function $P(H_{eff})$ at 4.2 K indicates that the magnetization of alloy 14 is spatially inhomogeneous. On the other hand, the anomalies of the temperature dependence of $d\sigma/d\Omega$ allows us to conclude that this inhomogeneity is due to the depolarizing influence of the local antiferromagnetism.

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Singularities of the thermodynamics of unsymmetrical disordered systems

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A theory is developed of phase transitions in asymmetrical disordered systems. A superionic crystal is considered by way of an example of such a system. Within the framework of the molecular-field approximation, expressions are obtained for the free energy and the equation of state. The state of the system depends on two dimensionless parameters, which are determined by the properties of the crystal. The specifics of the unsymmetrical system manifest itself in the fact that both single phase transitions and bitransitions are possible. New critical conditions corresponding to realization of bitransitions are obtained and expressions are derived for the corresponding temperatures.

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This paper is devoted to a theoretical investigation of first-order phase transitions that can be realized in asymmetrical systems with disorder. The study of the singularities of the thermodynamics of model disordered systems, both symmetrical (for example, spin systems, AB alloys, certain lattice models of adsorption) and asymmetrical (for example, A_nB_m alloys, superionic crystals) has been the subject of many papers.[1-6] At the same time, some asymmetrical systems should have a number of interesting singularities, which have not been considered earlier. In particular, as will be shown below, two genetically related phase transitions—bitransitions—may take place in such systems.

1. FORMULATION OF PROBLEM

An example of an asymmetrical system to be considered is a superionic crystal, although, as will be shown subsequently, the results are general in character and can be used also for the description of a rather large class of objects and phenomena.

Superionic crystals, which have been intensively investigated of late, are a special class of ionic crystals. One of the most characteristic features of these crystals is the jumplike changes of the *ionic conductivity*, by several times or by several orders of magnitude.

This change occurs at certain temperatures that are lower than the melting temperatures of these crystals. Anomalies in the temperature dependence of a number of thermodynamic and kinetic characteristics are simultaneously observed. This group of problems is the subject of a number of experimental[7-11] and theoretical[12-16] studies. These singularities are caused, in final analysis, by a jumplike disordering ("melting") of the sublattices of one of the sorts of ions (usually cations), whereas the sublattice of the other sort of ions remains ordered and ensures "rigidity" of the crystal.[17,18] 1) The asymmetry of the system manifests itself here in the fact that the number N' of the interstitial positions for the cations does not coincide with the number N of the sites of the disordered sublattice (usually $N'>N$). In ordinary ionic crystals, to find the equilibrium number n of the ions that have moved from their sites into the interstices (and have produced by the same token Frenkel defects[19,20]) one can start from the expression for the free energy, which is connected with the formation of the defects[3,20]

$$F(n)=E(n)-T\ln\left\{\frac{N!}{(N-n)!n!}\frac{N'!}{(N'-n)!n!}\right\}. \tag{1}$$

The first term in (1) is the energy of formation of n defects; in the simplest case $E(n)=wn$, where $w>0$ is the energy for the formation of one defect. The second term, where T is the absolute temperature in energy units, corresponds to the configuration entropy S: the first factor in the curly brackets is the number of possible manners in which n empty sites (vacancies) can be disposed among the total number of N cation sites, while the second is the same for n interstitial ions in N' interstices (for simplicity we consider only one sort of energywise equivalent interstitial positions). The equilibrium value of n is determined by the condition that the free energy be a minimum, i.e., from the equation $\partial F/\partial n=0$.

Assuming $E(n)=wn$ and using the relation $\ln z!\approx z\ln z-z\ (z\gg 1)$, we obtain from (1) an expression for n (the equation of state)

$$n^2/(N-n)(N'-n)=e^{-w/T}, \tag{2}$$

which coincides with the relation known[3,20] from the theory of ordinary ionic crystals. Equation (2) has only one positive solution $n(T)$, with n increasing monotonically with increasing T.

The change of the character of the oscillations as a result of the displacement of the cations from the sites into the interstices leads to the appearance of an additional term $nT\ln\chi$ in the free energy. Assuming also that ω_j and ω_j' $(j=1,2,3)$ are the frequencies of the normal vibrations of the cations in the sites and the interstices, respectively, we obtain

$$\chi=\prod_j\frac{\mathrm{sh}(\hbar\omega_j/2T)}{\mathrm{sh}(\hbar\omega_j'/2T)}, \tag{3}$$

with

$$\chi=\begin{cases}\prod_j(\omega_j/\omega_j'), & \hbar\omega_j,\hbar\omega_j'\ll T, \quad (4a)\\ \prod_j\exp\left[\frac{\hbar(\omega_j-\omega_j')}{2T}\right], & \hbar\omega_j,\hbar\omega_j'\gg T. \quad (4b)\end{cases}$$

We now recognize that the interstitial ions and the sites that they have left (vacancies) interact both directly and "crosswise" with one another, the total number of interacting pairs being proportional to n^2. Introducing the dimensionless defect concentration $x\equiv n/N\ (0\leqslant x\leqslant 1)$, we now write down the energy $E(n)$ in the form

$$E(x)=N(wx-\lambda x^2/2). \tag{5}$$

Here λ is a phenomenological constant, the sign and magnitude of which are determined by the resultant effect of the interactions (possibly indirect) of the interstitial ions with one another, the interactions of the remaining vacancies with one another, as well as the interactions between the vacancies and the interstitial ions, and depend on the nature of the crystal. The expression for the free energy, obtained after substituting (5) in (1), is equivalent to the well known Bragg-Williams approximation in the theory of alloys[4,5] or to the Curie-Weiss approximation in the theory of magnetism.[2,21] Similar approximations are used also in the description of regular solutions,[3] of the adsorption in the presence of interactions between particles,[22,23] of the properties of liquid crystals,[24] etc. We thus have

$$\begin{aligned}F(x)/N=wx-\lambda x^2/2-T[&-2x\ln x-(1-x)\ln(1-x)\\&+x\ln(\chi N'/N)+(x-N'/N)\ln(1-Nx/N')].\end{aligned} \tag{6}$$

The corresponding equation of state obtained from the condition $\partial F/\partial x=0$ is of the form

$$\frac{x^2}{(1-x)(N'/N-x)}=\chi\exp\left\{-\frac{w-\lambda x}{T}\right\}. \tag{7}$$

Equations (6) and (7) contain a complete formulation of the problem of the thermodynamic of superionic crystals, within the framework of the considered model. We emphasize that the specifics of the investigated system will not be used at all below. Since consideration of a number of other asymmetrical disordered systems leads to the same model equations (6) and (7), the results of the subsequent investigation are of interest for the analysis of the behavior of a rather large class of objects.

2. MATHEMATICAL INVESTIGATION OF THE PROBLEM. BITRANSITIONS

Assume for simplicity that $N'/N\gg 1$ and that χ is given by (4a) (it will be shown below that these assumptions are not essential). In this case we always have $N'/N\gg x$, and expressions (6) and (7) can be rewritten in the form

$$F(x)/N=wx-\lambda x^2/2-T[x(1+\ln\nu)-x\ln x^2-(1-x)\ln(1-x)], \tag{8}$$

$$1-x=x^2\nu^{-1}\exp\{(w-\lambda x)/T\}, \tag{9}$$

or

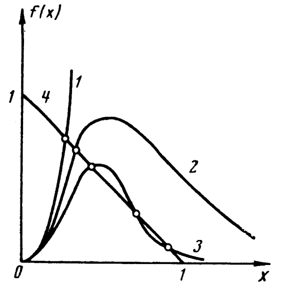

FIG. 1. Graphical solution of Eq. (9): the function $f(x) = x^2 v^{-1} \times \exp\{(\omega - \lambda x)/T\}$; the $f(x)$ curve at: 1) $\lambda = 0$, 2) $0 < \lambda < w$, 3) $\lambda > \omega$; 4) the line $1 - x$.

$$\frac{T}{\lambda} = \frac{\tilde{x} - x}{\ln[\nu(1-x)/x^2]}, \tag{10}$$

where $\nu \equiv \chi N'/N$ and $\tilde{x} \equiv w/\lambda$. The behavior of the considered system is determined completely by the two dimensionless parameters ν and $\tilde{x}$. We note that although $N'/N \gg 1$, the parameter ν can range from 0 to ∞, owing to the factor χ. Recognizing that λ can generally speaking be positive as well as negative, $\tilde{x}$ varies in the interval $[-\infty, \infty]$. However, as will be shown below, the jumplike changes of x which are of greatest interest here are possible only if $\lambda > 0$, i.e., $0 < \tilde{x} < \infty$. If we assume that at sufficiently low temperatures[2)] the crystal is completely ordered ($x \to 0$ as $T \to 0$), then it follows from (6) or (8) that $\lambda/2 < w$, i.e., $1/2 < \tilde{x} < \infty$. The interval $0 < \tilde{x} < 1/2$ corresponds to the situation when x is close to unity at low temperatures. As $T \to \infty$ we find from (9), regardless of the value of x, that $x_\infty^2/(1 - x_\infty) = \nu$, where $x_\infty \equiv x(T \to \infty)$, with $0 < x_\infty < 1$.

We first carry out a qualitative analysis of the behavior of the system. If $\lambda = 0$, then (9) coincides with equation obtained from (2) when account is taken of the substitution $w \to w - T \ln \chi$ and under the condition $N'/N \gg 1$. In this case (and also at $\lambda < 0$) Eq. (9) has one solution (see Fig. 1). At sufficiently large λ, however, as seen from Fig. 1, Eqs. (9) or (10) has three roots $\{x_1 \leqslant x_2 \leqslant x_3\}$ in the interval $0 < x < 1$. If the equation of state has a single root, then the free energy, regarded as a function of x (at fixed T) has one minimum at a value of x corresponding to this root (Fig. 2). In the case of three roots, the function $F(x)$ has two minima at the points x_1 and x_3 and one maximum at the point x_2. The crystal is in one of the two states (x_1 or x_3) corresponding to the absolute minimum of $F(x)$; the state x_2 corresponds to a maximum of $F(x)$ and is therefore unstable.

When T changes, the $F(x)$ curve is deformed in such a way that at certain temperatures T the value of $F(x_1(T))$ turns out to be equal $F(x_3(T))$. The latter means that a phase transition takes place in the system as a result of which x changes jumpwise from x_1 to x_3 (or from x_3 to x_1). The necessary condition for the transition is the onset of inflection points of the function $F(x)$, corresponding to the appearance of roots of the function $\partial^2 F/\partial x^2$. From (8) we obtain

$$w \to w - \sum_j \frac{\hbar}{2}(\omega_j - \omega_j'), \qquad \chi \to 1. \tag{11}$$

It follows from (11) that the values of λ/T corresponding to the appearance of real roots of the equation $\partial^2 F/\partial x^2 = 0$ are determined by the inequality $\lambda/T \geqslant \xi$, where $\xi = 3 + 2\sqrt{2}$; at $\lambda/T = \xi$ there appears a single real root $x = x_* = 2 - \sqrt{2}$. The obtained numbers ξ and x_* do not depend on the parameters γ and $\tilde{x}$ and are invariants of the problem.

The obtained invariants determine substantially the behavior of the system in the case of "weak" transitions. We shall call phase transitions weak if the jumplike change of x is small: $x_3 - x_1 \ll 1$. In this case, obviously, all three roots of Eqs. (9) or (10) are close to one another (see curve 3 of Fig. 2). The equation $\partial^2 F/\partial x^2 = 0$ has two roots, which are located inside the intervals $[x_1, x_2]$ and $[x_2, x_3]$ and are also obviously close to each other. Between the two roots of the equation $\partial^2 F/\partial x^2 = 0$ there should be located the single root of the equation $\partial^3 F/\partial x^3 = 0$. Differentiating (11), we easily verify that $\partial^3 F/\partial x^3 = 0$ at $x = x_*$.

Thus, all three roots $\{x_1, x_2, x_3\}$ are concentrated in the vicinity of the point $x = x_*$, with $x_2 \approx x_*$ while x_1 and x_3 are on opposite sides of the point x_* at equal distances from it. The transition takes place if the $F(x)$ curve is symmetrical about the point $x = x_*$ in its vicinity. It is precisely then, obviously, that we have $F(x_1) = F(x_3)$; this symmetry condition calls for satisfaction of the equality $\partial F/\partial x|_{x=x_*} = 0$. Substituting $x = x_*$ in (10) we obtain the temperature of the weak transition

$$T^{(w)} = \frac{\lambda(\tilde{x} - x_*)}{\ln(\nu/\nu_*)}, \tag{12}$$

where $\nu_* = x_*^2/(1 - x_*)$; the numerical value is $\nu_* = 2(\sqrt{2} - 1) \approx 0.828$. Substituting (12) in the equality $\lambda/T = \xi$ we obtain the equation for the first critical curve in the $(\tilde{x}, \nu)$ plane

$$\nu_1 = \nu_* \exp\{\xi(\tilde{x} - x_*)\}. \tag{13}$$

It is easy to verify that the condition $\lambda/T < \xi$ corresponds to

$$\begin{aligned} &\tilde{x} > x_* + \xi^{-1} \ln(\nu/\nu_*) \quad \nu < \nu_*, \\ &\tilde{x} < x_* + \xi^{-1} \ln(\nu/\nu_*) \quad \nu > \nu_*. \end{aligned} \tag{14}$$

Thus, weak transitions are realized near the critical curve (13) to its left at $\nu > \nu_*$ and to its right at $\nu < \nu_*$,

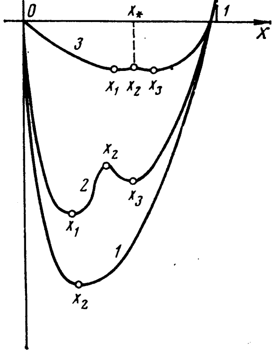

FIG 2. Schematic form of the dependence of F on x at different $\tilde{x}$ and T: 1—the equation of state has one solution; 2, 3—the equation of state has three solutions $\{x_1, x_2, x_3\}$; $x_* = 2 - \sqrt{2}$.

and "become enhanced" with increasing distance from this curve.

We consider now the transitions at $x_1 \ll 1$ and $x_3 = 1 - \varepsilon$, with $\varepsilon \ll 1$; we call these transitions "strong." From (9) we get

$$x_1 = \nu^{1/2} e^{-w/2T}, \quad x_3 = 1 - \nu^{-1} e^{(w-\lambda)/T}, \tag{15}$$

from which we see that strong transitions can be realized if $w/2T \gg 1$, $(\lambda - w)/T \gg 1$.

Assume now for simplicity that $x_1 \gg \varepsilon$, i.e., $2w > \lambda > 3w/2$, or $\frac{1}{2} < \tilde{x} < \frac{2}{3}$. With allowance for the foregoing inequalities, we obtain from (8)

$$F(x_1) \approx -2Tx_1 + O(x_1^2), \quad F(x_3) = \lambda(\tilde{x} - {}^1/_2) - T(1 + \ln \nu) + O(\varepsilon). \tag{16}$$

Bearing in mind that $F(x_1) = F(x_3)$ at the transition point, we get from (15) and (16) an equation for the strong-transition temperature $T^{(s)}$:

$$\lambda(\tilde{x} - {}^1/_2) = T^{(s)}[(1 + \ln \nu) - 2\sqrt{\nu} \exp\{-\lambda\tilde{x}/2T^{(s)}\}]. \tag{17}$$

We emphasize that the last term in the brackets in the right-hand side of (17) much be much less than unity, whereas the other terms in (17) can be either larger or smaller than unity. In particular, if the quantity $1 + \ln\nu$ is not small, then (17) has a single solution

$$T_1^{(s)} = \frac{\lambda(\tilde{x} - {}^1/_2)}{1 + \ln \nu}. \tag{18}$$

On the other hand, if the condition $0 < 1 + \ln\nu \ll 1$, is satisfied then, as can be easily seen, the right-hand side of (17) as a function of $T^{(s)}$ has a maximum. It starts from zero and is almost linear up to the maximum, after which it drops abruptly, crossing the $T^{(s)}$ axis at $T^{(s)} = T_0$, corresponding to the vanishing of the quantity in the square brackets in (17). Under the condition $0 < \tilde{x} - \frac{1}{2} \ll 1$ Eq. (17) has two solutions. The first is given by (18), and the second turns out to be quite close to T_0 and is therefore given by

$$T_2^{(s)} = \frac{\lambda\tilde{x}}{2}\left(\ln \frac{2\nu^{1/2}}{1 + \ln \nu}\right)^{-1}. \tag{19}$$

With increasing $\tilde{x} - \frac{1}{2}$, the solution $T_1^{(s)}$ and $T_2^{(s)}$ approach each other and merge, so that starting with a certain $\tilde{x} = \tilde{x}_{cr}(\nu)$, at which $T_1^{(s)} = T_2^{(s)}$, there are no solutions. Equating (18) and (19) with allowance for the fact that $1 + \ln\nu \ll 1$, we obtain approximately

$$\tilde{x}_{cr}(\nu) = \frac{1}{2} - \frac{1}{4}\frac{1 + \ln \nu}{\ln(1 + \ln \nu)}. \tag{20}$$

Thus, at $\frac{1}{2} < \tilde{x} < \tilde{x}_{cr}(\nu)$ with $1 + \ln\nu \ll 1$, two strong transitions take place in the system in any case, and are separated by a temperature interval $\Delta T = T_2^{(s)} - T_1^{(s)}$.

In connection with this result, let us carry out the general investigation of the existence of bitransitions in the system. In the phase-transition region there are three functions $x(T)$, and therefore $F(T, x(T)$ is a multiply valued function of T. A transition corresponds to the intersection of the two curves $F(T, x_1(T))$ and $F(T, x_3(T))$. The number of intersections determines the number of transitions (see Fig. 3).

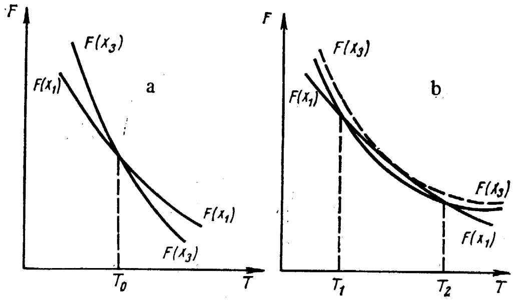

FIG. 3. Schematic plots of the free energy $F(T)$ corresponding to the solutions $x_1(T)$ and $x_3(T)$ as functions of T: a) the curves $F(x_1)$ and $F(x_3)$ intersect once, T_0 is the transition temperature; b) the curves $F(x_1)$ and $F(x_3)$ intersect twice, T_1 and T_2 are the temperatures of the transitions; dashed—the curves are tangent and T_1 and T_2 merge.

In the analysis presented above of the conditions for the "onset" (or vanishing) of a weak transition (see (11)–(14)) we used the system of equations

$$\frac{\partial F}{\partial x} = 0, \quad \frac{\partial^2 F}{\partial x^2} = 0, \quad \frac{\partial^3 F}{\partial x^3} = 0, \tag{21}$$

which determines the critical curve $\nu_{\text{I}}(\tilde{x})$ in the parameter plane, as well as the temperature corresponding to the onset (vanishing) of a transition on this curve. The presented system (21) is perfectly analogous to the system traditionally used in the investigation of first-order phase transitions (the meaning of the quantity x is determined here by the specifics of the system). Single phase transitions, the onset conditions for which are described by Eqs. (21), correspond to Fig. 3a. At the same time, the onset (or vanishing) of a pair of transitions is possible in principle[25] (see Fig. 3b). The corresponding condition is determined by the tangency of the two branches of the curves

$$\begin{gathered} F(T, x_1(T)) = F(T, x_3(T)), \\ \frac{d}{dT}F(T, x_1(T)) = \frac{d}{dT}F(T, x_3(T)). \end{gathered} \tag{22}$$

The two equations (22) together with the equation of state $\partial F/\partial x = 0$ determine a substantially different type of critical conditions than in (21). These conditions determine the critical curve (or curves) $\nu_{\text{II}}(\tilde{x})$ in the parameter plane, and also the temperature for the onset (or vanishing) of a bitransition (a pair of transitions) on this curve.

The foregoing analysis (see (17)–(20)) illustrate the fact that the critical conditions (22) can be realized in the investigated system.

We emphasize that in the general case, in the analysis of problems connected with phase transitions, it is necessary to take into account the possibility of realization of the formulated conditions (22), corresponding to the appearance of bitransitions in the system.

We proceed now to a detailed mathematical investi-

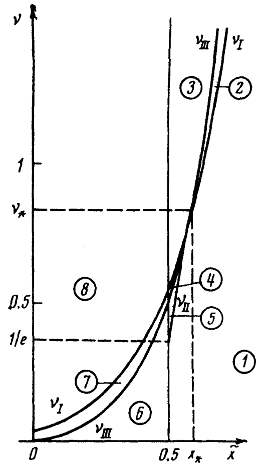

FIG. 4. Plane of the parameters $(\tilde{x}, \nu)$: ν_I, ν_{II}, and ν_{III} are the critical curves (see (13), (24), and (25).

gation of the properties of the considered system with allowance for the critical conditions (22). Recognizing that the functions $x_{1,3}(T)$ are determined from the equation $\partial F/\partial x = 0$, we obtain $dF(T, x_{1,3}(T))/dT = \partial F/\partial T = -S(x_{1,3})$. From this and from (22) it follows that at the point of the onset (or vanishing) of a pair of transitions, we have $E(x_1) = E(x_3)$ (which is equivalent to the equality $x_1 + x_3 = 2\tilde{x}$) and $S(x_1) = S(x_3)$. From the presented equations, and also from Eq. (10) and the condition $T(x_1) = T(x_3)$, we obtain after simple transformations

$$\begin{gathered}\tilde{x}^2 - \Delta^2/4 = \nu[(1-\tilde{x})^2 - \Delta^2/4]^{1/2}, \\ \frac{2\tilde{x}}{\Delta}\ln\frac{\tilde{x}-\Delta/2}{\tilde{x}+\Delta/2} + \frac{1-\tilde{x}}{\Delta}\ln\frac{1-\tilde{x}+\Delta/2}{1-\tilde{x}-\Delta/2} = -1,\end{gathered} \tag{23}$$

where $\Delta \equiv x_3 - x_1$ is the jump of the concentration at the points where the bitransition sets in.

Within the framework of the assumed model, the system (23) is exact and it determines the critical $\nu_{II}(\tilde{x})$ (see Fig. 4) and Δ. An analysis shows that at $\nu > \nu_*$ the system (23) has no solution at any x; consequently, there are no bitransitions in this case. At $1/e < \nu < \nu_*$, in the interval $\frac{1}{2} < \tilde{x} < x_*$, a solution of the system (23) exists and is furthermore unique.

If $0 \leqslant x_* - \tilde{x} \ll 1$, then $\Delta \ll 1$, corresponding to the critical condition for a weak bitransition (a pair of weak transition). In this case we obtain from (23)

$$\Delta^2 = \frac{40\sqrt{2}}{3}(x_* - \tilde{x}), \qquad \nu_{II}(\tilde{x}) \approx x_* + 2\xi^{1/2}(\tilde{x} - x_*). \tag{24a}$$

On the other hand if $0 < \tilde{x} - \frac{1}{2} \ll 1$, then $\Delta \approx 1$, corresponding to the critical condition for a strong bitransition. In this case

$$\begin{gathered}\Delta = 1 - 2[\delta + 4e^2\delta^2 + 32\delta^3 e^2 \ln\delta + \ldots], \\ \nu_{II}(\tilde{x}) = \frac{1}{e}[1 - 4\delta\ln\delta + \ldots],\end{gathered} \tag{24b}$$

where $\delta = \tilde{x} - \frac{1}{2}$. We note that the obtained function $\nu_{II}(\tilde{x})$ is equivalent to the previously obtained function $\tilde{x}_{cr}(\nu)$ —see (20). It is obvious that the "intermediate" region of the values of x corresponds to the critical condition for the "medium" bitransitions.

At $\nu < 1/e$, the system (22) has no solutions and there are no bitransitions.

With increasing distance to the left of the second critical curve (Fig. 4), the temperature interval between the produced pair of transitions broaden and a pair of arbitrary transitions (for example, a weak and a strong one) can be realized in the system.

It is convenient to illustrate the results by analyzing the equation of state in the form (10). It is easily seen that the function $T(x)$ vanishes at the three points $x = 0$, $x = 1$, and $x = \tilde{x}$. Thus, in the low temperature region Eq. (10) always has three solutions $x_1(T) \leqslant x_2(T) \leqslant x_3(T)$. If $\tilde{x} < 1$, then all the solutions are in the interval $[0, 1]$, but if $\tilde{x} > 1$, then one solution is situated in the physical interval $[0, 1]$. At sufficiently high T, there always exists only one solution that tends asymptotically to the value x_∞ (Fig. 5).

If $\tilde{x} < x_\infty$, the closed loop corresponding to the solution of x_1 and x_3 (Figs. 5c and 5d) is located under the asymptotic value $x = x_\infty$; if $\tilde{x} > x_\infty$, then the closed loop corresponds to the solutions x_2 and x_3 (Figs. 5a and 5b) and lie above the asymptotic value $x = x_\infty$. The condition

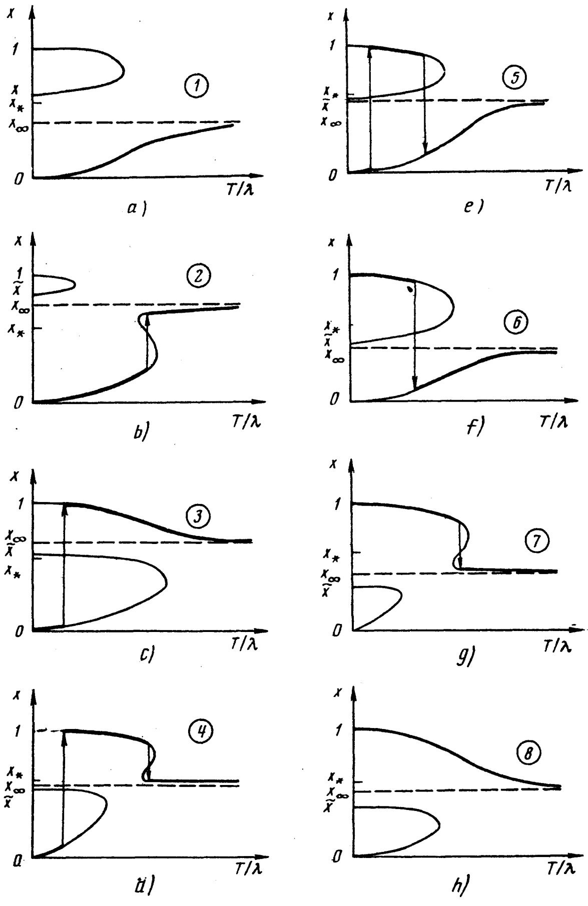

FIG. 5. Schematic form of the possible solutions of the equation of state and of the transitions between solutions. The numbers in the circles correspond to the regions in the $(\tilde{x}, \nu)$ plane—see Fig. 4. The thick lines represent the realized regimes, and the arrows the transitions between them.

$\tilde{x}=x_\infty$ yields the equation for the third critical point in the $(\tilde{x}, \nu)$ plane—see Fig. 4:

$$\nu_{\rm III}=\frac{\tilde{x}^2}{1-\tilde{x}}. \qquad (25)$$

The loop is lower if $\tilde{x}$ and ν are located to the left of this curve and higher if they are on the right.

3. QUALITATIVE ANALYSIS OF THE RESULTS

We present now a complete picture of the behavior of the system in the plane of the parameters $(\tilde{x}, \nu)$—Fig. 4. The three critical curves (see (13), (24), and (25)) and the line $x=\frac{1}{2}$ break up the parameter plane into eight regions.

In region 1, which is to the right of the curves $\nu_{\rm I}$ and $\nu_{\rm II}$ and of the line $\tilde{x}=\frac{1}{2}$, there are no transitions and x increases monotonically from the value $x=0$ at $T=0$ to $x=x$ at $T\to\infty$. This region corresponds to Fig. 5a, and if $\frac{1}{2}<\tilde{x}<1$ then the loop lies under the value $x=1$ (i.e., in the physical region of the parameter).

On crossing the curve $\nu_{\rm I}$, we land in region 2 (see Fig. 5b), where one transition on the S-shaped section of the lower branch of the curve is realized. The transition is weak in the immediate vicinity of the curve $\nu_{\rm I}$ (where the S-shaped section initiates) and becomes stronger with decreasing $\tilde{x}$. On crossing the curve $\nu_{\rm III}$, which corresponds to the transition of the loop downward, we land in region 3 (see Fig. 5c), which is bounded by the curves $\nu_{\rm I}$, $\nu_{\rm III}$, and the line $\tilde{x}=\frac{1}{2}$.

The concentration jump in the phase transition on the S-shaped section, as for example in region 2, cannot be accompanied by a jump through the value $x=x_\infty$ which is asymptotic as $T\to\infty$ (although the difference x_3-x_1 need not necessarily be small in such a transition). In region 3, a phase transition takes place with participation of loop-shaped curves. In the general case this transition must be accompanied by a jump to the value $x=x_\infty$ so that one of the states must have a concentration x larger than x_∞. The transitions accompanied by crossing of the asymptote will be called, in accord with[26], supertransitions. Thus, in the region 3 there is realized one transition which is a supertransition; it can be either strong (when x is near the value $\frac{1}{2}$) or weak (when $\tilde{x}$ is near x_* and ν is near ν_*).

On crossing the curve $\nu_{\rm I}$, we go over into the region 4. Inasmuch as on the right of $\nu_{\rm I}$ there is produced a weak transition (see (14)), we "acquire" on landing in region 4 a second transition, independent of the first—see Fig. 5d—and connected with the appearance of the S-shaped section on the upper branch of the curve. Thus, in region 4 there are realized two independent transitions, one of which is a supertransition.

Crossing curve $\nu_{\rm III}$, we land in region 5 between the curves $\nu_{\rm II}$, $\nu_{\rm III}$, and the line $\tilde{x}=\frac{1}{2}$. It is precisely this region that corresponds to the situation described by formulas (17)–(20), namely a pair of strong transitions; in the general case, a bitransition comprising a pair of supertransitions is realized in region 5—see Fig. 5e. Finally, crossing the curve $\nu_{\rm II}$, we land again in region 1.

From a comparison of Figs. 5a and 5e we see that the plots of the solutions in regions 1 and 5 are topologically equivalent, and the pair of supertransitions (see Fig. 5e) in the region 5 comes closer together as the $\nu_{\rm II}$ curve is approached and vanishes when this curve is crossed.

The point $\tilde{x}=x_*$, $\nu=\nu_*$ on the parameter plane, at which all three critical curves intersect, is singular: at $\tilde{x}=x_*=x_\infty$ degeneracy sets in and a single phase transition, furthermore of second order, takes place in the system (the quantity x is continuous and dx/dT is discontinuous). The temperature of this transition is $T=\lambda/\xi$.

Let us return to the case $\tilde{x}<\frac{1}{2}$. As already indicated, in this case at low temperatures the value of x is close to unity. In the region 6 (Fig. 5f) the solution curves are topologically equivalent to the curves corresponding to regions 1 and 5 (Figs. 5a and 5e), but the starting point is now $x=1$. Therefore with increasing temperature, one supertransition is realized here, accompanied by a jumplike decrease of x. (We note that there are no transitions in the analogous curves in the region 1, while in the region 5 we have a bitransition.) In region 7 (Fig. 5g) the solution curves are topologically equivalent to those shown in Fig. 5d, but now only one transition takes place here on the S-shaped section of the upper curve. Finally, region 8 corresponds to Fig. 5h, which is topologically equivalent to Fig. 5c, but now the system is on the upper curve at all T, and there are no transitions.

We emphasize that the existence of bitransitions is essentially connected with the asymmetry of the considered system: $N'\neq N$. When $N'=N$ (symmetrical systems), the equation of state (7) reduces to the form $x/(1-x)=\nu^{1/2}\exp\{-(w-\lambda x)/2T\}$. This case is analyzed in detail in[27].

It is easy to verify that the value of x_* corresponding to the onset of three close solutions (see (11)) turns out to be equal to $x_*=\frac{1}{2}$ in the symmetrical system, and there is no interval $\frac{1}{2}<\tilde{x}<x$, corresponding to the possibility of realizing two transitions. Therefore in a symmetrical system there are either no transitions, or there exists a single transition. The temperature of this transition (at all values of the difference x_3-x_1) is obtained from (12) by making the substitution $x_*=\frac{1}{2}$ (and $\nu_*=1$): $T_{\rm sym}=\lambda(\tilde{x}-\frac{1}{2})/\ln\nu$.

The considered case $N'\gg N$ is the "extremely asymmetrical" one. It is clear, however, that the results (in particular, the existence of eight characteristic regions on the $(\tilde{x}, \nu)$ plane and of double transitions) remain in force also in the general case of asymmetry $N'\neq N$ (Eqs. (6) and (7).[3)]

Let us make a few remarks concerning a number of other assumptions used in the calculations. It was assumed that w remains unchanged in the entire considered temperature interval. This assumption is in fact not restrictive, since allowance for a weak $w(T)$ dependence reduces, as can be easily seen, to a renormalization of the constants χ in Eqs. (6) and (7).

Consideration of other models for the description of the vibrations of the disordered particles reduces in exactly the same manner to a renormalization of χ. Next, it was assumed that all the states N' are energywise equivalent. Obviously, the results remain unchanged also in a number of cases when the system has several sorts of such states (for example, different interstitial positions). Indeed, if the energies of these states are close to one another (their difference is less than T), then these states can be effectively regarded as indistinguishable. In the opposite limit (when their difference is larger than T), we can confine ourselves to consideration of states with minimum energy. Finally, it was assumed that all the states N' are equally accessible, i.e., there is no blocking effect. We note in this connection that in the opposite limit of absolute blocking (one particle blocks $g > 1$ places), the calculation of the configuration entropy leads to the same final expressions (6) and (7), but with a renormalized ratio $N'/N \to N'/gN$; the parameter can also become renormalized in concrete models.

Thus, the investigated model, despite its relative simplicity, predicts a variety of possible temperature behaviors of the considered disordered systems. First, a continuous disordering of the initial sublattice is possible (Fig. 5a), or else a nearly continuous one accompanied by a relatively small discontinuity of x (Fig. 5b); the temperature of such a jump (weak transition) is given by formula (12).4)

Second, an abrupt jump from a state with "small" x to a state with a value $x \approx 1$ is possible, corresponding to a strong supertransition. The temperature of such a transition is given by formula (18). With further increase of the temperature, the system remains in this state, and x decreases with increasing T (Fig. 5c). Physically, the decrease of x with increasing T is due to the following: the state $x_3 > x_\infty$ is realized and is preserved because of the presence of a sufficiently strong interaction ($\tilde{x} < 1$). With increasing temperature, the influence of the interaction weakens effectively (the "particle gas" becomes ideal as $T/\lambda \to \infty$). Consequently, x decreases with increasing T to a value $x = x_\infty$.

Third, the temperature interval in which the state $x > x_\infty$ is realized can be finite. In particular, when this interval is bounded by a pair of strong supertransitions (Fig. 5a), the temperature limits of the interval are given by formulas (18) and (19).

It is possible also that the second jump is not a supertransition (Fig. 5d) and therefore does not take the system out of the state $x > x_\infty$, into which the system went over as a result of the first transition. If one transition is strong and the other is weak, then the temperatures of the transitions are given by formulas (18) and (12) respectively.

Finally, a case is possible when the system is disordered in the initial state ($\tilde{x} < \frac{1}{2}$). With increasing temperature this disorder can decrease either continuously (Fig. 5a) or accompanied by a weak transition (Fig. 5g). A jumplike ordering is also possible as a result of a strong supertransition at a temperature $T_1^{(s)}$ (18), so that at $T > T_1^{(s)}$ the system is "almost ordered" (Fig. 5f).

In the case of superionic crystals, the last situation corresponds to a jumplike vanishing of the high ion conducitivity with increasing temperature. This effect is analogous in its physical manifestation, in a certain sense, to the destruction of electronic superconductivity with increasing temperature.

The foregoing investigation has revealed the existence of a number of interesting possibilities of the thermodynamic behavior of asymmetrical disordered systems; the existence of supertransitions, bitransitions, and two successive transitions. This investigation was based on the use of two types of critical conditions for the onset of phase transitions—(21) and (22). Conditions (21) are traditionally used in the description of first-order phase transitions.

At the same time, we must emphasize the importance of the formulated conditions (22) for a sufficiently complete analysis of problems involving phase transitions. In particular, in the simple model system considered in the present paper we have demonstrated the possible existence of bitransitions as a result of realization of the conditions (22). In more complicated systems, a similar analysis can demonstrate in principle the existence of several bitransitions, or even a more complicated system of correlated transitions.

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1) In some crystals, the considered cation order can be accompanied by a restructuring of the rigid sublattice and by a change of its symmetry. For simplicity, we shall deal below with crystals in which no such restructuring takes place.

2) By "low" temperatures are meant those corresponding to the intermediate asymptotes, so that $x_1 \ll 1$ but (4a) is still valid; at even lower temperatures, when χ is given by (4b), the problem reduces to ours by making the substitution

$$\frac{1}{N}\frac{\partial^2 F}{\partial x^2} = -\lambda + T\left(\frac{2}{x} + \frac{1}{1-x}\right).$$

3) Equations analogous to (6) and (7) were obtained in [28], where a system of interacting defects in an irradiated crystal was investigated. Since, however, the critical conditions (22) were not investigated in [28], the possibility of the existence of bitransitions was not observed.

4) The weak and strong transitions mentioned here and below can, generally speaking, be "medium" transitions (when $x_3 - x_1 \lesssim 1$); the temperatures of "medium" transitions cannot be obtained analytically but can be determined by a numerical solution of the corresponding equations.

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