Double phase transitions in asymetrical systems

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The existence of double phase transitions in asymmetrical disordered systems is predicted. The conditions for the realization of such transitions and their temperatures are obtained.

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The purpose of the present communication is to point out the possibility of realizing double first-order phase transitions in asymmetrical disordered systems. A particular example of this system, which will be considered below for the sake of argument, are superionic crystals. These substances go over into a state of anomalously high ionic conductivity (superionic state) as a result of disordering of one of the sublattices. The asymmetry of the system is manifest here in the fact that the number of energywise equivalent interstitial positions N' in the crystal does not coincide with the number N of sites of the disordered (usually cationic) sublattice.

In the average-field (Bragg—Williams, Curie—Weiss) approximation, which, as is well known, is sufficiently effective for the description of the general character of the behavior of the system,[1-3] the free energy connected with the disordering effect takes the form

$$F(n) = wn - \frac{\lambda n^2}{2N} - T\ln\left\{\frac{N!}{(N-n)!n!}\;\frac{N'!}{(N'-n)!n!}\right\} - nT\ln\chi . \tag{1}$$

Here n is the number of cations that have moved from their sites into the interstices (defects), $w>0$ is the energy for the production of one defect, and $\lambda>0$ is a phenomenological constant describing the effective interaction (possibly indirect) of the defects with one another. The third term in (1) describes the contribution of the configuration entropy, while the fourth takes into account the change in the character of the cation vibrations on going from site to interstice. In the simplest case, χ is independent of T and 0 (see, e.g.,[4]). Assuming for simplicity $N'\gg N$ and using the relation $\ln z!\approx z\ln z - z$, we obtain from (1)

$$\frac{1}{N}F(x) = wx - \frac{\lambda}{2}x^2 - T[x(1+\ln\nu) - x\ln x^2 - (1-x)\ln(1-x)], \tag{2}$$

where $x\equiv n/N$ $(0\le x\le 1)$ and $\nu\equiv \chi N'/N$ $(0<\nu<\infty)$.

The equation of state follows from the condition $\partial F/\partial x = 0$.

$$T = \frac{\lambda(\tilde{x} - x)}{\ln[\nu(1-x)/x^2]}, \tag{3}$$

where $\tilde{x}\equiv w/\lambda$ $(0<\tilde{x}<\infty)$. In definite regions of the values of the dimensionless parameters ν and $\tilde{x}$, Eq. (3) has at certain T only one solution, and at other T three solutions $(0\le x_1\le x_2\le x_3\le 1)$, corresponding to the possible existence of phase transitions between x_1 and x_3 (x_2 is unstable). If the parameter ν is equal

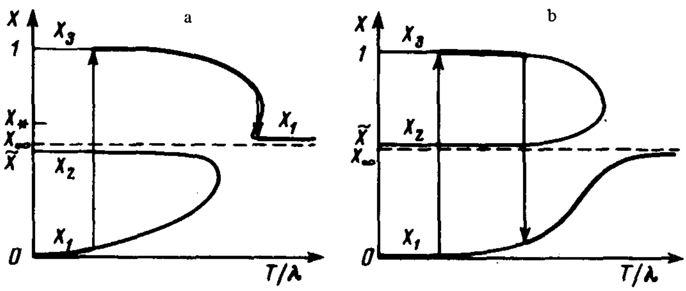

FIG. 1.

to a certain critical value (which depends on $\tilde{x}$), then the three solutions merge into one: $x_1 = x_2 = x_3 = x_* = 2 - \sqrt{2}$ (in this case the equation $\partial^2 F/\partial X^2 = 0$ has a single root, and $\lambda/T = \xi \equiv 3 + 2\sqrt{2}$). This situation corresponds to the onset (or vanishing) of an S-shaped section on the $x(T)$ curve, which is a solution of the equation of state (3)—see the upper curve of Fig. 1a. On the $F(T, x(T))$ curve this corresponds to the onset (or vanishing) of a self-intersection (see Fig. 2,

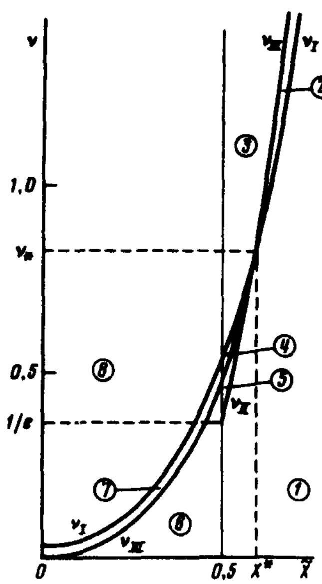

FIG. 2.

left-hand curve). At the intersection point ($T = T_{tr}$) we obviously have $F(x_1) = F(3)$, corresponding to a phase transition. Taking the foregoing into account, we obtain from (3)

$$\nu_I(\tilde{x}) = \nu_* \exp\{\xi(\tilde{x} - x_*)\}, \tag{4}$$

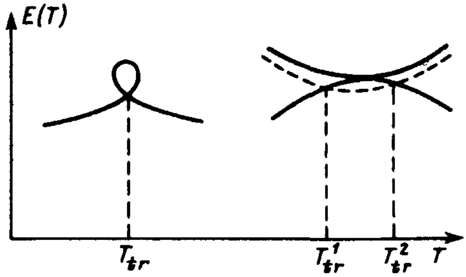

FIG. 3.

where $\nu_* = x_*^2/(1-x_*)$ In the $(\tilde{x}, \nu)$ parameter plane—see Fig. 3—the critical curve (4) corresponds to the onset or to the vanishing of one phase transition in the system. The condition $F(x_1) = F(x_3)$ can be realized also as a result of tangency of two branches of the function $F(T, x(T))$ (see Fig. 2). It is important that in this case two phase transitions are produced in the system. The equation of the corresponding critical point $\nu_{II}(\tilde{x})$—Fig. 3—is obtained from the tangency condition: $F(T, x_1(T)) = F(T, x_3(T))$; $dF(T, x_1(T))/dT = dF(T, x_3(T))/dT$. We then find from (2) and (3) that $\nu_{II}(\tilde{x})$ is defined in the interval $\frac{1}{2} \leq \tilde{x} \leq x_*$ and is given by

$$\nu_{II}(\tilde{x}) = \begin{cases} \frac{1}{e}\left[1 - 4\left(\tilde{x} - \frac{1}{2}\right)\ln\left(\tilde{x} - \frac{1}{2}\right)\right], & 0 \leqslant \tilde{x} - \frac{1}{2} << 1 \\ \nu_* + 2\xi^{1/2}(\tilde{x} - x_*), & 0 \leqslant x_* - \tilde{x} << 1. \end{cases} \quad (5)$$

The transitions in the system are of two types: (1) not accompanied by a jump through the asymptotic solution x_∞ of Eq. (3) as $T \to \infty$ $[x_\infty^2/(1-x_\infty) = y]$—see Fig. 1a, right-hand transition—and (2) accompanied by such a jump—supertransitions (see Figs. 1a and 1c).

The $\nu_{III}(\tilde{x})$ curve defined by the equation $\nu_{III}(\tilde{x}) = \tilde{x}^2/(1-\tilde{x})$ divides the plane of the parameters $(\tilde{x}, \nu)$ into two regions: on going through $\nu_{III}(x)$, the type of transition changes.

The vertical line $\tilde{x} = \frac{1}{2}$ divides the plane $(\tilde{x}, \nu)$ into two parts corresponding to two essentially different initial states of the system. As follows from (1), at $\tilde{x} > \frac{1}{2}$ and $T \to 0$ the system is in the state x_1, and at $\tilde{x} < \frac{1}{2}$ and $T \to 0$ it is in the state x_3.

Thus, the plane of the parameters $(\tilde{x}, \nu)$ is broken up into eight regions. An investigation shows that in region 1 there are no transitions, in regions 2 and 3 there is realized one transition $(x_1 \to x_3)$, and in region 3 this is a supertransition. The specifics of the asymmetrical system become manifest in regions 4 and 5. We enter into region 4 from 3 by crossing the $\nu_I(\tilde{x})$ curve, and this produces in the system and second transition on the S-shaped section of the $x(T)$ curve, see Fig. 1a. If the left-hand transition satisfies the condition $x_1 \ll 1$, $1 - x_3 \ll 1$ ("strong" transition), and the right-hand transition the condition $(x_3 - x_1) \ll 1$ ("weak" transition), then the corresponding transition temperatures T_{tr} obtained from (2) and (3) are

$$T_{tr}^{(s)} = \frac{\lambda(\tilde{x} - \frac{1}{2})}{1 + \ln \nu}; \qquad T_{tr}^{(w)} = \frac{\lambda(\tilde{x} - x_*)}{\ln \nu/\nu_*}. \qquad (6)$$

It is easy to verify that Eqs. (6) determine with good accuracy the temperatures of both transitions in practically the entire region 4. Going from the region 1 into the region 5 we cross the critical curve $\nu_{II}(\tilde{x})$. This is accompanied as indicated above, by the onset of two supertransitions in the system—Fig. 1c.

If both supertransitions are "strong," then the temperatures of the left- and right-hand transitions turn out to be equal

$$T_{tr}^{(s,l)} = \frac{\lambda(\tilde{x} - \frac{1}{2})}{1 + \ln \nu}; \qquad T_{tr}^{(s,r)} = \frac{\lambda \tilde{x}}{2}\left(\ln \frac{2\nu^{1/2}}{1 + \ln \nu}\right)^{-1}. \qquad (7)$$

For superionic crystals, particularly in this region, the superionic state is used only in a finite temperature interval.

At $0 < \tilde{x} < \frac{1}{2}$, where the initial state at $T=0$ is $x_3=1$, the picture is the following: in region 6 there is one supertransition ($x_3 \to x_1$); in region 7 there is one transition analogous to the right-hand transition of Fig. 1a; there are no transitions in region 8. We note that the jumplike decrease of the ionic conductivity with increasing temperature, predicted in regions 6 and 7 and due to the "loosening" of the interaction, is analogous to a certain degree to destruction of the superconducting state.

We emphasize in conclusion that in symmetrical systems ($N'=N$) the analog of the point $x=x_*$ is $x=\frac{1}{2}$; the interval $[\frac{1}{2}, x_*]$ contracts to a point, and there are no double transitions.

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