on the order parameter curve by that point Q which is equal to one-half value of the order parameter at $\tau = 0$ /2,5/ is not valid in general. It is exactly fulfilled at $\omega = 0$, approximately valid in the vicinity of the point $\omega = 0$, but completely wrong for ω far from zero in both directions as can be seen comparing Fig. 2 and Fig. 4 (Top).

We expect that some experimental examples will be found among recently investigated double perovskites /6/ which exhibit the Jahn-Teller mechanism of phase transition described above in the point (a). However, up to now, no investigation has been reported about the system where the splitting of the higher-lying doublet would result in the phase transition (as in Fig. 1c). It seems it may be quite reasonable that such a mechanism can occur among non-Jahn-Teller crystals dopped by the Jahn-Teller ions.

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