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Dielectric constants of solid electrolytes and transition to superionic state

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A mechanism whereby an ionic conductor goes into the superionic state is proposed. The disordering of the cation sublattices, which consists of a shift of a cation from a site to one of the interstices of the same unit cell, if the number of the interstices is large, leads to an increase of the dielectric constant ε of the crystal, since dipoles consisting of interstitial and site cations are produced in the system in this case. On the other hand, the shift of cations from sites to interstices with increasing ε consumes less energy, because of the larger polarization of the medium by the dipole. As a result, with increasing T, a first-order phase transition from a state with low ε (ordered cation sublattice) into a state with high ε (disordered cation sublattice) can occur. At large ε, conditions become easier also for the production of carriers, i.e., of excess cations in other unit cells and of the vacancies that remain after their departure, since the Coulomb interaction between them becomes weaker. The jump of ε leads therefore to a jump in the conductivity.

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It is customary to single out from among the solid electrolytes the group of superionic conductors, which have relatively high ionic conductivity ($\sigma > 10^{-3}\Omega^{-1}\ \mathrm{cm}^{-1}$) above a certain temperature.[1] As a rule, the transition to the high-conductivity state proceeeds jumpwise, with the resistance changing by several orders of magnitude. This jump differs substantially from the insulator-metal phase transition in electronic conductors in that the resistance in the high-conductivity phase, just as in the low-conductivity phase, depends exponentially on the temperature, but the activation energy in the former is much lower than in the latter. A transition into the superionic state is accompanied simultaneously by partial disordering of the lattice, wherein the translational symmetry is lost in the arrangement of the cations that carry the current, but is preserved for the low-mobility anions (it is customary to speak of melting of the cation sublattice and preservation of the anion sublattice).

A characteristic feature of materials that can become superionic is the complexity of their crystallographic structure. The latter manifests itself, in particular, in the large number of equivalent unit-cell interstices to which a cation can go from its normal stable position. It must therefore be emphasized that, despite the prevailing opinion, the very melting of the cation sublattice still does not automatically lead to high conductivity. In fact, the charge transfer consists of a transition of cations from some unit cells to others, i.e., its necessary condition is the presence of "polar states"—unit cells with either excess or deficit of cations. Yet the loss of translational symmetry of the cations can take place also without the cations going from cell to cell—simply by the cation going into one of the interstices within the same unit cell. This kind of "melting" is similar in essence to the "order-disorder" phase transition in ferroelectrics which, as is well known, is usually not accompanied by high conductivity. The reason is that in typical ferroelectrics the energy needed to produce the excess cations and their vacancies is high. It can be lower in solid electrolytes, but certainly exceeds the energy needed by the cation to leave a site and go to an interstice in the same unit cell.

At the same time, the physics of the melting of the cation sublattice in solid electrolytes is not clear (it differs from the disorder in ferroelectrics in that in the latter the cations become redistributed among equivalent positions within the unit cell, whereas in solid electrolytes the moves are from sites to interstices). In the previously advanced theories[2,3] it is postulated that attraction exists between the cations in the interstices, so that when the number of cations increases formation of more remote defects of this type is facilitated and a first-order phase transition into a state with a molten cation sublattice becomes possible. The physical nature of the attraction, and whether it exists at all, remains unclear. It is therefore desirable to construct a theory of superionic conductors without using yet-unfounded hypotheses. The present paper is an attempt to construct such a theory. We emphasize that the mechanism proposed below for the

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conductivity of superionic conductors is very likely not to be the only possible one. The degree to which it is realistic can be assessed only by a detailed investigation of a large class of such materials.

The principal idea of the paper is the following. Although the disordering of the lattice as a result of the move of the cations from sites to interstices does not lead by itself to the appearance of carriers (excess cations and their vacancies), it does facilitate substantially their formation. The reason is that the disorder is accompanied by an increase of the dielectric constant ε of the crystal, and this weakens the Coulomb interaction between the cation that departed to another unit cell and the vacancy left behind. Thus, the problem reduces to a determination of the character of the temperature dependence of the dielectric constant. Since by definition the number of carriers (excess of cations and vacancies) per unit cell is small, their presence can be neglected in the calculation of $\varepsilon(T)$, and the crystal can be regarded as an insulator (this is permissible even at carriers densities $\sim 10^{20}-10^{21}$ cm^{-3}).

The increase of ε because of the transition of the cations from sites to interstices is due to the fact that each such transition produces in the crystal an equivalent dipole whose positive charge is in the interstice and the negative charge in the site. Since the number of interstices is large, the dipole orientation can be practically arbitrary, i.e., the dipole can align itself with the external electric field and increase the dipole moment of the system (in contrast to an ordinary ferroelectric, where the ion position in the interstices is described by an equivalent spin 1/2, the position of the ion in our case can be described by the classical spin). The departure of the cation to the interstice increases greatly the polarizability of the unit cell, since the length of the produced equivalent dipole is very large—of the order of the lattice constant. In essence, the system of equivalent dipoles in the crystal lattice is the analog of a solution of polar molecules in a nonpolar liquid.

The increase of the number of equivalent dipoles with rising temperature should be due to purely statistical causes, even if we disregard the interaction of the equivalent dipoles with one another. Their number must then increase continuously with temperature, and the cation sublattice should become disordered at temperatures $\sim\Delta/\ln z$, where Δ is the energy of the transition of the cation from the site to the interstice and z is the number of interstices in the unit cell. In the absence of interaction between the dipole, this disorder, not being a cooperative phenomenon, is likewise not a phase transition. The situation changes qualitatively if account is taken of the interaction between the produced dipoles, which lowers the dipole-production energy $\Delta(n)$ with increasing dipole concentration n. The resultant positive feedback between the dipoles can lead, under favorable conditions, to a first-order phase transition from a state with small ε and n into a state with large ε and n.

The reason for the decrease of $\Delta(n)$ with increasing n is that the neighboring dipoles are oriented relative to each other so as to ensure a gain in the energy of their interaction with one another. Assume that some dipole distribution is produced and a new dipole is created in some unit cell. Then the neighboring dipoles should turn somewhat, so that some correlation should arise in their directions, i.e., a short-range order should exist in the directions of the dipoles. But this, generally speaking, does not mean the appearance of a ferroelectric long-range order, although in some cases it is apparently possible. The situation here is similar to that realized in a gas of charged particles. Screening of the charge by other charges, which is precisely a manifestation of the short-range order and their arrangement, lowers the energy of the system, although no long-range order is produced in the gas.

We shall take into account the influence of the dipoles on one another in a self-consistent manner. The energy of their interaction with one another is represented as the energy of polarization, by the dipole, of a medium having a dielectric constant that depends on the dipole concentration. A similar approach is used in Onsager's theory of the dielectric constant of a gas of polar molecules (see, e.g., Ref. 4), but there the dipole concentration is assumed fixed, whereas here it is determined from the self-consistency equation.

The abrupt increase of the dielectric constant in the first-order phase transition should be accompanied by a jump in the number of carriers, since the energy of production of a pair of carriers (an extra cation and a vacancy), which is the result of the departure of the cation "its own" to a "foreign" interstice, is of the order of $e^2/\varepsilon a$, where a is the lattice constant. It must be noted that in addition to the number of carriers, the carrier mobility, which is of the hopping type in solid electrolytes, also depends exponentially on the temperature. The transition from one unit cell to the neighboring one is a classical above-barrier motion. The corresponding potential barrier is determined mainly by the short-range forces and apparently does not change substantially with increasing ε. Thus, a phase transition with a jump of ε leads to a jumplike increase in the number of carriers and accordingly of the conductivity; it is also accompanied by a jumplike decrease of the conduction-activation energy.

1. DIELECTRIC CONSTANT

We assume the following model of the structure of a solid electrolyte: for each cation site there are $z \gg 1$ energywise equivalent interstitial positions equidistant from the site (here and below, unless otherwise stipulated, we refer to the sublattice that becomes disordered, while the second sublattice ensures the rigidity of the crystal). We consider only the dipole excitations described above. Their number n per cation is equal to

$$n=\frac{z\exp[-\Delta(n)/T]}{1+z\exp[-\Delta(n)/T]}, \tag{1}$$

where the energy $\Delta(n)$ of an individual excitation is itself a function of n. Indeed, the dipole moment **P** which arises when an ion goes from a site to an interstice polarizes the dielectric medium and as a result gains an energy $-\mathbf{P}\cdot\mathbf{E}_\varepsilon$, where $\mathbf{E}_\varepsilon$ is the electric field produced at the dipole by the medium polarized by the dipole. Naturally, the intensity of this field depends on ε and consequently on n. Short-range forces can be regarded as independent of temperature, and then $\Delta(n)$ is given by

$$\Delta(n)=\Delta_0-\mathbf{P}\mathbf{E}_\varepsilon+\mathbf{P}\mathbf{E}_{\varepsilon_0}. \tag{2}$$

Here Δ_0 and ε_0 are the excitation energy and the dielectric constant as $T\to 0$, i.e., in the absence of ions in the interstices.

By virtue of the condition $z\gg 1$, these defects are regarded as classical dipoles. The electric field $\mathbf{E}_\varepsilon$ and the dielectric constant ε are calculated within the frame-framework of the Onsager model, which is the simplest formalism suitable for the description of polar dielectrics.[4] According to this model, a point dipole is placed at the center of a vacuum sphere with radius R (R is the order of the lattice constant a). The remainder of the crystal is regarded as a continuous medium with dielectric constant equal to the actual ε of the system. Within the framework of this model

$$\mathbf{E}_\varepsilon=2\frac{\varepsilon-1}{2\varepsilon+1}\frac{\mathbf{P}}{R^3}. \tag{3}$$

The polarizability of the system under consideration consists of the polarizability of the lattice in the absence of cations in the interstices and the polarizability of the system of dipoles produced as a result of the transitions of the cations into the interstices. The system is thus the analog of a solution of dipole molecules in a nonpolar liquid. According to the Onsager model, the dielectric constant is then determined from the equation[4]

$$\begin{gathered}\varepsilon-1=\frac{4\pi N\alpha_0}{1-f\alpha_0}g+\frac{4\pi nN}{3T}P^2g,\\ g=\frac{3\varepsilon}{2\varepsilon+1},\quad f=\frac{2(\varepsilon-1)}{(2\varepsilon+1)R^3},\end{gathered} \tag{4}$$

where $N=a^{-3}$ is the number of unit cells per unit volume, and α_0 is their polarizability as $T\to 0$. We neglect here the lengthening of the dipole moments P under the influence of the polarized medium, inasmuch as under typical conditions the moment induced by the field is small compared with the dipole's own moment.

We note that the calculation of E_ε and ε within the framework of the Onsager model constitutes in effect allowance for the dipole-dipole interaction in the spirit of the self-consistent-field approximation.

The radius R in (4) is eliminated with the aid of the Onsager approximation, according to which the sphere occupies a volume equal to that of the unit cell

$${}^4/_3\pi NR^3=1, \tag{5}$$

and this, as seen from (4) with $n=0$, is equivalent to satisfaction of the Clausius–Mosotti relation for ε_0:

$$(\varepsilon_0-1)/(\varepsilon_0+2)={}^4/_3\pi N\alpha_0. \tag{5'}$$

Substituting (5) and (5′) in (4) we obtain an equation for ε:

$$\frac{(\varepsilon-\varepsilon_0)(2\varepsilon+1)^2}{3\varepsilon(2\varepsilon+\varepsilon_0)}=4\pi\frac{nP^2}{3Ta^3}. \tag{6}$$

This expression is not convenient for direct calculations, and we shall therefore use hereafter an interpolation formula of the Langevin type

$$\varepsilon=\varepsilon_0+2\pi nP^2/Ta^3, \tag{6'}$$

which is asymptotically valid both at $(\varepsilon-\varepsilon_0)/\varepsilon_0\ll 1$ and at $\varepsilon_0/\varepsilon\ll 1$. The interpolation (6′) is accurate enough: in the entire range of parameters it yields for ε values that differ from those calculated by Eq. (6) by not more than 10%. This accuracy is perfectly satisfactory, since none of the Onsager-theory results were obtained with higher accuracy.

Substituting (6′), (5′), (3), and (2) in (1), we obtain, accurate to terms of order $1/2\varepsilon$, the molecular-field equation for the determination of n:

$$\begin{gathered}\ln\frac{z(1-n)}{n}=Ax-x\frac{xn}{1+xn},\\ A=\Delta_0\Big/\frac{3}{2}\frac{P^2}{\varepsilon_0R^3},\quad x=\frac{3}{2}\frac{P^2}{\varepsilon_0R^3T}.\end{gathered} \tag{7}$$

The main physical parameter of the problem is the quantity A, equal to the ratio of Δ_0 to the maximum possible energy gain due to polarization. At $A\gg 1$ the number n increases continuously and monotonically with increasing temperature. When A decreases to values of the order of unity, a temperature region appears in which Eq. (7) does not have a unique solution (see Fig. 1 below); this indicates, as usual, in the absence of a change in symmetry, that a first-order phase transition takes place in the system. Since the linear dimension of the dipole is of the order of the lattice constant a, the quantity P^2/ε_0R^3 is of the order of $e^2/\varepsilon_0a\sim 0.5$–1 eV, i.e., it is of the order of Δ_0. Thus, a situation with $A\sim 1$ is possible in real crystals. In order for Eq. (7) to have several solutions belonging to the same continuous curve, it is necessary and sufficient that the plot of n against the dimensionless reciprocal temperature x have points at which $dx/dn=0$ $(dn/dx=\infty)$.

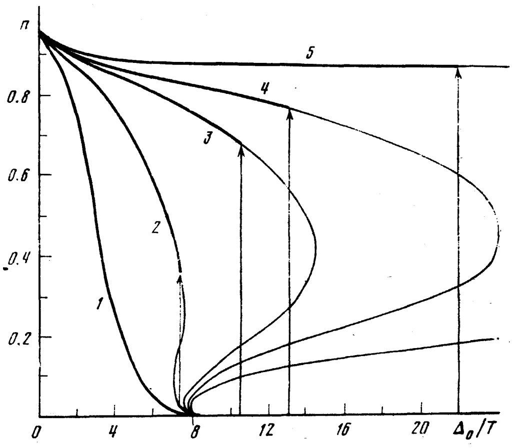

FIG. 1. Dependence of the number of dipole excitations n on the dimensionless reciprocal temperature at $z=20$ ($A_{\max}\approx 1.4$) and at different values of the parameter A ($1-A=\infty$; $2-A=1.3$; $3-A=1.1$; $4-A=1.05$; $5-A=1$). The thick lines denote the physically realized states, the arrows mark the phase transitions.

Differentiating (7) with respect to n and recognizing that $dx/dn = 0$, we get

$$1/n(1-n) = x^2/(1+xn)^2. \tag{8}$$

It is clear from the foregoing that phase transitions can occur in the system if A does not exceed a certain value $A_{\max}$, which, can be calculated from the condition that Eqs. (7) and (8) be simultaneously solvable. Substituting x from (8) in (7), we obtain an equation for n at the points $dx/dn = 0$:

$$[((1-n)n)^{1/2} - n]\ln\frac{z(1-n)}{n} + \left(\frac{n}{1-n}\right)^{1/2} = A. \tag{9}$$

The expression in the left-hand side of (9) is maximal at $[(1-n)/n]^{1/2} = 1 + 2^{1/2}$. Correspondingly

$$A_{\max} = {}^1/_2(2^{1/2}-1)[\ln z(3+2\cdot 2^{1/2})+2] \approx 0.779 + 0.207\ln z. \tag{10}$$

2. FREE ENERGY AND PHASE TRANSITIONS

For a more detailed investigation of the phase transition that occurs if $A < A_{\max}$ (in particular, to determine the transition temperature), it is necessary to make up a functional for the free energy. In the spirit of the self-consist-field approximation the free energy F per cell is given by

$$F = \int_0^n \Delta(n)\,dn - \frac{T}{N}\ln(C_N{}^{nN} z^{nN}), \quad C_N{}^{nN} = \frac{N!}{(N-nN)!(nN)!}, \tag{11}$$

where N is the number of cells per unit volume. The first term in (11) is the energy of defect formation; C_N^{nN} is the number of possible ways of exciting nN ions in N cells, while the second factor is the number of methods of placing nN ions in the interstices.

Using (2), (3), and (6′), (11), and Stirling's formula for the factorial of a large number ($\ln y! \approx y\ln y - y$), we obtain

$$F = T[(A-1)xn + \ln(1+xn) - n\ln z + (1-n)\ln(1-n) + n\ln n]. \tag{12}$$

We note that Eq. (7), as usual, follows from the condition $\partial F/\partial n = 0$. Using the dependence of n on the dimensionless reciprocal temperature x [Eq. (7)], we can simplify expression (12) for the free energy:

$$F = T\left[\ln(1+xn) - \frac{xn}{1+xn} + \ln(1-n)\right]. \tag{13}$$

At $A < A_{\max}$ there is a temperature region in which Eq. (7) has three solutions for each value of x. We designate them n_1, n_2, and n_3 in increasing number of excitations, and the corresponding values of the free energy (13) are designated F_1, F_2, and F_3. The largest number of excitations n_3 and the smallest n_1 correspond to minima of the free energy, while n_2 corresponds to a maximum. At a certain temperature T_c the three energies F_1 and F_2 become equal

$$F_1(T_c) = F_3(T_c). \tag{14}$$

Below T_c we have $F_1 < F_3$ and the "ordered" state ($n_1 \ll 1$) is stable, while above T_c we have $F_1 > F_3$ and the system is in a "molten" state ($n_3 \sim 1$). Thus, at a temperature T_c a first-order phase transition takes place in the system and is accompanied by a jump in the number of excited ions ("melting" of the lattice) and accordingly by an increase of the dielectric constant.

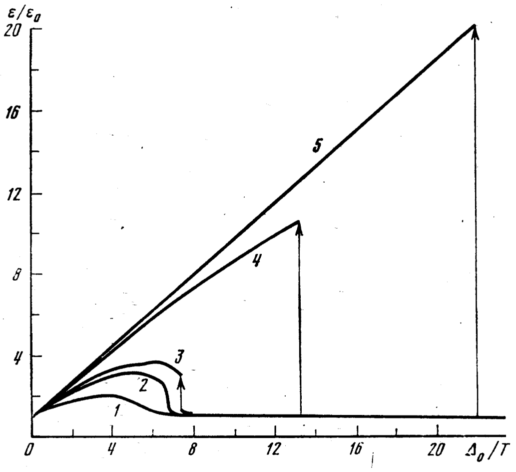

FIG. 2. Dependence of the dielectric constant on the dimensionless reciprocal temperature at $z = 20$ ($A_{\max} \approx 1.4$) and at different values of the parameter A ($1 - A = 2$; $2 - A = 1.45$; $3 - A = 1.3$; $4 - A = 1.05$; $5 - A = 1$). The arrows mark the phase transitions.

The transition temperature is obtained by simultaneously solving (14), (13), and (7).

Figure 1 shows the results of the numerical calculation of the function $n(\Delta_0/T)$ and of the transition temperatures at $z = 20$ ($A_{\max} \approx 1.4$) and at various values of A. At $A = 1.3$ the value of n is altered by the transition by more than one order of magnitude, while at $A = 1.05$ the change exceeds four orders of magnitude.

To estimate the change of the dielectric constant, we rewrite (6′) in the form $\varepsilon = \varepsilon_0(1 + xn)$, where x is defined in (7). The dependence of $\varepsilon/\varepsilon_0$ on the reciprocal temperature at the different values of the parameter A is shown in Fig. 2. As seen from Fig. 2, in the phase transition the dielectric constant can increase by more than one order of magnitude. When the inequality $A < A_{\max}$ is satisfied with sufficient margin, ε follows closely in the disordered state the Langevin interpolation ($\varepsilon \sim T^{-1}$). Deviations from linearity of ε in T^{-1} are due to the fact that at $T > T_c$ the number of dipole excitations continues to increase with temperature. When A approaches $A_{\max}$ this can lead to an increase of ε with increasing temperature in the region $T > T_c$ (curve 3 of Fig. 2). It is interesting that in the case $A > A_{\max}$, when there is no phase transition in the system and accordingly there is no jump of ε, sizable anomalies of the dielectric constant should be observed. Thus, even at $A = 2$ (curve 1 of Fig. 2) ε increases with temperature by more than two times, and with further increase of temperature its change is close to that given by Langevin.

If A is less than $A_{\max}$ by at least 10%, then the values of n_1 are exponentially small and n_3 is of the order of unity. Therefore it is perfectly sufficient to use in the calculation the approximation

$$\varepsilon \approx \varepsilon_0 \quad (xn \ll 1), \qquad \varepsilon \approx \varepsilon_0 xn = 2\pi P^2 n/Ta^3 \quad (xn \gg 1),$$

which is asymptotically exact in the indicated limits within the framework of the Onsager model. This confirms the applicability of the interpolation (6′) for the investigation of the phase transition.

So far we have disregarded the change of the character of the oscillations when the ions move from the sites to the interstices. To take this change into account it is necessary to add to the free energy (11), (12)

$$\Delta F=-nT\ln\prod_i(\omega_i/\omega_i'),$$

where ω_i and ω_i are the frequencies of the normal vibrations in the sites and the interstices, respectively. As seen from (11) and (12), this leads only to a renormalization of z: all the equations must contain in place of z

$$z'=z\prod_i(\omega_i/\omega_i').$$

Since usually the coupling in the interstices is weaker than at the sites (thus, $\omega_i < \omega_i$), this can increase effectively the number z and by the same token weaken the criterion for the presence of the phase transition (10).

Nor does allowance for the presence of carriers (excess cations and vacancies) alter the results, since these can be regarded as separated from the dipole excitations by a sufficiently large energy gap, and their number thus remains exponentially small also in the "molten" state. Their presence leads only to a screening of the dipole-dipole interaction. At a screening radius greatly exceeding the lattice constant, however, a situation to which incidentally the high values of ε contribute, this results only in small corrections to the polarization energy.

A behavior of ε similar to that obtained in our model was recently observed experimentally in the superionic conductor Li_3N.[5] At low temperatures, the low-frequency dielectric constant ε is the same as in the infrared region. With increasing T, the value of ε first increases, but at 80–170 K it decreases like $1/T$ (no measurements were made at high temperatures because of the high conductivity). The authors of the cited article attribute the Langevin decrease of ε to local ionic motion within the unit cell, but no direct experimental proof has yet been obtained for this statement. The local "melting" by itself, as indicated above, is not enough for high conductivity to appear. Owing to the increase of ε, it only decreases the activation of the conductivity, but still to a finite value. Therefore, if the temperature is not too high (as was apparently the case under the experimental conditions) the resistance can be high enough. We note also that the conductivity of Li_3N exhibits no anomalies with further increase of temperature, and merely increases exponentially.

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