Features of the thermodynamics of superionic conductors

Yu. Ya. Gurevich and Yu. I. Kharkats

Institute of Electrochemistry of the Academy of Sciences of the USSR

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This article reviews the theoretical and experimental studies on a number of the thermodynamic aspects of superionic conduction, the intensive study of which began in the past decade. We discuss the relation of superionic conductivity to the disordering of one of the sublattices of the crystal, disordering phase transitions caused by the interaction of point defects, and the mechanism of polymorphic transitions associated with partial disordering. We analyze the effect of jumpwise variation of the ionic conductivity induced by an external electric field, the thermodynamics of domain states in superionic conductors, and the effect of pressure on the phase transitions and the ionic conductivity.

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1. INTRODUCTION

Superionic conductors constitute a special class of substances that have attracted steady attention in recent years from a very wide circle of investigators. The flow of scientific papers on superionic conductors is now counted in hundreds of articles per year, and the corresponding publications amount to an appreciable fraction of the contents of a number of leading physical and chemical journals. The unusual, in many ways paradoxical properties of these substances are of interest both from the standpoint of fundamental problems of solid-state physics and physical chemistry, and in connection with purely applied problems.[1-7]

One of the most important features that distinguish superionic conductors is their anomalously high ionic conductivity. While the ionic conductivity of ordinary solids, e.g., ionic crystals, at temperatures not too close to the melting point does not exceed 10^{-8}–10^{-9} (ohm · cm)$^{-1}$, the ionic conductivity of "good" superionic conductors under the same conditions amounts to 10^{-1}–1 (ohm · cm)$^{-1}$ [for comparison we recall that the electronic conductivity of metals is 10^4–10^6 (ohm · cm)$^{-1}$]. In order of magnitude, the ionic conductivity of superionic conductors is close to the values characteristic of alloys and concentrated solutions of strong electrolytes. Correspondingly the superionic conductors are also called solid electrolytes. Thus the problem involves substances that possess distinctive hybrid properties—the conductivity of a liquid alloy or solution and the mechanical strength and elasticity of a solid.

The vigorous development of studies involving superionic conductors began essentially in the late sixties. The direct impetus toward this in many ways was the synthesis of the compound Ag_4RbI_5[18,19] and its subsequent use as a solid electrolyte in batteries designed to operate under outer-space conditions (advantages: miniaturization, mechanical strength, reliability). The compound Ag_4RbI_5, which has even at −150 °C a high conductivity in silver ions, and which reaches a conductivity of ~0.3 (ohm · cm)$^{-1}$ at room temperature, is now one of the "record-makers" among superionic conductors.

At the same time, the problem of superionic conductivity arose in physics long before the synthesis of the stated solid electrolyte, and it has a long history. Faraday already knew of the existence of solid crystalline materials that possess a considerable ionic conductivity. Subsequent studies in this field bear the names of Warburg and Nernst,[20,21] who also studied ceramic and glassy solid phases. Finally, a very important contribution was made by the studies of Tubandt and Lorenz performed not long before World War I.[22] In studying the electrical properties of silver halides they established that solid silver iodide AgI—in contrast to the chloride and the bromide—possesses an extremely high ionic conductivity in the solid state

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that is now called the α-phase. The high-conductivity state arises at 147 °C and is accompanied by a jumpwise increase in the ionic conductivity by more than three orders of magnitude. Subsequently the conductivity increases relatively slowly and reaches 2.6 (ohm × cm)$^{-1}$ at 555 °C, corresponding to the melting point of the crystal. Then it decreases again in jumpwise fashion (by about 7%) upon melting. As the most recent studies[13,23-28] have shown, the described behavior is typical of a number of superionic conductors, e.g., MAg_4I_5 (where M = Rb, K, NH_4, CuI), Cu_2S, CaF_2, YF_3, etc. (in the latter two compounds the superionic conduction is due to fluoride anions).

At present a multitude of compounds have been synthesized and studied that have a high ionic conductivity, in which the current carriers are the cations of sodium, potassium, lithium, or anions of oxygen or the halogens, etc.[16,29-33] Materials exist in which ions of several types are simultaneously mobile.[34-37] The electronic conductivity of superionic conductors is usually negligibly small, although compounds exist (e.g., silver chalcogenides, certain bronzes) in which it plays an appreciable role. The set of problems associated with electronic conductivity has been treated in Refs. 17, 38–29.

The temperatures at which a high ionic conductivity [$\geq 10^{-2}$ (ohm · cm)$^{-1}$] is reached are also marked by considerable variety. Here the overall temperature range of superionic conductivity "covered" by the entire set of currently known superionic conductors (many tens of compounds) amounts to more than 1500 °C. Figure 1 shows some examples.

With a certain degree of arbitrariness, one can classify the superionic conductors into several types on the basis of features of the structure and character of the ionic conductivity.[12]

The first type (to which special attention is paid below) contains crystals with structural disorder, in particular, such as solid electrolytes based on AgI. Their distinguishing feature is the existence of a certain critical temperature characteristic of each substance at which a jumpwise change in the ionic conductivity occurs. One simultaneously observes also anomalies in the temperature behavior of a number of thermodynamic and kinetic characteristics.[1-44] The stated features ultimately arise from jumpwise disordering—partial or total—of the sublattice formed by one of the types of ions. The other sublattice, i.e., the bulk structure, formed by the other type (or types) of ions retains its "rigidity" and thus maintains the mechanical strength of the crystal as a whole. Qualitative concepts of the "melting" of one of the sublattices were first expressed in Ref. 22. X-ray and neutron diffraction analysis of superionic conductors[40-43] have convincingly confirmed them in the subsequent decades. Thus, crystals with structural disorder, which we shall call superionic crystals, can exist in two qualitatively different phases. At temperatures below critical, they behave like ordinary ionic crystals (dielectric phase). At temperatures above critical they transform to a special state—the superionic state (electrolyte phase). In this state the crystals are superionic conductors.

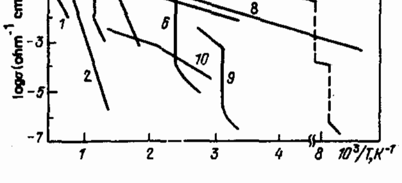

FIG. 1. Temperature-dependence of the conductivity for different superionic conductors. 1—$ThO_2 - Y_2O_3$, 2—CaF_2, 3—Li_2SO_4, 4—PbF_2, 5—Ag_3SI, 6—AgI, 7—$RbAg_4I_5$, 8—Na-β-alumina, 9—Ag_2HgI_4, 10—CeF_3.

The second type of superionic conductors contains compounds whose high ionic conductivity arises from a high concentration of impurity ions that activate the disordering of the structure. If, for example, one dopes the crystalline lattice of ZrO_2 with CaO, the Ca^{2+} ions are incorporated into the Zr^{4+} sublattice, while the O^{2-} ions fill out the oxygen sublattice. However, in view of the difference in charges of the calcium and zirconium ions, oxygen vacancies necessarily arise in this mixed crystal. Whenever there are enough of them, the conductivity rises substantially for the oxide ions, which acquire the ability to move from vacancy to vacancy. Typical solid electrolytes with impurity disorder are compounds of the type of MO_2–M′O and MO_2–M''_2O_3, where M is Zr, Hf, or Ce; M′ is Ca, Sr, or Ba; and M″ is Sc or Y. In contrast to the crystals having structural disordering, the compounds with impurity disordering usually do not show a sharp temperature jump in the ionic conductivity, although the latter increases considerably with the temperature.

Finally, also amorphous glassy materials that have an ionic conductivity due to the presence of electrically active impurities are included among the superionic conductors.[44-45] A number of crystalline superionic conductors possess high ionic conductivity also in the amorphous state (see, e.g., Ref. 46).

Thus the observed jumpwise variation of the ionic conductivity of superionic crystals is ultimately explained by a sharp change in the number of ions in states possessing high mobility. This variation arises from a first-order phase transition accompanied by disordering (melting) of one of the sublattices of the crystal.

What we have said implies that studying the features of the thermodynamics of superionic crystals is an important step on the path to understanding the processes associated with the effect of the anomalously high ionic conductivity of solids. The temperature-dependent phase transitions in superionic crystals have been studied in a considerable number of papers, both of experimental[47-56] and theoretical nature.[57-67] As a result considerable successes have been attained along this line recently that allow one to speak of the possibility of qualitative (and in individual cases even quantitative) description of the phenomena that take place. This review is devoted to the current state of the thermodynamic theory of the structural disordering of superionic crystals.

2. THERMODYNAMICS OF DISORDERING IN IONIC CRYSTALS

The fundamental distinguishing characteristic of superionic conductors—the anomalously high ionic conductivity—is closely associated in nature with the features of their thermodynamic behavior. Since ionic conduction in solids is effected by the migration of point defects (e.g., ions via the interstices), one of the basic factors that governs the conduction is the concentration of these defects. It is determined from the model thermodynamic calculations first performed by Frenkel'[68-69] for quantitative description of ionic conduction in ordinary ionic crystals.

The modern concepts employed for treating the thermodynamic and kinetic properties of superionic conductors involve the same set of ideas.

The free energy of the crystal is represented in the form of two terms

$$\mathscr{F} = \mathscr{F}^{(0)} + \mathscr{F}^{(d)}. \tag{1}$$

Here $\mathscr{F}^{(0)}$ is the free energy of the ideal defect-free crystal, and $\mathscr{F}^{(d)}$ is the free energy involved in disordering. For crystals characterized by a fixed regular skeleton formed by one type (or several types) of ions and by a relatively disordered arrangement of another type of ions, the quantity $\mathscr{F}^{(d)}$ can be written in the form[7,76]

$$\mathscr{F}^{(d)}(n) = E(n) - T \ln\left[\frac{N_1!}{(N_1-n)!\,n!} \times \frac{N_2!}{(N_2-n)!\,n!}\right]. \tag{2}$$

Here N_1 is the number of energetically equivalent interstitial positions; N_2 is the number of nodes of the sublattice subject to disorder (usually $N_1 > N_2$) (Fig. 2); n is the number of ions that have moved from their nodes to interstices (and of the Frenkel' defects thus formed); and T is the absolute temperature in energy units.

The first term in (2) is the energy of formation of n defects. In the simplest case we have $E = wn$, where $w > 0$ is the energy of formation of a single defect. The second term corresponds to the configurational entropy S; the first factor in the square brackets is the number of possible ways of arranging n empty nodes (vacancies) among the total number N_2 of nodes of the sublattices subject to disorder (for the sake of definiteness, the cation lattice); the second factor is the number of possible ways of arranging n interstitial ions (cations) at N_1 interstices (for simplicity we treat here only one type of energetically equivalent interstitial positions; for the corresponding generalization see, e.g., Ref. 48). The equilibrium value of n is determined by the condition of minimum free energy, i.e., by the equation $\partial\mathscr{F}/\partial n = 0$.

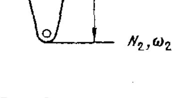

FIG. 2. Schematic shape of the energy profile for ions at nodes and in interstitial positions. N_1 and N_2 are the numbers of nodal and interstitial positions, $\omega_{1,2}$ are the corresponding frequencies.

Under the assumption that $E(n) = wn$, and with account taken of the relationship $\ln z! \approx z \ln z - z (z \gg 1)$, Eq. (2) gives rise to an equation for n (the equation of state):

$$\frac{n^2}{(N_1-n)(N_2-n)} = e^{-w/T}. \tag{3}$$

This is the equation used to describe the concentration of defects in ordinary ionic crystals. Equation (3) has only one positive solution $n(T)$, with n increasing monotonically with increasing T from zero for $T = 0$ to N_2 for $T \to \infty$.

The change in the nature of the lattice vibrations caused by the displacement of the cations from the nodes to the interstices gives rise to an additional term in the free energy of (2) of the form $-nT\ln\chi$, with the form of the function $\chi(T)$ depending on the model chosen.[70,72] If we assume, in particular, that $\omega_1^{(j)}$ and $\omega_2^{(j)}$ $(j = 1, 2, 3)$ are the frequencies of the normal vibrations of the cations, respectively in the interstices and at the nodes, and that $\omega_{1,2}^{(j)} \ll T$, after simple calculations we get[59,63]

$$\chi = \prod_j \frac{\omega_1^{(j)}}{\omega_2^{(j)}}.$$

Now let us bear in mind the fact that the interstitial ions and the nodes (vacancies) produced by them generally interact, both among themselves and "crosswise" with one another. Now we consider that the total number of interacting pairs here is proportional to n^2, and introduce the dimensionless concentration $x = n/N_2 (0 \leq x \leq 1)$. In view of what we have stated, we can write the energy $E(n)$ in the form

$$E(x) = N_2\left(wx - \frac{\lambda x^2}{2}\right). \tag{4}$$

Here λ is a phenomenological constant, whose sign and magnitude determine the resultant interaction effect (perhaps indirect) of the ensemble of interstitial ions and vacancies in the crystal; $\lambda > 0$ corresponds to effective attraction, and $\lambda < 0$ corresponds to effective repulsion.[1)]

The expression for the free energy that we obtain after substituting (4) into (2) is equivalent to the well-known Bragg-Williams approximation in the theory of alloys[76,77] or the Curie-Weiss approximation in the theory of magnetism.[71] Approximations analogous in nature are also employed in describing regular solutions,[71,78] adsorption involving interaction between the particles,[78-81] the properties of liquid crystals,[82] etc. This type of approach is rather effective in treating

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[1)] The analysis of the various concrete interactions that give rise to λ lies outside the scope of this review (see, e.g., Refs. 57 and 63). We shall merely point out that, in particular, taking account of the elastic deformations in the crystal upon forming defects[73] and also the rearrangement of its phonon spectrum in second-order perturbation theory[74,75] lead to an effective attraction.

the thermodynamic behavior of the system as a whole, i.e., describing its overall behavior over a relatively wide temperature range (although it requires refinement for analyzing narrow temperature ranges in the immediate vicinity of singular points[83,84]).

Thus, we obtain the following expression for the free energy $\mathscr{F}^{(d)}$ of the crystal from (2) and (4)[63,64]:

$$\frac{\mathscr{F}^{(d)}}{N_2} \equiv F(x) = wx - \frac{\lambda x^2}{2} - T\Big[-2x\ln x - (1-x)\ln(1-x) + x\ln\frac{\chi N_1}{N_2} + \Big(x - \frac{N_1}{N_2}\Big)\ln\Big(1 - \frac{N_2 x}{N_1}\Big)\Big]. \quad (5)$$

The corresponding equation of state derived from the condition $\partial F/\partial x = 0$ has the form[2)]:

$$\frac{x^2}{(1-x)\,[(N_2/N_1)-x]} = \chi \exp\Big(-\frac{w-\lambda x}{T}\Big). \quad (6)$$

Relations similar to (5) and (6), which differ in details inessential for the treatment below, have been employed in a number of studies.[57-62,93,95] Let us offer another remark on the cited relationships, which we shall analyze below, following Refs. 63 and 64.

In Refs. 85 and 86 an expression for the energy $E(x)$ having the following form has been employed in place of (4):

$$E(x) = N_2\Big(wx - \frac{\lambda f(x)}{2}\Big). \quad (4')$$

Here we assume with respect to $f(x)$ only that $f(x) = f'(x) = 0$ for $x = 0$, and that $f(x)$ is a monotonic function in the interval $[0, 1]$. Here it turned out that the behavior of a system with its energy in the form (4′) is qualitatively very similar to that obtained in the case $f(x) = x^2$. Accordingly we can assume that the analysis performed below possesses a sufficient degree of generality.

Equations (1), (5), and (6) contain a complete formulation of the problem of the thermodynamic behavior of superionic crystals within the framework of models of the type employed in the theoretical studies.[57,66]

3. DISORDERING PHASE TRANSITIONS CAUSED BY INTERACTION OF DEFECTS

Let us assume, following Refs. 63 and 64, that $N_1/N_2 \gg 1$, and that the quantity χ does not depend on the temperature (as will be seen from the material below, these assumptions are not essential). In this case we always have $N_1/N_2 \gg x$, and Eqs. (5) and (6) acquire the form

$$F(x) = wx - \frac{\lambda x^2}{2} - T\,[x(1+\ln\nu) - x\ln x^2 - (1-x)\ln(1-x)], \quad (7)$$

$$1 - x = \nu^{-1}x^2 e^{(w-\lambda x)/T}, \quad (8)$$

or

$$\frac{T}{\lambda} = \frac{\tilde{x} - x}{\ln[\nu(1-x)/x^2]}. \quad (9)$$

Here we have $\nu \equiv \chi N_1/N_2$ and $\tilde{x} \equiv w/\lambda$. The behavior of the system being studied is fully determined by the two dimensionless parameters ν and $\tilde{x}$. We note that, although $N_1/N_2 \gg 1$, the parameter ν can vary over the interval from 0 to ∞ owing to the factor χ. If we consider that the quantity λ generally can be either positive or negative, then $\tilde{x}$ varies over the interval $(-\infty, \infty)$. Thus, if we introduce the $(\tilde{x}, \nu)$ parameter plane into the treatment, then each concrete thermodynamic system (crystal undergoing disorder) corresponds to some point in the region $0 < \nu < \infty$, $-\infty < \tilde{x} < \infty$. The jumpwise changes in x which are of greatest interest here can occur only if $\lambda > 0$, i.e., $0 < \tilde{x} < \infty$, i.e., in the first quadrant of the $(\tilde{x}, \nu)$ parameter plane. If we assume the crystal to be fully ordered at low enough temperatures ($x \to 0$ as $T \to 0$), then, as is implied by (7), we have $\lambda/2 < w$, i.e., $1/2 < \tilde{x} < \infty$. The interval $0 < \tilde{x} < 1/2$ corresponds to the situation in which x is close to unity at low temperatures. As $T \to \infty$, we obtain from (8), apart from the dependence on the value of $\tilde{x}$, $x_\infty^2/(1 - x_\infty) = \nu$. Here we have $x_\infty = x(T \to \infty)$, with $0 \leqslant x_\infty \leqslant 1$.

Let us first analyze qualitatively the behavior of the system. If $\lambda = 0$, then (8) coincides with the equation that we get from (3) upon taking account of the substitution $w \to w - T\ln\chi$ and the condition $N_1/N_2 \gg 1$. Here (and also when $\lambda < 0$), Eq. (8) has one solution [Fig. 3(a)]. However, for sufficiently large λ, as we see from Fig. 3(a), Eq. (8) [or (9)] has three roots ($x_1 \leqslant x_2 \leqslant x_3$) in the interval $0 \leqslant x < 1$. If the equation of state has a single root, then the free energy treated as a function of x (for fixed T) has a single minimum at the value of x corresponding to this root [Fig. 3(b)]. 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 exists in whichever of the two states (x_1 and x_3) corresponds to the absolute minimum of $F(x)$. The state x_2 corresponds to the maximum of $F(x)$ and hence is unstable. Upon varying T the curve $F(x, T)$ is deformed, so that at certain temperatures $T = T_{tr}$ the value $F[x_1(T)]$ proves to be equal to $F[x_3(T)]$. The latter implies that a phase transition takes place in the system, whereby the quantity x changes jumpwise from x_1 to x_3 (or from x_3 to x_1).

Thus a necessary condition for a transition is the appearance of an inflection point in the function $F(x)$, which corresponds to the appearance of roots of the function $\partial^2F/\partial x^2$. Equation (7) implies that

$$\frac{\partial^2 F}{\partial x^2} = -\lambda + T\Big(\frac{2}{x} + \frac{1}{1-x}\Big). \quad (10)$$

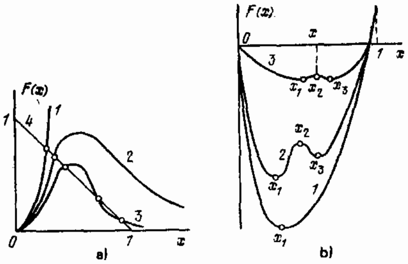

FIG. 3. (a) Graphical solution of the equation of state (8), and (b) the corresponding $F(x)$ relationship as given by (7). a) The function $f(x) = x^2\nu^{-1}\exp[(w - \lambda x/\tilde{T}]$ (1—$\lambda = 0$; 2, 3—$\lambda > 0$; 4—straight line $1 - x$); b) 1—single solution of Eq. (8); 2, 3—three solutions of the equation of state; $x_* = 2 - \sqrt{2}$.

[2)] If the crystal is at constant pressure p, then we must replace the quantity w in (5) with $h = w - pv_0$, which is the enthalpy of formation of a defect. Here v_0 is the free volume of formation of a defect. We note further that the quantity $\chi = \exp(s_f/k)$, where s_f is the entropy of formation of a defect, and k is the Boltzmann constant.

Equation (10) implies that the values of λ/T that correspond to the appearance of real roots of the equation $\partial^2F/\partial x^2=0$ are determined by the inequality $\lambda/T > \xi$, where $\xi=3+2\sqrt{2}$. When $\lambda/T=\xi$, the single real root $x=x_*=2-\sqrt{2}$ arises. The numbers ξ and x_* do not depend on the parameters ν and x, and are invariants of the problem. They are precisely what determines the behavior of the system in the case of "weak" transitions. Phase transitions are termed weak when the jumpwise change in x is small: $x_3-x_1 \ll 1$. Evidently, in this case all three roots of the equation of state (8) are close together [see Fig. 3(b), curve 3]. The transition occurs when the curve $F(x)$ is symmetrical about the point $x=x_*$ in its vicinity: precisely here, evidently, we have $F(x_1)=F(x_3)$. This condition requires fulfillment of the equality $\partial F/\partial x|_{x=x_*}=0$. This determines the temperature T_{tr} of the weak transition:

$$T_{tr}^{(w)}=\frac{\lambda(\tilde{x}-x_*)}{\ln(\nu/\nu_*)}. \tag{11}$$

Here we have $\nu_*=x_*^2/(1-x_*)$; numerically $\nu_*=2(\sqrt{2}-1)\simeq 0.828$. Substitution of the value $T_{tr}^{(w)}$ into the equality $\lambda/T=\xi$ yields the equation of the critical curve in the $(\tilde{x},\nu)$ parameter plane:

$$\nu_{w}=\nu_* e^{\xi(\tilde{x}-x_*)}. \tag{12}$$

Weak transitions are realized with varying T in systems whose representative points lie near the critical curve of (12). Here, as we can easily convince ourselves, these points must lie to the left of it if $\nu>\nu_*$, and to the right of it if $\nu<\nu_*$. Upon being "generated" on this curve, weak transitions are "strengthened" upon moving away from it into the corresponding region (Fig. 4).

Now let us treat "strong" transitions, in which $x_1 \ll 1$, while $x_3=1-\varepsilon$, with $\varepsilon \ll 1$. Equation (8) implies that

$$x_1=\sqrt{\nu}e^{-w/2T}, \quad x_3=1-\nu^{-1}e^{(w-\lambda)/T}. \tag{13}$$

We see from (13) that strong transitions can be realized when $\lambda\tilde{x}/2T \gg 1$, and $\lambda(1-\tilde{x})/T \gg 1$. In the case $x_1 \ll \varepsilon$, i.e., $1/2<x<2/3$, we obtain approximately from (5):

$$\begin{aligned} F(x_1)&=-2Tx_1+O(x_1^2),\\ F(x_3)&=\lambda\left(\tilde{x}-\frac{1}{2}\right)-T(1+\ln\nu)+O(\varepsilon). \end{aligned} \tag{14}$$

When we take into account the fact that $F(x_1)=F(x_3)$ at the transition point, Eqs. (13) and (14) yield an equation for the temperature of the strong transition:

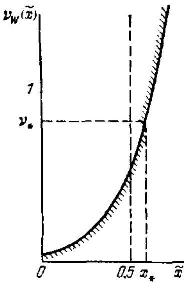

FIG. 4. Critical curve $\nu_w(\tilde{x})$ for creation of weak transitions (the hatching marks the regions where weak transitions are realized).

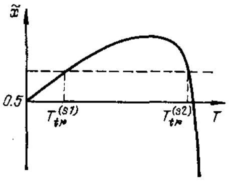

FIG. 5. Diagram of the graphical solution of Eq. (15) in the case in which two transitions exist.

$$\lambda\left(\tilde{x}-\frac{1}{2}\right)=T_{tr}^{(s)}\left(1+\ln\nu-2\sqrt{\nu}e^{-\lambda\tilde{x}/2T_{tr}^{(s)}}\right). \tag{15}$$

The last term in the parentheses on the right-hand side of (15) is necessarily much smaller than unity. Therefore, if the quantity $1+\ln\nu>0$ is not small, (15) has the single solution

$$T_{tr}^{(s,1)}=\frac{\lambda[\tilde{x}-(1/2)]}{1+\ln\nu_t}, \tag{16}$$

This gives the temperature of the strong transition.

At the same time, if the condition $0<1+\ln\nu \ll 1$ is satisfied, then, as we can easily see, Eq. (15) has two solutions (Fig. 5) for small enough values of the differences $\tilde{x}-1/2$. The first of them is approximately given by (16) and the second by the expression

$$T_{tr}^{(s,2)}=\frac{\lambda\tilde{x}}{2}\left(\ln\frac{2\sqrt{\nu}}{1+\ln\nu}\right)^{-1}. \tag{17}$$

As we see from Fig. 5, as the quantity $\tilde{x}-1/2$ increases, the solutions $T_{tr}^{(s,1)}$ and $T_{tr}^{(s,2)}$ approach one another and merge, so that there are no solutions beyond some critical value $\tilde{x}=\tilde{x}_{cr}$ at which $T_{tr}^{(s,1)}=T_{tr}^{(s,2)}$.

Thus, if $0<1+\ln\nu \ll 1$ and $1/2<\tilde{x}<\tilde{x}_{cr}(\nu)$, in any case two strong transitions occur in the system and are separated by the temperature interval $\Delta T=T_{tr}^{(s,1)}-T_{tr}^{(s,2)}$.

The result obtained from the example that we have discussed is of fundamental significance, and it pertains to a broad class of thermodynamic systems. In this connection, let us take up the general study of the existence in a system of double transitions[87,88] (bitransitions).

At a certain value of the parameters and temperatures there are three functions $x(T)$. Therefore, $F[T,x(T)]$ constitutes a many-valued function of T. The 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. 6).

In analyzing the conditions for "creation" (or disappearance) of a weak transition that was given above [see (10)–(13)], in essence we employed the system of equations

$$\frac{\partial F}{\partial x}=0, \quad \frac{\partial^2 F}{\partial x^2}=0, \quad \frac{\partial^3 F}{\partial x^3}=0. \tag{18}$$

This determines the critical curve $\nu_w(\tilde{x})$ in the parameter plane and also the temperature that corresponds to creation (or disappearance) of the transition on this curve. The presented system of equations (18) is fully analogous to that traditionally employed for studying

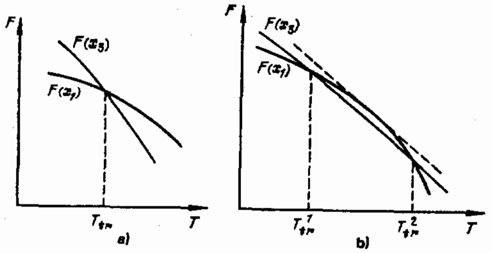

FIG. 6. Schematic shape of the $F(T)$ relationship corresponding to the solutions $x_1(T)$ and $x_3(T)$. a) The curves $F(x_1)$ and $F(x_3)$ intersect once (T_{tr} is the temperature of the transition), b) the curves $F(x_1)$ and $F(x_3)$ intersect twice ($T_{tr}^{(1)}$ and $T_{tr}^{(2)}$ are the temperatures of the transitions; dotted lines—the curves touch, and the values of $T_{tr}^{(1)}$ and $T_{tr}^{(2)}$ merge).

first-order phase transitions within the framework of a single equation of state[76,78,89]; here the meaning of the quantity x is determined by the specifics of the system. Figure 6(a) corresponds to single phase transitions whose conditions of creation are described by the equations (18).

At the same time, in principle a pair of transitions can be created (or disappear). The corresponding conditions are determined by the contact of the two branches of the $F(x)$ curve:

$$F(T,\ x_1(T)) = F(T,\ x_3(T)),$$
$$\frac{\mathrm{d}}{\mathrm{d}T}F(T,\ x_1(T)) = \frac{\mathrm{d}}{\mathrm{d}T}F(T,\ x_3(T)). \tag{19}$$

Together with the equation of state $\partial F/\partial x = 0$, the two equations of (19) define a type of critical conditions substantially differing from those of (18). These conditions define a critical curve (or curves) $\nu_b(x)$ in the parameter plane, as well as the temperature of creation (or disappearance) of the bitransition on this curve.

The treatment conducted above—cf. (15)–(17)—illustrates the fact that the critical conditions of (19) can be realized in the system under study.

Let us stress that, in the general case in analyzing problems involving phase transitions, we must take into account the possibility of realizing formulated conditions that correspond to the appearance in the system of bitransitions (see, e.g., Ref. 90).

Without taking up here the detailed calculation of the corresponding critical curve for a system under study,[63,64] let us point out only that the curve of creation (or disappearance) of bitransitions joins points in the $(\tilde{x},\nu)$ parameter plane that have the coordinates (x_*,ν_*) and $(1/2, e^{-1})$ (Fig. 7).

One can conveniently analyze the possible $x(T)$ relationships by using the equation of state in the form of (9). We can easily see that the function $T(x)$ vanishes at three points: $x=0$, $x=1$, and $x=\tilde{x}$. Thus, in the low-temperature region there are formally always three solutions of Eq. (9); $x_1(T) \leqslant x_2(T) \leqslant x_3(T)$. Here, if $\tilde{x} < 1$, they all lie in the physical interval $[0,1]$; if $\tilde{x} > 1$, one solution lies in the interval $[0,1]$. As we can easily see, at high enough T there is always only one solution, which asymptotically approaches the value x_∞. Thus a transition occurs from three solutions at

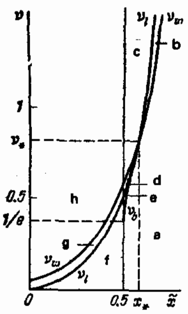

FIG. 7. The $(\tilde{x},\nu)$ parameter plane. Here ν_w, ν_b, and ν_l are the critical curves—cf. (12), (19), and (20).

$T=0$ to one solution at $T=\infty$. Topologically this can occur upon merger of any two solutions with increasing temperature. Thus these solutions form a closed loop (Fig. 8).

If $\tilde{x} < x_\infty$, then the solutions x_1 and x_2 form a closed loop and it lies below the asymptotic value x_∞; if $x > x_\infty$, the closed loop corresponds to the solutions x_2 and x_3 and lies above the value $\tilde{x} = x_\infty$. Thus the condition $\tilde{x} = x_\infty$ describes a certain additional characteristic curve in the $(\tilde{x},\nu)$ parameter plane. As Eq. (8) implies, we have $\tilde{x}_\infty^2/(1-x_\infty)=\nu$. Therefore the equation of the curve $\tilde{x}=x_\infty$ has the form

$$\nu_l = \frac{\tilde{x}^2}{1-\tilde{x}}. \tag{20}$$

When ν and $\tilde{x}$ lie to the left of this curve in the parameter plane, the loops lie below, or above when they lie to the right.

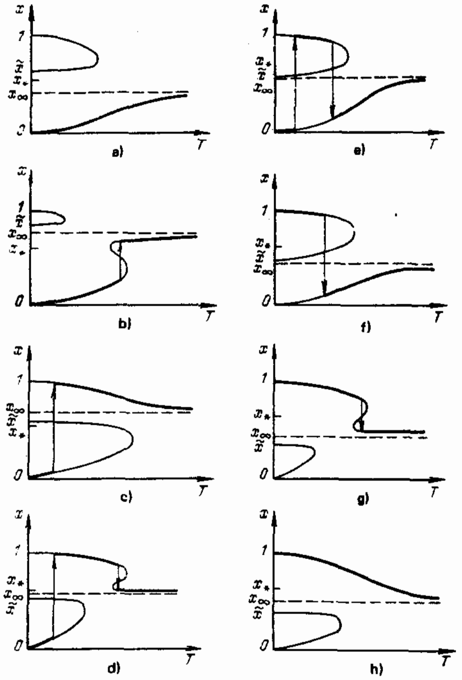

FIG. 8. Schematic shapes of the possible solutions of the equation of state and the transitions between solutions. Heavy lines—realizable regimes, arrows—transitions between them.

Now let us present the whole picture of the behavior of the system in the $(\tilde{x}, \nu)$ parameter plane—Fig. 7. The three critical curves ν_w, ν_b, and ν_1 and the straight line $\tilde{x}=1/2$ divide the parameter plane into eight regions.

In the region (a), which lies to the right of the curves ν_w and ν_b and the line $x=1/2$, there are no transitions, and x increases monotonically from the value $x=0$ at $T=0$ to $x=x_\infty$ as $T\to\infty$. This region corresponds to Fig. 8(a), and if $1/2<\tilde{x}<1$, the loops lie below the value $x=1$, i.e., in the physical region of the parameters. If $\tilde{x}>1$, there are no loops. Although there is no jumpwise change in $x(T)$ here, the existence of the interaction can substantially increase the steepness of the $x(T)$ curve as compared with the corresponding curve for ordinary ionic crystals.

Upon crossing the curve ν_w, we arrive in the region (b) [see Fig. 8(b)]; here a single transition is realized in the S-shaped region of the lower branch of the curve. The transition is weak in the immediate vicinity of the curve ν_w (where the S-shaped region is created), and it strengthens as $\tilde{x}$ decreases.

We note that, on the curve ν_w itself, the first-order phase transitions being discussed degenerate into second-order phase transitions.

Upon crossing the curve ν_1, which corresponds to shifting the loop to the lower side, we arrive in region (c) [see Fig. 8(c)], which is bounded by the curves ν_w, ν_1, and the line $\tilde{x}=1/2$.

A jump in the concentration in a phase transition in the S-shaped region [as, e.g., in region (b)] cannot involve jumping through the value $x=x_\infty$ (although the difference x_3-x_1 need not be small in such a transition). In region (c) the phase transition involves the looped curves. In the general case this transition is necessarily accompanied by a jump through the value $x=x_\infty$. Therefore one of the states necessarily has a concentration x greater than x_∞. In agreement with Ref. 91, we shall call transitions accompanied by crossing of the asymptote supertransitions. Thus one transition is realized in region (c), which is a supertransition. It can be either strong (when $\tilde{x}$ is close to $1/2$) or weak (when $\tilde{x}$ is close to x_* and ν close to ν_*).

Upon crossing the curve ν_w, we pass into region (d). Since a weak transition arises to the right of ν_w, when we enter region (d), we "acquire" a second transition [Fig. 8(d)] involving the appearance of an S-shaped region in the upper branch of the curve. Thus two transitions are realized in region (d), one of them being a supertransition.

Upon crossing the curve ν_b, we arrive in the region (e) between the curves ν_b, ν_1, and the line $\tilde{x}=1/2$. This is precisely the region described by Eqs. (16) and (17)—two strong transitions. Generally two supertransitions are realized in region (e) [Fig. 8(e)]. Finally, upon crossing curve ν_b, we arrive again in region (a).

We see from comparing Figs. 8(a) and (e) that the curves of the solutions in regions (a) and (e) are topologically equivalent, while the two supertransitions [see Fig. 8(e)] in region (e) approach one another as we approach the curve ν_b, and both of them vanish as we cross it.

Now let us turn to the case $\tilde{x}\leqslant 1/2$. As we have already pointed out, now the quantity x is close to unity in the low-temperature region. In region (f) [see Fig. 8(f)], the curves of the solutions are topologically equivalent to those corresponding to regions (a) and (e) [see Figs. 8(a), (e)]. However, the starting point now is $x=1$. Hence a single supertransition is realized here with increasing temperature, accompanied by a jumpwise change in x. In region (g) [see Fig. 8(g)], a single transition occurs in the S-shaped region of the upper curve. Finally, in region (h) the system lies on the upper curve for all T, and there are no transitions.

We stress that the existence of double transitions essentially involves the asymmetry of the system being treated: the number of cationic nodes does not equal the number of equivalent interstitial positions $(N_1\neq N_2)$. When $N_1=N_2$ (symmetric systems), the equation of state (8) is reduced to the form

$$\frac{x}{1-x}=\sqrt{\nu}\exp\left(-\frac{w-\lambda x}{2T}\right). \tag{21}$$

This special case has been analyzed in detail in Ref. 92 and later in Ref. 57. We can easily convince ourselves that the value x_* corresponding to the appearance of three close-lying solutions proves in the symmetric system to be $x_*=1/2$, and there is no interval of values $1/2<\tilde{x}<x_*$ that corresponds to the possible realization of two transitions. Therefore in a symmetric system there are either no transitions or a single transition. One can obtain its temperature for any values of the difference x_3-x_1 from (11) by substituting $x_*=1/2, \nu_*=1$:

$$T_{\mathrm{tr}}^{\mathrm{sym}}=\frac{\lambda\,[x-(1/2)]}{\ln\nu}. \tag{22}$$

The case $N_1\gg N_2$ that we have treated is "asymmetric in the extreme." However, evidently, the results presented here continue to hold in the general case of asymmetry $N_1\neq N_2$—Eqs. (5) and (6).

We note also that the peculiar degeneracy possessed by the symmetric system $N_1=N_2$ is also removed upon deviation from the quadratic interaction law $\lambda x^2/2$.[85,86]

The thermodynamics of disordering of one of the sublattices has been discussed[93] under somewhat more general assumptions within the framework of similar model hypotheses. Here the number of ions subject to disordering can be either smaller or larger than the number of low-energy positions (nodes). In essence, the same model was treated later in Ref. 94, and also in Ref. 95, where "weak" transitions at a special value of the parameters N_1/N_2 were analyzed in detail.

The effect of impurities at low concentration, which create extra energy levels, on the temperature of phase transitions has been analyzed theoretically.[96]

4. POLYMORPHIC TRANSITIONS ACCOMPANIED BY DISORDERING

It was assumed in the theoretical studies discussed above[57-66,85-88,92-96] that interaction between defects plays the determining role in the process of disordering of one of the sublattices, while the sublattice that conserves the "rigidity" of the crystal remains invariant or undergoes a change of secondary type. Experimental indications exist (see, e.g., Refs. 13, 97, 98) that this is precisely the situation in a number of cases. At the same time, crystals exist in which a rearrangement of the fixed sublattice (polymorphic transition) occurs simultaneously with the disordering and apparently plays the central role.[1,13] Thus, in the general case the processes of disordering and of polymorphic transition in the rigid sublattice prove to be correlated.

The usual treatment of polymorphic transitions in crystals rests on concepts of an interconnection between the rearrangement of the lattice and the phonon spectrum of the crystal as the physical principle that gives rise to the transition.[99,100]

Namely, as the crystal is heated, the contribution of the phonon subsystem to the free energy increases. Hence, at a certain temperature, a transition of the whole crystal to another, higher-energy modification becomes thermodynamically favorable, with simultaneous "disposal" of the energy of the lattice vibrations. However, if the polymorphic transition is accompanied by a substantial disordering of one of the sublattices, we can assume that the thermodynamics of the transition is governed specifically by the disordering process, while the role of the change in the phonon contribution to the free energy is relatively small. In other words, situations can exist in which polymorphic transitions undergone by one of the sublattices of an ionic crystal are due to the disordering of another of its sublattices.

Phase transitions that occur by the stated mechanism have been treated in Refs. 67 and 101. Later, an essentially analogous idea has been employed in Refs. 102 and 103. Let us examine two crystalline modifications (α and β) between which a polymorphic transition occurs as the temperature is varied.[3)] The free energy $\mathcal{F}_{\alpha,\beta}$ of each modification can be represented, in line with Eq. (1), in the form

$$\mathcal{F}_{\alpha,\beta}=\mathcal{F}^{(0)}_{\alpha,\beta}+\mathcal{F}^{(d)}_{\alpha,\beta}. \tag{23}$$

Initially let us assume that the interaction in the system of defects is inessential. Then the quantities $\mathcal{F}^{(d)}_{\alpha,\beta}$ that enter into (23) are given for each of the modifications by Eq. (7), where $\lambda=0, w=w_{\alpha,\beta}$, and $\nu=\nu_{\alpha,\beta}$, while the quantities $x_{\alpha,\beta}$ that characterize the degree of disordering of each of the modifications are given by equations that follow from (8):

$$\frac{x_\alpha^2}{1-x_\alpha}=\nu_\alpha e^{-w_\alpha/T},\qquad \frac{x_\beta^2}{1-x_\beta}=\nu_\beta e^{-w_\beta/T}. \tag{24}$$

Upon using (24) and (7) with $\lambda=0$, we can rewrite the expressions for $F_{\alpha,\beta}\equiv\mathcal{F}^{(d)}_{\alpha,\beta}/N_2$ in the form

$$F_{\alpha,\beta}=T\,[\ln(1-x_{\alpha,\beta})-x_{\alpha,\beta}]. \tag{25}$$

The quantities $x_{\alpha,\beta}$ are determined by the equations (24), and hence $F_{\alpha,\beta}$ depends on $w_{\alpha,\beta}$ and $\nu_{\alpha,\beta}$.

The polymorphic transition between the different modifications of the crystal occurs under the condition that the free energies should be equal: $\mathcal{F}_\alpha=\mathcal{F}_\beta$. Upon taking (23) into account, we can write this condition in the form

$$\mathcal{F}^{(d)}_\beta-\mathcal{F}^{(d)}_\alpha=\mathcal{F}^{(0)}_\alpha-\mathcal{F}^{(0)}_\beta\equiv\delta\mathcal{F}^{(0)}. \tag{26}$$

As $T\to 0$, the quantity $\delta\mathcal{F}^{(0)}$ is determined by the difference of internal energies of the crystal modifications α and β, which arises from purely structural factors. In the general case at $T\neq 0$, the quantities $\mathcal{F}^{(0)}_{\alpha,\beta}$ contain a contribution from the phonon components, and hence they depend on the temperature. This situation leads to the polymorphic transitions in typical ionic crystals. On the other hand, compounds can exist, in particular superionic crystals, in which the difference $\mathcal{F}^{(0)}_\alpha-\mathcal{F}^{(0)}_\beta$ proves to be a very weak function of the temperature (in any case this is true at low enough temperatures).

In considering the treatment of polymorphic transitions under conditions in which the variation of the contribution of the phonon components in the $\alpha-\beta$ transition is inessential, while the transition is primarily due to disordering, we shall assume that

$$\delta\mathcal{F}^{(0)}=\mathcal{F}^{(0)}_\alpha-\mathcal{F}^{(0)}_\beta=N_2\Delta. \tag{27}$$

Here Δ is a constant that does not depend on the temperature.

Thus, upon taking (25) into account, Eq. (26) implies the following relationship at the transition point:

$$T^{(p)}_{tr}\left[\ln\frac{1-x_\beta}{1-x_\alpha}-(x_\beta-x_\alpha)\right]=\Delta. \tag{28}$$

Together with (28), the equations of (24) enable one to determine the temperature $T^{(p)}_{tr}$ of a polymorphic transition accompanied by disorder and the concentrations $x_\beta\,(T^{(p)}_{tr})$ and $x_\alpha\,(T^{(p)}_{tr})$ of interstitial cations before and after the transition.

According to (24), the functions $x_{\alpha,\beta}(T)$ increase monotonically with increasing T from $x=0$ at $T=0$ to $x^\infty_{\alpha,\beta}$ at $T=\infty$. Further, as is implied by (25), since the functions $F_{\alpha,\beta}$ decline monotonically with increasing $x_{\alpha,\beta}$, the $F_{\alpha,\beta}$ are monotonically decreasing functions of the temperature. If, in particular, we have $x^\infty_\alpha>x^\infty_\beta$ (which corresponds to $\nu_\alpha>\nu_\beta$), then as $T\to\infty$ the curve $F_\alpha(T)$ has a steeper slope than the curve $F_\beta(T)$. Hence, if $\Delta>0$, then there necessarily must be an intersection (which is the only one) of the curves $F_\alpha(T)+\Delta$ and $F_\beta(T)$. This corresponds to the existence of a single solution of the system of equations (24) and (28)—cf. Fig. 9. Analogously there is a single solution if $\nu_\alpha<\nu_\beta$ and $\Delta<0$.

Evidently, with an arbitrary relationship among the parameters, three situations are topologically possible: the curves $F_\alpha(T)$ and $F_\beta(T)$ do not intersect; they intersect once; or they intersect twice (Fig. 9).

This corresponds to the lack of solutions (transitions), the existence of a single solution (transition), or the existence of two transitions.

The problem has been studied in detail[67] with application of the critical conditions (19). As before, depend-

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[3)] It is not essential for what follows and hence is not fixed precisely which index (α and β) denotes the low-temperature modification of the crystal.

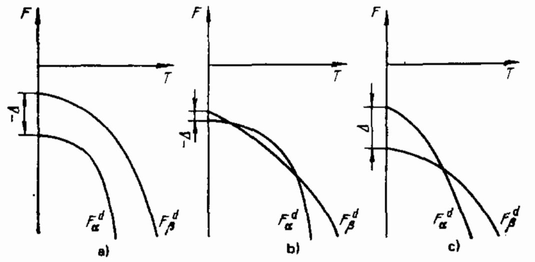

FIG. 9. Schematic illustration of the relative arrangement of the curves $F_\alpha(T)$ and $F_\beta(T)$. For the sake of definiteness we set $w_\alpha > w_\beta$, $\nu_\alpha > \nu_\beta$. a) There are no solutions, b) two transitions exist, c) single transition.

ing on the values of Δ, $\nu_{\alpha,\beta}$, and $w_{\alpha,\beta}$, it proves convenient to characterize the system by a point on a certain parameter plane. Here this plane is divided by the characteristic curves into separate regions. In principle the choice of this type of plane is ambiguous, and is governed by questions of convenience. If, in particular, we introduce the parameter plane $(\nu_\alpha - \nu_\beta, \Delta)$, the coordinate axes bound the regions of existence of single transitions, and thus constitute the characteristic curves (Fig. 10). The region of existence of two transitions is bounded by the coordinate axes and by the critical curve, which starts at the point $\Delta_0 = x_\infty (w_\beta - w_\alpha)$ on the Δ axis (where $x_\alpha^\infty = x_\beta^\infty = x^\infty$) and asymptotically approaches the $\nu_\alpha - \nu_\beta$ axis. Analytic expressions for describing the shape of the curve of double transitions is contained in Ref. 67.

Let us take up in greater detail the thermodynamic characteristics of an individual transition (we take an "individual" transition to mean either a single transition or one of a pair). The temperature T_p is found by substituting the solutions $x_{\alpha,\beta}$ of Eq. (24) into (28). In the most important limiting cases, the solutions of the transcendental equation that one obtains are found in explicit form.

If the energy of rearrangement of the lattice is relatively large ($|\Delta| > w_{\alpha,\beta}$), the transition occurs in the region of relatively high temperatures ($T > w_{\alpha,\beta}$), where the $x_{\alpha,\beta}$ are approximately equal to their asymptotic values $x_{\alpha,\beta}$. In this case one obtains the following for $T_{\mathrm{tr}}^{(\mathrm{p})}$:

$$T_{\mathrm{tr}}^{(\mathrm{p})} = \Delta\left[\ln\frac{1-x_\beta^\infty}{1-x_\alpha^\infty} - (x_\beta^\infty - x_\alpha^\infty)\right]^{-1}. \tag{29}$$

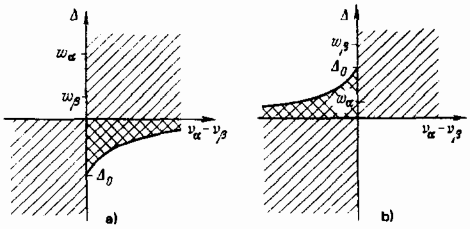

FIG. 10. Parameter plane $(\nu_\alpha - \nu_\beta, \Delta)$. a) $w_\alpha > w_\beta$, b) $w_\alpha < w_\beta$. In the unhatched regions there are no transitions. A single transition exists in the singly-hatched regions, and two transitions in the doubly-hatched regions.

The temperature $T_{\mathrm{tr}}^{(\mathrm{p})}$ is positive (and hence describes a real transition) when $\Delta > 0$ and $x_\alpha^\infty > x_\beta^\infty$, and when $\Delta < 0$ and $x_\alpha^\infty < x_\beta^\infty$. The discussed high-temperature transition mainly arises from the entropy terms $(-TS_{\alpha,\beta})$ in the free energies of the α- and β-modifications. We stress that here the degree of disordering can vary quite considerably. In particular, if $x_\alpha^\infty \ll 1$, while $x_\beta^\infty \lesssim 1$ (or $x_\alpha \lesssim 1$, while $x_\beta^\infty \ll 1$), we can set $x_\alpha^\infty = 0$ (or $x_\beta^\infty = 0$) in Eq. (29). In the limit as $x_\beta \to 1$, according to (24) and (29), we have the following in the case $\Delta < 0$:

$$T_{\mathrm{tr}}^{(\mathrm{p})} = \frac{|\Delta|}{1+\ln\nu_\beta}. \tag{30}$$

The expression (30) is an analog of the expression (16) given above for the temperature $T_{\mathrm{tr}}^{(\mathrm{s},1)}$ of a strong transition involving disordering caused by interaction between defects in the absence of rearrangement of the fixed sublattice.

If the energy of rearrangement Δ is small ($|\Delta| < w_{\alpha,\beta}$), the transition occurs at relatively low temperatures $T_{\mathrm{tr}}^{(\mathrm{p})} < w_{\alpha,\beta}$. Here we have $x_{\alpha,\beta} \approx \sqrt{\nu_{\alpha,\beta}}\exp(-w_{\alpha,\beta}/2T)$. If we assume that $\Delta < 0$ and $w_\alpha > w_\beta$ for the sake of definiteness, so that $x_\beta \gg x_\alpha$, then Eq. (28) implies that

$$2T_{\mathrm{tr}}^{(\mathrm{p})}\sqrt{\nu_\beta}\, e^{-w_\beta/2T_{\mathrm{tr}}^{(\mathrm{p})}} = -\Delta.$$

An approximate solution of this equation is

$$T_{\mathrm{tr}}^{(\mathrm{p})} = \frac{w_\beta}{2\ln(w_\beta\sqrt{\nu_\beta}/|\Delta|)}. \tag{31}$$

The overall pattern of the dependence of the concentration of disordered ions on the temperature (for the case $w_\alpha > w_\beta$ for definiteness) is shown in Fig. 11 for various values of $\nu_\alpha - \nu_\beta$ and Δ. As we see from Fig. 11, the $x_\alpha(T)$ and $x_\beta(T)$ relationships can either intersect [Fig. 11(a)–(c)—half-plane $\nu_\alpha > \nu_\beta$ in Fig. 10(a)] or not [Fig. 11(d), (e)—half-plane $\nu_\alpha < \nu_\beta$ in Fig. 10(a)]. Double transitions are realized only when the curves $x_\alpha(T)$ and $x_\beta(T)$ intersect. Here the temperatures of both transitions lie below the temperature of the intersection $T_0 = (w_\alpha - w_\beta)/\ln(\nu_\alpha/\nu_\beta)$. Single polymorphic transitions are realized both when the curves $x_\alpha(T)$ and $x_\beta(T)$ do not cross and when they do. In the latter case the transition temperature necessarily lies above T_0. The temperature of the single transition [see Fig. 11(c), (d)] is

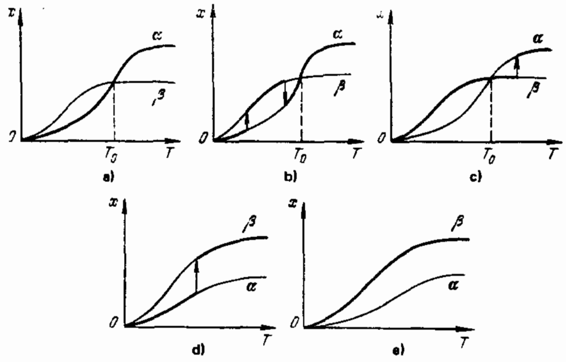

FIG. 11. Typical relationships of the concentrations of interstitial ions $x_{\alpha,\beta}$ to the temperature T and diagrams of polymorphic transitions ($w_\alpha > w_\beta$). Heavy lines—realizable regimes, arrows—transitions between them. Cases a–c) correspond to cases a–c) in Fig. 9.

given by the formulas (29) [in the special case of (30)] if the quantity $|\Delta|$ is large enough, or by the formula (31) (if the quantity $|\Delta|$ is small enough). In the case of a bitransition [Fig. 11(b)], the lower temperature for small $|\Delta|$ is also given by the formula (31), while the higher temperature is close to T_0.

Thus, polymorphic transitions can be closely connected with disordering of one of the sublattices of the crystal. In the case of "ordinary" crystals, the main observable effect is specifically a polymorphic transition with a relatively small change in ionic conductivity. In the case of superionic crystals, the main effect can prove to be a strong jumpwise change in the ionic conductivity accompanied by a polymorphic transition.

Let us now briefly take up the question of what extra features arise in phase transition accompanied by disordering under conditions in which both factors discussed above (interaction between point defects and rearrangement of the fixed sublattice) make comparable thermodynamic contributions toward generating these transitions.[101]

Upon using the equation of state (6) for each of the modifications α and β with the appropriate values of the parameters $N_{1,2}$, χ, w, and λ, we can rewrite the expression (5) for the free energy of disordering in these modifications in the form

$$F_{\alpha,\beta}=\frac{\lambda_{\alpha,\beta}x^2_{\alpha,\beta}}{2}+T\left\{\ln(1-x_{\alpha,\beta})+\left(\frac{N_1}{N_2}\right)_{\alpha,\beta}\ln\left[1-x_{\alpha,\beta}\left(\frac{N_2}{N_1}\right)_{\alpha,\beta}\right]\right\}. \tag{32}$$

The function $F_{\alpha,\beta}$ depends on T and on the parameters of the system, not only explicitly, but also via $x_{\alpha,\beta}$, according to Eq. (6). The polymorphic transition between the α- and β-modifications occurs when the condition (26) is satisfied. However, now we must bear in mind the fact that, under certain conditions, (discussed in detail in Sec. 3), the equation of state in each of the modifications can have three solutions $0\leq x_1\leq x_2\leq x_3\leq 1$. Two of these, x_1 and x_3, correspond to minima of $F_{\alpha,\beta}$ treated as a function of x, while the middle solution x_2 corresponds to maxima of $F_{\alpha,\beta}$ and hence is unstable. Disordering without change in the structure of the fixed component (phase transition within one modification) corresponds to the conditions

$$F_\alpha(x_{\alpha1}(T))=F_\alpha(x_{\alpha3}(T)) \text{ and } F_\beta(x_{\beta1}(T))=F_\beta(x_{\beta3}(T)).$$

Transitions accompanied by change in crystalline modification occur at temperatures determined by solving any of the following equations:

$$F_\alpha[x_{\alpha1}(T),T]=F_\beta[x_{\beta3}(T),T], \tag{33a}$$

$$F_\alpha[x_{\alpha3}(T),T]=F_\beta[x_{\beta1}(T),T], \tag{33b}$$

$$F_\alpha[x_{\alpha1}(T),T]=F_\beta[x_{\beta1}(T),T], \tag{33c}$$

$$F_\alpha[x_{\alpha3}(T),T]=F_\beta[x_{\beta3}(T),T]. \tag{33d}$$

Here the $F_{\alpha,\beta}$ are determined by (23) with (32) taken into account.

Equations (23), (32), and (33) give rise to a general equation for the temperature of polymorphic transitions involving *disordering:*

$$T^{(p)}_{tr}\left\{\ln\frac{1-x_\beta}{1-x_\alpha}+\left(\frac{N_1}{N_2}\right)_\beta\ln\left[1-x_\beta\left(\frac{N_2}{N_1}\right)_\beta\right]-\left(\frac{N_1}{N_2}\right)_\alpha\ln\left[1-x_\alpha\left(\frac{N_2}{N_1}\right)_\alpha\right]\right\}-\frac{\lambda_\alpha x^2_\alpha}{2}+\frac{\lambda_\beta x^2_\beta}{2}=\delta\mathscr{F}^{(0)}/N_2. \tag{34}$$

The functions $x_{\alpha,\beta}(T)$ that enter into (34) are solutions ($x_{\alpha1}$ or $x_{\alpha3}$ and $x_{\beta1}$ or $x_{\beta3}$) of Eq. (6) for the appropriate modification.

Let us assume that a polymorphic transition occurs between the α and β modifications with a relative degree of disordering in the β modification higher than in the α modification—case (33a). Upon assuming that $x_{\alpha1}\ll 1$, while $x_{\beta3}=1-\varepsilon_\beta$, with $\varepsilon_\beta\ll 1$, and using Eqs. (13) and (34) to obtain the temperature $T^{(p)}_{tr}$ of the polymorphic transition ($\alpha\to\beta$ or $\beta\to\alpha$), we have[101]

$$T^{(p)}_{tr}=\frac{[w_\beta-(\lambda_\beta/2)]-(\delta\mathscr{F}^{(0)}/N_2)}{\eta_\beta}. \tag{35}$$

Here we define

$$\eta_\beta\equiv\ln\left[\chi_\beta\left(\frac{N_1}{N_2}\right)_\beta\right]+\left[1-\left(\frac{N_1}{N_2}\right)_\beta\right]\ln\left[1-\left(\frac{N_1}{N_2}\right)_\beta\right].$$

Formula (35) is a generalization of (16) and transforms into it when the quantity $\delta\mathscr{F}^{(0)}/N_2$ is small and $(N_1/N_2)\gg 1$.

Figure 12 shows the schematic form of the temperature-dependences of the quantities x_α and x_β.

As before [cf. (17)], for certain values of the parameters in the crystal, a pair of genetically associated polymorphic transitions (a bitransition) can be realized and develop according to the scheme $\alpha\to\beta\to\alpha$ [cf. Fig. 12(b)].

Case (33b) is fully analogous to (33a). In particular, the corresponding temperature is obtained from (35) by replacing $\beta\to\alpha$.

In case (33c), if $x_{\alpha,\beta}\ll 1$, the terms describing the interaction between the defects in each modification (proportional to $x^2_{\alpha,\beta}$) can be omitted. Correspondingly the behavior of the crystal is analogous to that treated in the preceding section. Finally, case (33d) also can be easily analyzed[101] under the assumption that $x_{\alpha,\beta}=1-\varepsilon_{\alpha,\beta}$, with $\varepsilon_{\alpha,\beta}\ll 1$. Without taking this up in more detail here, we point out only that in the two latter cases, as in the first two, the jumpwise change in the actual number of interstitial ions is generally not at all small. In particular, if $N_{2\alpha}\neq N_{2\beta}$, then, even though $x_\alpha\approx x_\beta\approx 1$, the quantities $n_\alpha=N_{2\alpha}x_\alpha$ and $n_\beta=N_{2\beta}x_\beta$ can differ very substantially.

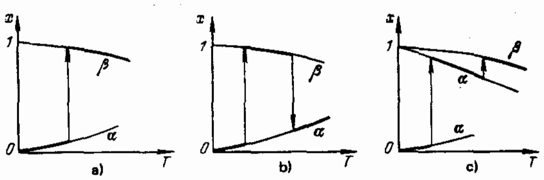

FIG. 12. Possible relationships of $x_{\alpha,\beta}$ to the temperature T in "strong" polymorphic transitions with account taken of the interaction between defects. Heavy lines—realizable regimes, arrows—transitions between them. a) Single transition, b) bitransition, *c) two successive transitions.*

The polymorphic transition can be preceded by jumpwise disordering within the low-temperature modification. In this case an additional disordering can arise from the polymorphic transition, so that the overall form of the temperature-dependence of the concentration of interstitial ions constitutes a curve with two "steps" [see Fig. 12(c)]. This type of $x(T)$ relationship differs qualitatively from those discussed above.

Finally, one can show within the framework of the overall scheme [see (33) and (34)] that, for certain values of the parameters in the crystal, three correlated polymorphic transitions are realized, occurring in the sequence $\alpha \to \beta \to \alpha \to \beta$ or $\beta \to \alpha \to \beta \to \alpha$.

5. EXPERIMENTAL DATA ON PHASE TRANSITIONS IN SUPERIONIC CONDUCTORS

The most thorough comparison of the conclusions of the theory with experiment requires data on the temperature-dependence of the excess heat capacity involved with disordering in the vicinity of phase transitions in superionic conductors. The numerous measurements of the temperature course of ionic conductivity accompanied by a jumpwise change also make it possible to draw conclusions on the features of the thermodynamic behavior of these materials.

One can derive from the various theoretical models the variation $x(T)$ of the concentration and use it to calculate the value of the heat capacity of disordering. We should note that the experimentally measured heat capacity is composed of the heat capacity of the defect-free crystal and the "excess" heat capacity involving disorder. Correspondingly, in processing the experimental data to find this excess heat capacity, one must subtract the contribution from the heat capacity of the defect-free crystal. Usually one does this by choosing a definite model for describing the phonon spectrum (see, e.g., Ref. 48).

Within the framework of the model of disordering caused by interaction between defects, we have the following expression for the heat capacity C_V at constant volume per particle[4)] [62,93]:

$$C_V = k\left(\frac{w}{T}\right)^2\left(1-\frac{\lambda x}{w}\right)\left[\frac{2m+(m+1)x}{x(1-x)(m-x)}-\frac{\lambda}{T}\right]^{-1}. \qquad (36)$$

Here k is the Boltzmann constant and $m \equiv N_1/N_2$. The expression given here is considerably simplified in the case of strong transitions. Upon assuming, moreover, that $m \gg 1$, we obtain from (36):

$$C_V = \begin{cases} \dfrac{k}{2}\left(\dfrac{w}{T}\right)^2 \nu^{1/2} e^{-w/2T}, & T < T_{\mathrm{tr}}^{(\mathrm{s})}, \\ k\,\dfrac{(w-\lambda)^2}{T^2}\,\nu^{-1} e^{(w-\lambda)/T}, & T > T_{\mathrm{tr}}^{(\mathrm{s})}. \end{cases} \qquad (36')$$

The first attempt to process experimental data[48] on the heat capacity of the superionic conductor Ag_4RbI_5 in the vicinity of the phase transition at 122 K by the formulas of (36′) was undertaken in Ref. 61. In Ref. 62 formula (36) was used to process the data analogously for a number of superionic conductors—AgI, Ag_4RbI_5, Ag_2S, etc. As an example, Fig. 13 compares the theoretical [according to (36)] and experimental C_V curves for AgI. As we see from Fig. 13, and also from analogous data on other materials, one can satisfactorily fit the low-temperature regions of the $C_V(T)$ relationships. The deviation in the temperature region above the phase transition apparently involves the fact that a polymorphic transition occurs simultaneously with the disordering, and contributes to the jump in C_V at $T = T_{\mathrm{tr}}^{(\mathrm{s})}$.

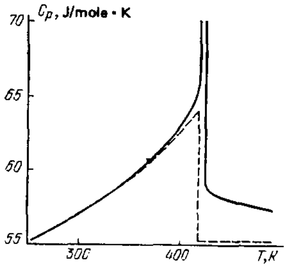

FIG. 13. Comparison of the experimental and theoretical curves for the heat capacity of disordering in Ag_2S.[62]

The data on the heat capacity in the vicinity of the transition at 122 K in Ag_4RbI_5 have been processed[104] by using a model of the polymorphic transition but without taking into account the interaction of defects (see Sec. 4). According to this model, the heat capacity C_V of disordering is described by an expression that stems from (24) and (25):

$$(C_V)_{\alpha,\beta} = k\,\frac{w_{\alpha,\beta}\,x_{\alpha,\beta}(1-x_{\alpha,\beta})}{T^2(2-x_{\alpha,\beta})}. \qquad (37)$$

Figure 14, which is taken from Ref. 103, shows a processing of the data that illustrates the qualitative agreement of theory and experiment for the excess heat capacity of Ag_2S. Figure 15, taken from Ref. 105, shows this for Ag_2Se within the framework of the model of a polymorphic transition.

Besides direct thermodynamic measurements, a number of studies has investigated other features of the behavior of superionic conductors that also can yield information on the thermodynamics of disordering. The temperature anomalies of the ionic conductivity of the superionic crystal Ag_4RbI_5 have been studied[106] in the vicinity of the phase transition at $T = 209$ K. Thorough study on monocrystalline specimens showed that a small jump in ionic conductivity occurs in the vicinity of this temperature (in contrast to the break that was studied by prior investigators—see, e.g., Ref. 5). This jump was interpreted as manifesting a first-

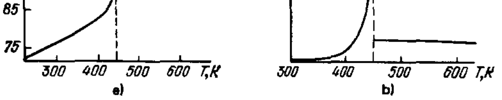

FIG. 14. Comparison of the experimental (a) and theoretical (b) curves for the heat capacity of disordering in AgI.[103]

[4)] In line with what we have said above—see footnote[2)]—one obtains the value of C_p by replacing w with h. Actually for solids the quantities C_p and C_V differ very little.

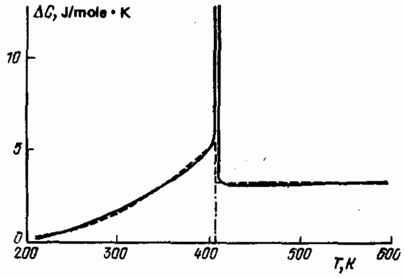

FIG. 15. Comparison of the experimental and theoretical curves for the heat capacity of disordering for Ag_2Se.[105]

order phase transition ("weak" in the terminology of Sec. 1).

Subsequent processing of the data on the conductivity jump using the variations found for this transition made it possible to find the values of the thermodynamic parameters $w = 5.6\times10^{-2}$ eV and $\lambda = 9.6\times10^{-2}$ eV for the superionic conductor Ag_4RbI_5. These values proved to be close to those found[61] by processing the heat capacity data near the phase transition in the same compound at 122 K ($w = 6\times10^{-2}$ eV, $\lambda = 10^{-1}$ eV).

The data on the ionic conductivity of high-temperature superionic conductors of the fluorite type (CaF_2, SrF_2, $SrCl_2$) obtained in Ref. 107 have been compared[59,96] with theoretical models describing the thermodynamics of disordering. It was shown[59] within the framework of the concepts of disordering presented in Sec. 3 that first-order temperature phase transitions can be realized in these compounds. A calculation was performed[95] with account taken of the fact that there is practically no jump in the conductivity σ. It showed that the first-order transition degenerates into a second-order transition for certain relationships among the parameters. Here one can expect, in agreement with the experimental data, that the $\sigma(T)$ relationship will show a sharp bend, rather than a jump. We note that actually the calculation performed in Ref. 95 simply corresponds to a choice of the parameters characterizing the system in which they lie near the critical curve ν_w in the parameter plane (Figs. 4 and 7) that corresponds to generation of weak transitions.

The $\sigma(T)$ relationship has been studied[109] in Na_2WO_4 crystals. It was found that the behavior of $\sigma(T)$ can indicate the existence of two close-lying first-order phase transitions accompanied by an increase, then a decrease, in the ionic conductivity (Fig. 16). This type of behavior qualitatively agrees well with the concepts discussed above that bitransitions can be realized in disordering systems.[87,88] Another experimental indication that bitransitions can exist in superionic crystals of $Ag_{21}I_{16}WO_{16}$ was found in Ref. 108, where the temperature-dependence of Raman scattering was studied.

We point out also that, in line with the results discussed in Sec. 4, multiple transitions can exist, whose diagrams prove in a number of cases to be rather complex. Individual polymorphic transitions can follow disordering transitions that occur within the framework of a single crystal modification, and also precede such transitions. The multiple changes observed in a number of superionic crystals in the nature of the ionic conduction correspond qualitatively to the complex pattern that was derived.

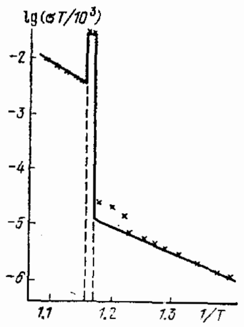

FIG. 16. Temperature-dependence of the ionic conductivity for the compound Na_2WO_4.[109]

6. THE EFFECT OF JUMPWISE VARIATION OF THE IONIC CONDUCTIVITY INDUCED BY AN ELECTRIC FIELD

The preceding sections have discussed ion disordering as a function of the temperature of the crystal. At the same time the degree of disorder can generally be altered by the action of external fields.

The possibility of disordering in an electric field of a surface layer of a crystal having a thickness of the order of the Debye screening length, involving the redistribution of mobile carriers, has been discussed in Ref. 110.

The thermodynamics of disordering of one of the sublattices throughout the volume of a crystal placed in an external electric field was first analyzed theoretically in Ref. 111. This study showed that a jumpwise change in the concentration of interstitial ions in a crystal can arise at a certain critical value of the field. A somewhat different mechanism, which also leads to ion disordering in the bulk of the crystal under the action of an electric field, has been treated in Ref. 112. In this type of phase transition induced by an electric field, the ionic conductivity of the crystal must also vary in jumpwise fashion. An effect of this type was first detected experimentally in Ref. 113.

The theory developed in Ref. 111 of a phase transition induced by an electric field to a state of superionic conductivity is based on concepts of the substantial role of the interaction of a Frenkel' defects in the crystal and of the effect of the electric field on the energy of formation of defects.

When an electric field is applied to a crystal, the energy of transfer of a cation to an adjacent interstice depends on the direction and intensity $\mathscr{E}$ of the electric field. In the simplest case all the interstitial positions in the unit cell can be classified into two groups: those lying in the direction of the field, and against the field. For interstices of the first type the energy of formation will be diminished: $w_1 - w - de\mathscr{E}$, while it will be increased for interstices of the second type: $w_2 = w$

$+de\mathscr{E}$. Here d is of the order of the characteristic dimension of the unit cell of the crystal.

In treating the thermodynamics of disordering, we must now take into account the fact that in an electric field ions are distributed over interstices of the two types and over the lattice positions. Let us denote by x_1 and x_2 the occupancies of the interstices of the first and second type. Then, within the framework of the mean-field approximation, we can derive an expression for the free energy of disordering[111]:

$$F = E(x_1, x_2) - (x_1 - x_2)\, de\mathscr{E}$$
$$- T\left[(x_1 + x_2)\ln\frac{\nu}{2} - x_1 \ln x_1 - x_2 \ln x_2 - (1 - x_1 - x_2)\ln(1 - x_1 - x_2)\right]. \tag{38}$$

Here E is the internal energy of the system undergoing disorder. The conditions of thermodynamic equilibrium $\partial F/\partial x_1 = 0$ and $\partial F/\partial x_2 = 0$ imply that

$$\frac{x_1}{1 - x_1 - x_2} = \frac{\nu}{2}\exp\left[-\frac{w(x_1, x_2) - de\mathscr{E}}{T}\right], \tag{39}$$

$$\frac{x_2}{1 - x_1 - x_2} = \frac{\nu}{2}\exp\left[-\frac{w(x_1, x_2) + de\mathscr{E}}{T}\right]. \tag{40}$$

Here $w(x_1, x_2)$ is the energy of formation of a defect in the absence of the electric field. In the simplest model that takes into account the interaction of defects, the function w is linear: $w = w_0 - \lambda(x_1 + x_2)$.

The system of equations (39)–(40) determines the equilibrium occupancies of the interstices of the first and second types $x_1(\mathscr{E})$ and $x_2(\mathscr{E})$. Investigation shows that the functions $x_1(\mathscr{E})$ and $x_2(\mathscr{E})$ have a many-valued region for sufficiently large values of λ/T. Here, at the critical value of the electric-field intensity, a phase transition must be realized, accompanied by a jump in x_1 and x_2.

By adding Eqs. (39) and (40) for $w = w_0 - \lambda(x_1 + x_2)$ we can derive an equation that gives the dependence on the electric-field intensity of the total occupancy of the interstitial positions $x = x_1 + x_2$:

$$\cosh(de\mathscr{E}/T) = \frac{x}{(1 - x)\nu}\exp\left(\frac{w_0 - \lambda x}{T}\right). \tag{41}$$

The right-hand side of (41) amounts to the function $f(x)$, which has a maximum and a minimum for sufficiently large values of λ/T. Correspondingly the $x(\mathscr{E})$ relationship has a many-valued region (Fig. 17). One can find the critical condition for λ/T from the conditions $df/dx = 0$ and $d^2f/dx^2 = 0$, and it gives $\lambda/T \geqslant 4$. This condition coincides with the condition for many-valued character of the $x(T)$ relationship as defined by Eq. (21) (Fig. 17).

Since the $x(\mathscr{E})$ relationship has an S-shaped region, and correspondingly so do the $x_1(\mathscr{E})$ and $x_2(\mathscr{E})$ relationships, x_1 and x_2 must vary in jumpwise fashion at some critical value of the electric-field intensity. The condition for the transition is that the free energies of the corresponding states should be equal:

$$F(x_1^{(1)}(\mathscr{E}), x_2^{(1)}(\mathscr{E}), \mathscr{E}) = F(x_1^{(3)}(\mathscr{E}), x_2^{(3)}(\mathscr{E}), \mathscr{E}). \tag{42}$$

The critical electric-field intensity that gives rise to the phase transition, as defined by Eq. (42) as well as (39)–(41), is given by the relationship

$$\ln\cosh\frac{de\mathscr{E}_{\rm tr}}{T} = \frac{w_0 - (\lambda/2)}{T} - \ln\nu. \tag{43}$$

If, moreover, the condition is satisfied that $de\mathscr{E}_{\rm tr} > T$, Eq. (43) implies that

$$de\mathscr{E}_{\rm tr} = w_0 - \frac{\lambda}{2} - T\ln\frac{\nu}{2}. \tag{44}$$

When the condition $de\mathscr{E}_{\rm tr} < T$ is satisfied, one can derive the following expression from (43):

$$de\mathscr{E}_{\rm tr} = \sqrt{2\left(w_0 - \frac{\lambda}{2}\right)T - 2T^2\ln\nu}. \tag{45}$$

Thus the analysis that we have conducted shows that, when one applies an electric field to a crystal, one can bring about a jumpwise disordering of the cation sublattice at a certain critical value of the field. This leads to an increase in the concentration of interstitial cations throughout the volume of the crystal.

The investigation performed in Ref. 111 allows us to conclude that a highly-conductive state of a crystal can be attained by a "melting" of the cation sublattice induced by an electric field that occurs without heating the crystal. Moreover, an analysis of the behavior of the system at values of the parameters that do not allow temperature-dependent phase transitions, while a field-induced phase transition can be realized, implies that the state of superionic conductivity is attainable in crystals that cannot be brought into the highly conductive state by heating alone.

A relatively simple model of the distribution of the cations over the interstitial positions and a very simple interaction law in the system of Frenkel' defects were employed in Ref. 111. One can easily see that all the derived laws must be conserved also in more complex models that take into account the attractive interaction of defects and a more complicated structure of the interstitial positions.

For example, let the crystal possess several (l) groups of interstices that are differently arranged with respect to the direction of the electric field. Then a treatment analogous to that in Ref. 111 yields a system of equations for the occupancies of the interstices:

$$\frac{x_i}{1 - \sum\limits_{m=1}^{l} x_m} = \nu_i \exp\left(-\frac{w_0 - \mathbf{d}_i e\vec{\mathscr{E}} - \sum\limits_{m=1}^{l}\lambda_{im}x_m}{T}\right). \tag{46}$$

The solutions of the system of equations (46) have the same characteristic features as the system of equations (39)–(40). Just as in the case of the simplest model, applying an electric field to the crystal lowers the effective energy of formation of a defect and renormalizes the entropy factor. The model of jumpwise

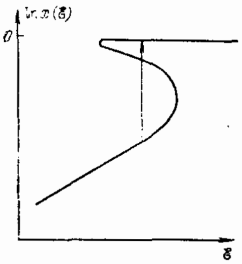

FIG. 17. Schematic shape of the $x(E)$ relationship as defined by Eq. (41) for $\lambda/T > 4$.

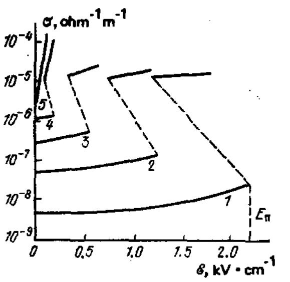

FIG. 18. Dependence of the electric conductivity σ of crystals of α-$AgSbS_2$ on the electric field intensity E.[144] The temperature T((K)=300 (1), 345 (2), 390 (3), 440 (4), and 500 (5).

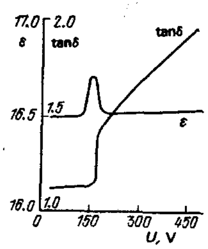

FIG. 19. Dependence of the dielectric properties of the crystal α-$AgSbS_2$ on the displacement voltage at the frequency 20 MHz.[114] $T = 300$ K.

disordering of a sublattice of the crystal that was treated in Ref. 111 also permits generalizations that allow for a rearrangement of the fixed sublattice of the crystal occurring simultaneously with disordering.

The first experimental data on detection of a phase transition in ionic crystals induced by an electric field and accompanied by a jump in ionic conductivity were published in Refs. 113–115.

Figure 18 shows the results of measuring the electric conductivity of α-$AgSbS_2$ as a function of the electric-field intensity $\mathscr{E}$ at different temperatures. At relatively small fields the conductivity σ is practically independent of $\mathscr{E}$. The authors associate this with the predominance in this field-intensity region of the electronic component of σ. With further increase in $\mathscr{E}$ ($\mathscr{E} > 300$ V/cm), one observes a linear increase in σ, which they ascribe to an increase in the ionic component caused by the gradual disordering of the cationic Ag^+ sublattice in the electric field. In this region the ionic conductivity already begins to predominate over the electronic conductivity.

When a critical value of the field intensity is reached, one observes a jumpwise increase in the conductivity, here of ionic character, by a factor of 6.2×10^3. This behavior agrees with the concepts discussed above of the jumpwise disordering of an ionic sublattice. When the electric field is removed, the highly conductive state of the crystal is "remembered." The time of transition from the high-conductivity state back to the low-conductivity state for α-$AgSbS_2$ at $T = 300$ K amounts to $t_\alpha = 24$ h.[113] With increasing temperature the value of t_α decreases. In just the same way, as we see from Fig. 18, the value of the critical field for the jumpwise transition and the amplitude of the jump decrease. As Eqs. (45) and (46) imply, the stated regularities also agree with the theoretical views presented in Refs. 111 and 112.

The observed effect is accompanied by anomalies in the behavior of the effective dielectric permittivity ε of the crystal and the tangent of the dielectric loss angle $\tan\delta$. Figure 19 shows the variation in crystals of α-$AgSbS_2$ of the capacitance[114] at the frequency of 20 MHz, which is related to ε by the formal relationship $C = \varepsilon/4\pi d$ (d is the dimension of the specimen), as a function of the displacement potential $U = \mathscr{E}d$ at $T = 300$ K. This figure also shows the variation of $\tan\delta$. As we see by comparing the cited relationships with the dependence of the logarithm of the dc current I through the specimen as a function of U, the anomalies in ε and $\tan\delta$ are unambiguously associated with the jump in the ionic conductivity at the critical field value.

As we know, the jumpwise disordering in ionic conductors that arises when the critical temperature is reached is accompanied by an anomalous behavior of the elastic properties of the crystal.[116,117] Similar anomalies have been found under the action of a field.[118] The velocity v of propagation and the damping coefficient α of ultrasonic waves at different intensities of the electric field applied to the crystal were measured by the method described in Ref. 119. It was found that α sharply increases while v declines in the vicinity of the critical value of $\mathscr{E}$. These data agree qualitatively with the model of Ref. 116, which associates the damping coefficient of ultrasound with the concentration of defects in the crystal. As was pointed out in Ref. 118, they agree with the concepts of a sharp change in the concentration of interstitial ions in the vicinity of a phase transition induced by an electric field.

Thus, the aggregate of the theoretical and experimental studies performed up to now indicates the possible appearance at critical electric fields of a jumpwise disordering of an ionic sublattice accompanied by a jumpwise variation in the ionic conductivity.

In closing we note that the set of phenomena that we have discussed above requires further painstaking study. Further, we stress that the described effect of jumpwise disordering induced by a field makes it possible in principle to realize the superionic state of a crystal at sufficiently convenient temperatures from the applied standpoint, e.g., room temperature, and this opens up interesting potentialities of practical utilization.

7. THERMODYNAMICS OF DOMAIN STATES IN SUPERIONIC CONDUCTORS

The high concentration of mobile ions in superionic conductors and the substantial role of interactions can lead to cooperative effects as well as jumpwise disordering. The former can also be manifested in the kinetics of charge transport. In particular, the interaction between the disordered ions can lead to formation

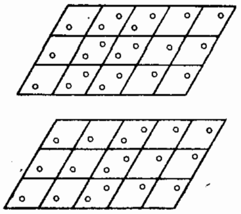

FIG. 20. Schematic view of the structure of domains formed by the distribution of the Na$^+$ cations according to the model of Ref. 130.

in the crystal of regions having short-range order, regions with an elevated or depressed concentration of interstitial ions, and more complex domain-type macroscopic structures.

Theoretical approaches to description of domain states in superionic conductors have been developed in a considerable number of papers.[120-130] A number of general problems associated with domain states in disordered crystals and with the possible experimental study of these states have been treated in Refs. 131–138. One of the first models of a domain distribution of Na$^+$ cations in the nonstoichiometric compound $Na_{1+x}Al_{11}O_{17}$ has been discussed in Ref. 130. It was considered in this model that the Na$^+$ cations are uniformly distributed in regions of β-Al_2O_3 of stoichiometric composition, which are separated by "walls" made of β-alumina containing double the amount of Na$^+$ cations as compared with β-Al_2O_3 (Fig. 20). The existence of small regions having an elevated content of Na$^+$ ions has been confirmed by x-ray data.[139]

Another domain model has been proposed to describe the distribution of Na$^+$ cations in the stoichiometric compound β-Al_2O_3.[120,126,127] It was proposed that the volume of the crystal is divided into a multitude of domains of two types, in each of which the Na$^+$ cations occupy a definite position. Here the Na$^+$ cations occupy positions of different types in adjacent domains. At the same time close-range order is realized in each domain in the distribution of carriers.

As the calculations of Ref. 126 show, the energy of a domain per cation can become low enough so that the domain wall can move with a low activation energy.

Concepts of the existence of microdomains in crystals of α-AgI and α-Ag_2S have been developed in Ref. 124, where it was noted that appreciable differences exist in the thermodynamic behavior of stoichiometric and nonstoichiometric α-AgI. These differences have been interpreted as resulting from domain ordering of the excess Ag$^+$ ions. According to Ref. 124, the ordering of the Ag$^+$ ions can lead with decreasing temperature to the formation of microdomains with a wall thickness much smaller than the characteristic dimensions of the domains themselves.

A thermodynamic theory that demonstrates the possibility of formation of domains in superionic crystals showing structural disordering has been developed in Refs. 128 and 129. Within the framework of the model of interacting defects (see Sec. 3), the expression for the free-energy density F can be written in the form

$$F=\mu_1^0x_1-\mu_2^0x_2-\frac{\lambda_1x_1^2}{2}-\frac{\lambda_2x_2^2}{2}-\lambda_{12}x_1x_2+T\,[x_1\ln x_1+(1-x_1)\ln(1-x_1)+x_2\ln x_2+(1-x_2)\ln(1-x_2)]+x_1T\ln Z_1-x_2T\ln Z_2. \tag{47}$$

In homogeneous states of the crystal, in which we have $x_1=x_2$ independently of the coordinates, upon taking into account the relationships $\chi=Z_1/Z_2$ and $\lambda=\lambda_1+\lambda_2+2\lambda_{12}$, Eqs. (47) transforms into (5) with $N_1=N_2$.

In (47) we have taken into account the fact that the concentrations x_1 and x_2 of interstitial cations and cation vacancies at an arbitrary point of the crystal do not agree. Moreover, they must satisfy the integral equation

$$\int_{\mathscr{V}}(x_1-x_1)\,d\mathscr{V}=0. \tag{48}$$

This corresponds to the equality of the total number of interstitial ions and vacancies in the entire volume $\mathscr{V}$ of the crystal.

The condition for thermodynamic equilibrium in a system with a variable number of particles (in this case interstitial cations and cation vacancies) corresponds to the minimum of the functional

$$\Omega=\int[F(x_1,\,x_2)-\mu_1x_1-\mu_2x_2]\,d\mathscr{V}. \tag{49}$$

Here $\mu_1=\partial F/\partial x_1$ and $\mu_2=\partial F/\partial x_2$ are the chemical potentials of the cations and vacancies.

The condition $\mu_1=\mu_2=\mu$ and (47) give rise to a system of equations that determine the functions $x_1(\mu,T)$ and $x_2(\mu,T)$:

$$\mu=w+T\ln\frac{x_1}{1-x_1}-T\ln Z_1-\lambda_1x_1-\lambda_{12}x_2, \tag{50}$$

$$-\mu=T\ln\frac{x_2}{1-x_2}+T\ln Z_2-\lambda_2x_2-\lambda_{12}x_1. \tag{51}$$

As the analysis performed in Refs. 128 and 129 showed, the functions $x_1(\mu,T)$ and $x_2(\mu,T)$ are many-valued in certain intervals of μ and of the temperature. By using the different branches of the solutions of $x_1(\mu,T)$ and $x_2(\mu,T)$, one can describe inhomogeneous states of the crystal that correspond to its subdivision into regions (domains) of two types. In regions of the first type we have $x_1>x_2$, but $x_2>x_1$ in regions of the second type, while the integral condition (48) is satisfied. The condition of minimum value of the functional Ω [cf. (49)] gives rise to a relationship connecting the values of the carrier concentrations x_1 and x_2 for the domains of the two different types (i and j), which are conjugate to one another:

$$F^i-\mu\,(x_1^i-x_2^i)=F^j-\mu\,(x_1^j-x_2^j). \tag{52}$$

The set of equations (47)–(52) enables one to determine the values of μ, x_1^i, x_2^i, x_1^j, and x_2^j, and to find the relationship between the volumes occupied by regions of the two types.

Investigation shows that the domain states of the type treated in Ref. 128 can be realized only in a certain region of the three-dimensional space of the interaction parameters λ_1, λ_2, and λ_{12}.

At relatively high temperatures the crystal always exists in a homogeneous state characterized by the condition $x_1 = x_2 = x$, where x is determined by an equation of state of the type of (6). At certain temperatures $T < T_d^{\max}$ the inhomogeneous state of the crystal corresponding to subdivision of the volume into domains of two types becomes thermodynamically more stable. The temperature $T_d^{\max}$ depends on the relationship among the parameters λ_1, λ_2, and λ_{12}. The inhomogeneous states of the crystal can exist down to $T = 0$ or, with certain relationships among the parameters, down to a certain minimum temperature $T = T_d^{\min}$, below which the homogeneous state again becomes thermodynamically more stable.

An interesting feature of the process of disordering involving inhomogeneous states is the possibility of "blocking" a phase transition when the temperature T_{tr} of the phase transition falls within the interval $[T_d^{\min}, T_d^{\max}]$ where domain states of the crystal are more stable.

At present there are as yet not enough quantitative data characterizing the properties of domain states of superionic crystals for comparing the theoretical views with experiment.

8. EFFECT OF PRESSURE ON PHASE TRANSITIONS AND CONDUCTIVITY OF SUPERIONIC CONDUCTORS

One can extract useful information on the mechanism of disordering in ionic crystals leading to a transition to a state of superionic conduction, and also on the kinetics of charge transport in superionic conductors, from experiments on the dependence of the properties of these materials on pressure.[140-146]

Since in many superionic crystals the transition to the highly conductive state is a first-order phase transition, the pressure-dependence of the transition temperature T_{tr} is described by the Clausius-Clapeyron relationship[147]:

$$\frac{dT_{tr}}{dP} = \frac{V_\beta - V_\alpha}{S_\beta - S_\alpha}. \tag{53}$$

Here $V_{\alpha,\beta}$ and $S_{\alpha,\beta}$ are the specific volumes and entropies of the α- and β-phases between which the transition occurs. If we take into account the fact that the different phases of the crystal generally possess different values of K_α and K_β of the isothermal compressibility, we can represent the relationship (53) in the form

$$\frac{dT_{tr}}{dP} = [V_\beta^0 - V_\alpha^0 - (V_\beta K_\beta - V_\alpha K_\alpha)P](S_\beta - S_\alpha)^{-1}. \tag{54}$$

Here the $V_{\alpha,\beta}^0$ are the values of the specific volumes at the pressure $P = P_0$ that we take as the initial pressure.

The experimental pressure-dependence of the transition temperature to the highly conductive state for the crystal Ag_4RbI_5, which takes place at atmospheric pressure at $T_{tr}^{(s,1)} = 122$ K, is shown in Fig. 21, which is taken from Ref. 140. The same diagram shows the data on the $T_{tr}^{(2)}(P)$ relationship for the "weak" transition at higher temperature in the same material, which occurs at atmospheric pressure at $T_{tr}^{(2)} = 218$ K.[5] Up to pressures of the order of 3×10^3 bar, the $T_{tr}^{(1)}(P)$ relationship proves linear (10^3 bar equals 0.1 GPa). At higher pressures the differences between the compressibilities of the γ and β phases begin to play a role. As is implied by Eq. (54) (where α plays the role of γ), this behavior can be explained by the greater specific volume of the β-phase as compared with the γ-phase and the greater value of the modulus of compressibility K_β than K_γ. The pressure-dependence of the temperature of the "weak" transition $T^{(2)}$ also can be processed by Eq. (54) and represented by a linear and by a quadratic term in P. However, the linear term proves here to be substantially smaller than in the case of the "strong" transition $T_{tr}^{(1)}$.

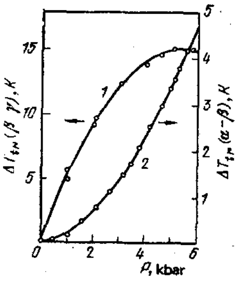

FIG. 21. Dependence of the temperatures T_{tr} of the phase transitions on the pressure P for the superionic conductor Ag_4RbI_5.[140] 1—$T_{tr}^{(1)}(P)$, 2—$T_{tr}^{(2)}(P)$.

Experiments on the effect of pressure on the temperature of transition to the highly conductive state for another typical superionic crystal AgI have been performed in Refs. 140 and 143. The transition temperature is described well by a linear relationship that corresponds to a decrease of the volume of the crystal by about 5.6% in going from the low-temperature β-phase to the α-phase at $T_{tr} = 420$ K.

Equation (53) can be also analyzed within the framework of the concepts discussed above on the thermodynamics of phase transitions under the condition that one specifies further details of the parameters of the theory. It was pointed out[57] that the volume of the crystal must also vary jumpwise when the change in the concentration of defects occurs jumpwise. If the transition is "strong", then the change in specific volume amounts to $v_0 N_2$, where v_0 is the "free volume" of formation of a single defect. Let us assume that the contribution of the polymorphic transition of the fixed sublattice to the thermodynamics of the transition is inessential (cf. Sec. 3) and employ Eq. (7) with account taken of (16) to find the value of $S_\alpha - S_\beta$, then we obtain from (53)[148]:

$$\frac{dT_{tr}}{dP} = \frac{N_2|v_0|T_{tr}}{w - \lambda/2} = \frac{N_2|v_0|}{\ln \nu + 1}. \tag{55}$$

In the simplest model the parameter ν is connected to the ratio of the vibration frequencies ω_2 of ions at

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[5] Historically the low-temperature transtion at $T_{tr}^{(1)}$ has been termed $\gamma \to \beta$, and the high-temperature transition at $T_{tr}^{(2)} \beta \to \alpha$, in line with the terminology for the three phases $\gamma \to \beta \to \alpha$.

the nodes to the frequencies ω_i at the interstital positions. If these frequencies vary similarly as functions of the pressure, then the denominator in (55) does not depend on P. Upon taking the linear dependence of v_0 on P into account, the function $T_{tr}(P)$ can actually be represented as the sum of linear and quadratic terms in P; cf. (54). Under more general assumptions this relationship generally does not hold. For example, if the frequencies $\omega_{1,2}$ depend on P according to the Grüneisen relationsip[147] $d\ln\omega_{1,2}/dV=\gamma_{1,2}$, with $\gamma_1\neq\gamma_2$, then the function $T_{tr}(P)$ also contains logarithmic terms.

We note that the values of the parameters entering into (54) and (55) are at present not yet known reliably enough for superionic conductors. We can only state with certainty that the quantity $|v_0|$ is anomalously high for a number of materials.[141]

In describing the effect of pressure on the conductivity of superionic conductors, until now use has been made only of the relations that arise from the standard theory of reaction rates[149-150] under the assumption of absence of collective effects, in particular, interactions between defects. Thus, in Ref. 140 the conductivity associated with a hopping mechanism for interstitial ions was written in the same form as for ordinary ionic crystals[6]:

$$\sigma=-\frac{ne^2}{T}\eta a^2\omega e^{-\Phi_m/T}. \qquad (56)$$

Here a is the hopping distance, ω is the mean frequency of approach to the activation barrier, which is usually identified with the Debye frequency ($\omega=\omega_D$), η is a steric factor of the order of several units, and Φ_m is the Gibbs free energy for the activation process. The quantity n (the concentration of interstitial ions) is written in Ref. 140 in the form $n=\sqrt{N_1N_2}\exp(-\Phi_f/2T)$, which corresponds to (6) in the limit $\lambda=0, x\ll 1$. Here Φ_f is the Gibbs free energy for formation of a defect. In line with general thermodynamic principles, we can represent the quantities Φ_f and Φ_m in the form

$$\Phi_f=w-Ts_f-Pv_0, \qquad (57)$$

$$\Phi_m=E_m-Ts_m-Pv_m. \qquad (58)$$

Here w, s_f, and v_0 are the energy, entropy, and volume for creation of an isolated defect, E_m, s_m, and v_m are the corresponding characteristics of the activation process within the framework of the theory of Ref. 149, and P is the pressure.

According to the relationship $V=-(\partial\Phi/\partial P)_T$ and (56)–(58), the total effect activation volume $v=(v_0/2)+v_m$ has the form

$$v=-T\left(\frac{\partial\ln\sigma}{\partial P}\right)_T+T\left(\frac{\partial\ln\omega}{\partial P}+\frac{2\partial\ln a}{\partial P}\right). \qquad (59)$$

The last two terms in (59) can be expressed in terms of the isothermal compressibility K and the Grüneisen constant. As a result one obtains the formula usually employed in processing the experimental data:

$$v=-T\left(\frac{\partial\ln\sigma}{\partial P}\right)_T+T\left(\gamma K-\frac{2}{3}K\right). \qquad (60)$$

If we assume that $v_0\ll v_m$, we can identify the quantity v with v_m.

There are two fundamental approaches to calculating theoretically the activation volumes v_m. One of them is carried out within the framework of the model of an elastic continuum,[151,152] and this leads to the relationship

$$v_m=\left[\left(\frac{\partial\ln G}{\partial P}\right)_T-K\right]\Phi_m. \qquad (61)$$

Here G is the shear modulus. Equation (61) allows further model simplifications upon associating G with the frequencies of acoustic phonons and then employing the Grüneisen relationship. The approach that we have described enables one to explain qualitatively the dependence of v_m on the macroscopic characteristics of the crystal. However, it can claim to agree with the experimental data only in order of magnitude.[152]

The other approach to calculating v_m is based on the dynamic theory of diffusional hopping.[153-155] Here the dependence of v_m on Φ_m is associated with the effect of the pressure on the effective frequency ω of the phonons that govern the process of activational hopping. Within the framework of this theory the dependence of v_m on Φ_m is given by the relationship

$$v_m=\frac{1}{\omega^2}\left(\frac{\partial\omega^2}{\partial P}\right)_T\Phi_m. \qquad (62)$$

Apparently the greatest contribution to the dynamics of ion hopping must arise from the short-wavelength optical modes.

However, currently there are no reliable data on the dependence of the frequency of optical phonons in superionic conductors on the pressure that would enable one to employ (62) for calculating v_m. Moreover, we note that the value of v_m can be extracted from a comparison of the data on the dependence of $\ln\sigma$ on P for crystals having intrinsic and impurity conduction based on the same ions (see, e.g., Refs. 160–161). In the latter case there is no contribution from v_0 to $(\partial\ln\sigma/\partial P)_T$.

If one knows v_m, one can determine v_0 from data on the pressure-dependence of the ionic conductivity. Comparison of v_0 with the molar volume v_s of the material (recalculated per molecule) makes it possible to decide on the type of point defects that govern the conductivity. In the case in which Frenkel' defects are formed, we usually have $v_0/v_s<1$, while for Schottky defects $v_0/v_s>1$.

Experimental studies have been performed[140] on the pressure-dependence of the ionic conductivity of Ag_4RbI_5 over a broad temperature range. It was found that the magnitude of the effect is very small in the highly conductive state, while the $\ln[\sigma(P)]$ relationships are nonlinear. The activation volumes were estimated by Eq. (60) from the experimental values of $(\partial\ln\sigma/\partial P)_T$ and the known[156,157] values of K and γ. In the low-temperature phase having low ionic conductivity, the magnitude of the effect proved considerably larger. Here one can calculate v_m by Eq. (60) while neglecting the contribution from the last terms. The total activation volumes

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[6] There are a number of misprints in the corresponding formula in Ref. 140.

proved respectively to be $v = -0.2$ cm^3/mole (for the β-phase of Ag_4RbI_5) and $v = 8$ cm^3/mole (γ-phase of Ag_4RbI_5 at 115 K). Analogous measurements for the superionic conductor AgI yielded values $v \approx 0.56$ cm^3/mole at 435 K (in the high-conductivity phase) and $v = -10$ cm^3/mole at 400 K in the low-conductivity phase.[7)]

Thus the values of v in the high-conductivity phases of Ag_4RbI_5 and AgI proved to be appreciably smaller than the values of v for the low-conductivity phases of the same compounds. The values of v in the high-conductivity phases also prove to be smaller than the values of the activation volumes in ionic crystals with conduction based on silver ions (AgBr, AgCl[158,159]), as well as a number of other ionic crystals. This fact can serve to indicate the substantial difference between the kinetics of ion transport in superionic conductors and ordinary salts.

9. CLOSING REMARKS

As is implied by the analysis of the results of the theoretical and experimental studies on the thermodynamics of superionic conductors, substantial progress has been made at present in understanding the physical essence of the phenomenon of superionic conductivity, although a number of important and interesting problems yet wait to be solved. An ever wider group of investigators in the field of theoretical physics, solid-state physics, physical chemistry, materials science, and in a number of applied fields is now becoming involved in the study of the various properties of these unusual materials. The problematics involved in the phenomenon of superionic conductivity has distinctly been singled out in recent years as an independent and rather extensive field of science.

At the same time, the thermodynamic aspect of superionic conduction is closely associated with a number of other rather well studied phenomena in solids, such as disordering in alloys, solid solutions, and ferroelectrics. In this regard we stress that some of the theoretical results discussed above, which involve first-order phase transitions in nonsymmetrical systems subject to disordering, directly pertain to a broader class of objects. In particular, results of this kind are the possible existence of bitransitions—two successive genetically associated first-order phase transitions in systems subject to disordering, and the possible induction of polymorphic transitions of crystal structures by the disordering of one of the sublattices of the crystal.

The effect of jumpwise change in the ionic conductivity induced by an external electric field may be of special interest—both from the purely scientific and the applied standpoints.

The intensively conducted studies on the structural, thermodynamic, and kinetic characteristics of superionic conductors unquestionably open up possibilities for more detailed analysis of the features and types of phase transitions in these materials.

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