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Some Problems in the Theory of Solid Electrolytes

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Modern theoretical views on solid electrolytes (i.e. solids whose ionic conductivity is anomalously high) are reviewed, and various mechanisms for the creation of disorder in one of the ionic sublattices are analysed, together with schemes for the phase transitions to the superionic state and with the dependence of the characteristics of these transitions on the parameters of the crystal and on the charge transfer phenomena in the solid electrolyte. Problems in the microscopic description of ionic transport in solid electrolytes are examined, and the theoretical foundations of the experimental methods used to study the properties of solid electrolytes are discussed.

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I. INTRODUCTION

In recent years solid electrolytes have increasingly claimed the attention of researchers (physicists, chemists, materials scientists) as well as of technologists, engineers, and system designers[1-11]. One of the most important features of solid electrolytes (their anomalously high ionic conduction) can be exploited at temperatures well below the melting point of the material. For example, whereas the ionic conductivity of "normal" solids at room temperature is not greater than 10^{-7}–10^{-8} Ohm^{-1} m^{-1}, that of "good" solid electrolytes is approximately 10 Ohm^{-1} m^{-1} at the same temperature, i.e. it is similar to the conductivity of melts and of concentrated (liquid) solutions of electrolytes. Thus materials of this type can be said to have "hybrid" properties, combining the conductivity of a melt or of a liquid solution with the mechanical strength and elasticity of a solid.

Solid electrolytes (also called "superionic conductors") can be arbitrarily classified into various types, depending on the magnitude of their ionic conductivity and on their structural features.

The first type includes crystals in which one of the sublattices (cation or anion) is structurally disordered. Many (several tens) of these compounds have already been discovered and studied, and their number is increasing[4,7,11]. The most typical example of this type of solid electrolyte is the compound $RbAg_4I_5$, with a room-temperature conductivity (due to the disordered Ag^+ cations) of ~25 Ohm^{-1} m^{-1}. This is 16 orders of magnitude higher than the ionic conductivity of common salt at the same temperature.

Another type of solid electrolyte includes substances which owe their high ionic conductivity to a high concentration of impurity ions able to activate the structural disorder. For example, if CaO is added to the ZrO_2 lattice the Ca^{2+} ions distribute themselves over the Zr^{4+} sublattice, and the O^{2-} ions complete the oxygen sublattice. However, because of the difference in charge between Ca^{2+} and Zr^{4+}, oxygen vacancies must appear in the mixed crystal, leading to disorder in the oxygen sublattice. These compounds are impurity solid electrolytes, or solid electrolytes with impurity-induced disorder. Examples are provided by the MO_2–M'O series of compounds (where M = Zr, Hf, Ce, and M' = Ca, Sr, Ba), whose ionic conductivity (due to oxygen ions) is ~1–10 Ohm^{-1} m^{-1} at 1000–1500°.

Lastly, amorphous glassy solids with a measurable ionic conductivity due to the presence of electrically active impurities[12,13], and ion-exchange resins, are also occasionally classified among solid electrolytes.

Most of the solid electrolytes with structural disorder show, at some characteristic critical temperature, a discontinuous change in ionic conductivity by a large factor (even by several orders of magnitude). Above this critical temperature the crystal is in a state of high ionic conductivity, and behaves as a solid electrolyte. In other words, we have a rational method of identifying superionic crystals among all the known crystalline compounds. Below their critical temperature (i.e. in their dielectric phase) these materials behave as "normal" crystals, and above their critical temperature they are converted into a qualitatively different state: the superionic (electrolyte) phase.

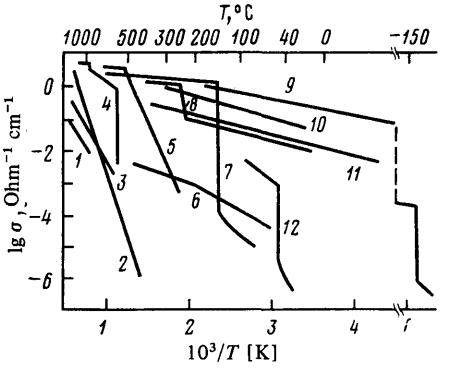


Figure 1. Temperature dependence of the conductivity of some solid electrolytes[5]: *1*) ThO_2–Y_2O_3, *2*) CaF_2, *3*) ZrO_2–CaO, *4*) Li_2SO_4, *5*) PbF_2, *6*) CeF_3, *7*) AgI, *8*) Ag_3SI, *9*) $RbAg_4I_5$, *10*) $Ag_6I_4WO_4$, *11*) Na–β-Al_2O_3, *12*) Ag_2HgI_4.

Unlike the superionic crystals, solid electrolytes with disorder due to impurities do not usually show a discontinuity in the temperature dependence of ionic conduction, though anomalies in this dependence may arise from phase transformations resulting in impurity redistribution.

The structure and the ionic conductivity of solid electrolytes of both these types are fully discussed in Refs.1–11. Therefore we shall not dwell on this set of problems, except to mention that the temperatures at which

solid electrolytes of the first class become good ionic conductors are usually much lower than those for the second class, and often even lie below room temperature. High ionic conductivity (≥ 1 Ohm^{-1} m^{-1}) is observed in a temperature range of over 1500 K, which includes all the known solid electrolytes: some examples are shown in Fig.1.

The electronic conductivity of solid electrolytes is usually much lower (by several orders) than their ionic conductivity, though it plays an important role in some materials. The theory of electronic conduction is dealt with in Refs.14–16, and will not be discussed here.

The problems in the behaviour of solid electrolytes lie at the "junction" of solid-state physics, crystallography, solid-state chemistry, and electrochemistry. By exploiting the wide range of experimental approaches offered by all these disciplines a very comprehensive fund of information (both specific, and generalised) has been generated. The aim of this review is to present some new theoretical concepts in the science of solid electrolytes and to discuss the theoretical foundations of the physicochemical methods used in their investigation.

II. THERMODYNAMICS OF SOLID ELECTROLYTES

The distinguishing feature of all solid electrolytes, which is ultimately responsible for their anomalously high ionic conductivity, is the presence of disorder (full, or partial) in one of the crystal sublattices. In the superionic crystals, for example, this disorder consists in the random distribution of the ions of one kind over the interstitial positions, whose number in these compounds is usually greater than the number of disordered ions. Because the relevant activation energy is very small, the interstitial ions have a very high mobility. In other words, the dynamic effect (anomalously high ionic conductivity) is unambiguously related to a thermodynamic effect (lattice disorder). The system can be described in terms of the somewhat arbitrary concept of an "ionic liquid" pervading a rigid crystalline skeleton consisting of ordered ions, analogous to the concept of an electronic liquid in metals†.

The most important problem in the thermodynamics of solid electrolytes is to explain and to describe quantitatively the sudden disordered ("melting") of one of the crystal sublattices. The formation of disorder is accompanied not only by a discontinuous increase in ionic conductivity but also by other anomalous effects in the temperature dependence of various thermodynamic and kinetic parameters[17,22].

The discontinuity in the number of highly mobile ions in interstitial positions is a phase transformation of the first kind. This transition may be produced in a number of ways, depending on the properties of the sublattice which remains rigid. In particular, the rigid sublattice may be quite unaffected by the disorder transition, or it may undergo secondary structural changes. In this case collective interactions in the system of crystal defects can be expected to play a major role. The theory of the disordering of one sublattice through collective interactions while the other sublattice remains unchanged has been developed by many workers[23–32]. However, there are crystals in which the disordering of one sublattice is accompanied by a rearrangement (polymorphic change) in the other sublattice which may have an important effect. The case of negligible interaction in the defect system, such that the disorder is induced exclusively by the lattice rearrangement, is analysed in Ref.33 (see also Ref.34); several special features of phase transitions involving disorder with comparable thermodynamic contributions from both factors are discussed in Ref.35.

One special feature of the thermodynamic behaviour of solid electrolytes is the possibility of forming domain structures. Some of the problems associated with domain formation are discussed in Refs.36–39.

1. Structural Disorder Induced by Lattice Rearrangement

Structural disorder in the absence of collective interactions in the defect system, and due entirely to a polymorphic transition, is the simplest to describe mathematically[33].

The traditional treatment of polymorphic changes in crystals relates these transitions to changes in the vibrational (phonon) spectrum of the solid[40,41]. Thus, it is assumed that the contribution of the phonon subsystem to the free energy increases with the temperature of the crystal, so that at some temperature $T_{tr}^{(p)}$ the transition of the crystal into a higher-energy modification (with "dumping" of the lattice vibration energy) becomes thermodynamically favourable.

However, if the polymorphic transition is accompanied by a substantial amount of disordering of one of the sublattices it is reasonable to assume that the thermodynamics of the process will be determined predominantly by the disordering process, with a much smaller contribution from the changes in phonon spectrum. In other words, polymorphic transitions in one sublattice may be induced by disorder in the other sublattice.

We shall use as our starting point some standard thermodynamic expressions from the theory of ionic crystals[2,3,42]. The free energy F of the crystal can be written as the sum

$$F = F^{(0)} + F^{(d)}, \qquad (1)$$

where $F^{(0)}$ is the free energy of the ideal (defect-free) crystal, and $F^{(d)}$ is the free energy resulting from the presence of disorder. The quantity $F^{(d)}$ can be expressed as

$$F^{(d)} = wn - T \ln \left\{ \frac{N_2!}{(N_2 - n)!\, n!} \frac{N_1!}{(N_1 - n)!\, n!} \right\} - nT \ln \chi, \qquad (2)$$

where N_1 and N_2 are the numbers of interstitial sites and of lattice sites per unit volume respectively, n is the number of ions per unit volume transferred from lattice sites to interstitials (and thus giving rise to Frenkel' defects in the crystal), w is the energy of formation of one defect#, T is the absolute temperature (expressed in energy units), and χ is a quantity related to the entropy of formation of one defect. In the simplest model $\chi = (\omega_2/\omega_1)^3$, where ω_1 and ω_2 are the vibration frequencies of the disordered ions in the interstitial sites and in the lattice sites respectively. The concentration n corresponding to thermodynamic equilibrium is defined by the condition of minimum disorder free energy: $\partial F/\partial n = 0$ [since $F^{(0)}$ is not a function of n]. Differentiating Eqn.(2), and using the expression

$$\frac{d}{dz} \ln z! = \ln z, (z \gg 1),$$

†For example, in $RbAg_4I_5$ the ionic liquid is formed by the disordered Ag^+ ions, and the rigid sublattice by the Rb^+ and I^- ions; in solid electrolytes with impurity disordering the "liquid" can consist, in principle, of vacancies.

#We can allow for effects associated with changes in volume of the crystal by replacing w by h (the enthalpy of formation of one defect).

we obtain the following expression for n:

$$n^2/(N_2-n)(N_1-n) = \chi \exp(-w/T) . \quad (3)$$

Assuming N_1 to be substantially higher than N_2 (as in the great majority of solid electrolytes) we can simplify Eqn.(3) to

$$x^2/(1-x) = \nu \exp(-w/T) , \quad (4)$$

where $\nu = \chi N_1/N_2$, and $x = n/N_2$ is a dimensionless concentration ($0 < x < 1$) used as a quantitative description of the degree of disorder. Using Eqn.(4) we can rewrite Eqn.(2) for $F^{(d)}$ as

$$F^{(d)} = N_2 T[\ln(1-x) - x] . \quad (5)$$

It follows from (3) and (4) that the function $x(T)$ increases monotonically with T from $x = 0$ at $T = 0$ to the value $x = x_\infty$ formally corresponding to the limit at $T = \infty$ and given [according to Eqn.(4)] by the expression

$$x_\infty = -\nu/2 + (\nu^2/4 + \nu)^{1/2} .$$

Hence, and using Eqn.(5), we find that $F^{(d)}$ decreases monotonically as T increases, with $F^{(d)} = 0$ at $T = 0$ and $F^{(d)}$ varying linearly with T for $T \gg w$.

Let us now consider two crystalline modifications (α and β), having free energies $F_\alpha(T)$ and $F_\beta(T)$. The modification having the lower free energy is present when the system is in thermodynamic equilibrium. As the temperature changes, the functions $F_\alpha(T)$ and $F_\beta(T)$ change at different rates, and the cross-over temperature (when $F_\alpha = F_\beta$) corresponds to the phase transition between the α and β modifications. This transition causes a rearrangement of the crystal lattice (polymorphic change) accompanied by a sudden change in the degree of disorder.

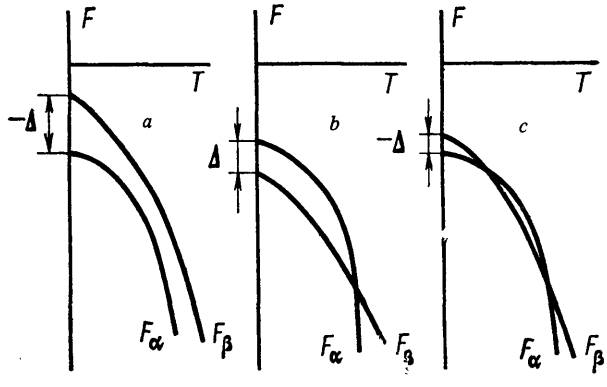


Figure 2. Idealised temperature dependences of the free energy F for α and β modifications: (*a*) no transitions, (*b*) single transition, (*c*) double transition.

The condition $F_\alpha = F_\beta$ can be written, using Eqn.(1),

$$F_\beta^{(d)} - F_\alpha^{(d)} = N_2\Delta , \quad (6)$$

where, by definition, $N_2\Delta = F_\alpha^{(0)} - F_\beta^{(0)}$, and the quantity Δ in our case is approximately independent of T and is determined by the difference in internal energy between the α and β crystalline modifications. The different mutual dispositions of the $F_\alpha(T)$ and $F_\beta(T)$ curves which are possible according to Eqns.(5) and (6) are shown in Fig.2. Case *a* corresponds to the absence of phase transitions, the crystal remaining in the α modification at all temperatures. In case *b* the low-temperature α modification is converted into the high-temperature β modification at the intersection point. Case *c* corresponds to two polymorphic transitions in succession ($\alpha \to \beta \to \alpha$, or bitransition).

From Eqns.(4)–(7) we can obtain a system of three equations defining the polymorphic phase transition temperatures $T_{tr}^{(p)}$ and the concentrations x_α and x_β of the interstitial ions before and after the transition:

$$T_{tr}^{(p)}\{\ln[(1-x_\beta)/(1-x_\alpha)] - (x_\beta - x_\alpha)\} = \Delta \quad (7)$$

$$x_\alpha^s/(1-x_\alpha) = \nu_\alpha \exp(-w_\alpha/T_{tr}^{(p)})$$

$$x_\beta^s/(1-x_\beta) = \nu_\beta \exp(-w_\beta/T_{tr}^{(p)}) , \quad (8)$$

Using Eqns.(5) and (6), the heat of the phase transition for a single particle is given by the expression

$$Q_p = \Delta + w_\alpha x_\alpha(T_{tr}^{(p)}) - w_\beta x_\beta(T_{tr}^{(p)}) , \quad (9)$$

and the specific heat of the disordering process ΔC for the α and the β modifications is

$$(\Delta C)_{\alpha,\beta} = w_{\alpha,\beta}x_{\alpha,\beta}(1-x_{\alpha,\beta})/T^2(2-x_{\alpha,\beta}) . \quad (10)$$

A detailed analysis of the conditions leading to single and to double transitions (bitransitions) is given in Ref.33, together with expressions for the corresponding transition temperatures.

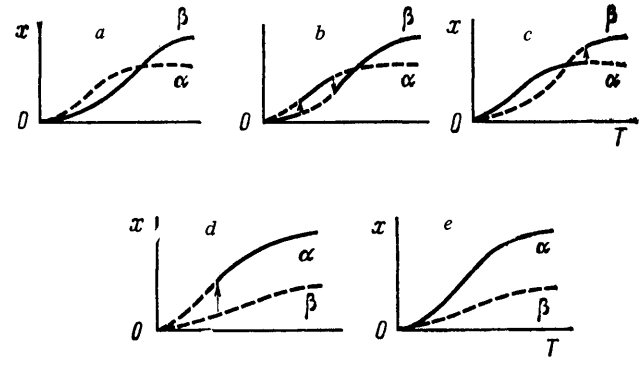


Figure 3. Possible temperature dependences of the degree of disorder $x_{\alpha,\beta}$, and schematic representation of the phase transitions for different relative values of the parameters Δ, $w_\alpha < w_\beta$, ν_α, and ν_β;[33] the full lines show the realisable situations, the arrows show transitions between these situations.

These expressions for the degree of disorder x as a function of temperature with allowance for polymorphic ($\alpha \rightleftharpoons \beta$) transitions are not trivial: different types of relationship are shown in Fig.3. We should stress that the relative amounts of disorder, and therefore also other characteristics of the solid electrolytes, can change by large amounts.

2. Structural Disorder Induced by Defect Interactions

We shall now consider how collective interaction between defects can be incorporated into a general thermodynamic scheme for describing the behaviour of the crystal.

Interstitial ions and the empty sites which they leave behind (vacancies) can interact both among themselves and with members of the other group (cross-over interaction), the total number of interacting pairs being proportional to n^2 in the case of $n \gg 1$. As a result, if in the absence of interactions the internal energy E of the system of n defects is $E = wn$, allowing for the collective interactions gives

$$E = wn - \frac{\lambda}{2}\frac{n^2}{N_a} ,$$

where λ is a phenomenological constant whose sign and value are determined by the nature of the inter-particle (including indirect) interactions in the ensemble of interstitial ions and vacancies. The case of $\lambda > 0$ corresponds to effective attraction, $\lambda < 0$ to repulsion.

An analysis of the specific interactions which contribute to λ is beyond the scope of this review. We shall only stress that contribution to effective attraction is possible not only from self-consistent Coulombic interactions[43] but also from the elastic deformations accompanying the formation of defects in the crystal[44], and from the changes in vibrational spectrum of the crystal predicted by second-order perturbation theory[45].

Replacing wn in Eqn.(2) by the corrected expression for E, and using the condition $\partial F^{(d)}/\partial n = 0$, we obtain instead of Eqn.(4) the equation of state[27-29]

$$x^2/(1-x) = \nu \exp[-(w-\lambda x)/T] \quad . \qquad (11)$$

The average field approximation used in the derivation of (11) is equivalent to the standard Bragg–Williams approximation in the theory of alloys[46] or to the Curie–Weiss approximation in the theory of magnetism[47]. Effectively the same approximation is used to describe regular solutions, adsorption with inter-particle interactions[48,49], the properties of liquid crystals[50], etc.

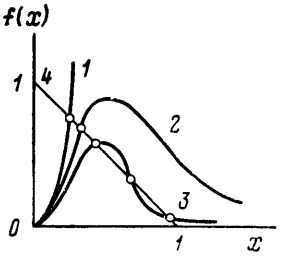


Figure 4. Graphical solution of Eqn.(11) ($f(x) = x^2\nu^{-1} \exp[(w - \lambda x)/T]$): *1*) for $\lambda = 0$, *2*) $0 < \lambda < w$, *3*) $\lambda > w$, *4*) is the $(1 - x)$ straight line.

Let us now consider, as in Refs.27 and 28, the thermodynamic behaviour of the system. If $\lambda = 0$ Eqn.(11) reduces to (4), and under these conditions (as well as for $\lambda < 0$) Eqn.(11) has only one solution (Fig.4). However, as Fig.4 shows, for large positive values of λ Eqn.(11) has three solutions $\{x_1 \leq x_2 \leq x_3\}$ in the range $0 \leq x \leq 1$. If the equation of state has only one solution, the free energy at a fixed value of T will have one minimum at the value of x corresponding to this root (Fig.5). In the case of three roots the function $F(x)$ has two minima (at the points x_1 and x_3) and one maximum (at the point x_2). The crystal is found in the state (x_1 or x_3) corresponding to the lower of the two minima in $F(x)$; the state x_2 corresponds to a local maximum in $F(x)$ and therefore is unstable.

Changes in T alter the shape of the $F(x)$ curve, and at a particular temperature $F[x_1(T)]$ becomes equal to $F[x_3(T)]$. This indicates a phase transition of the first kind which makes the parameter x (the degree of disorder) change discontinuously from x_1 to x_3 (or from x_3 to x_1). These phase transitions can arbitrarily be classified into weak or strong[27]. Weak transitions are those in which the jump in the value of x is small ($x_3 - x_1 \ll 1$); the strong transitions correspond to $x_1 \ll 1$ and $x_3 = 1 - \varepsilon$, with $\varepsilon \ll 1$. From the condition $F[x_1(T)] = F[x_3(T)]$, and using the equation of state (11), we obtain the following expression for the transition temperature in the two cases:

$$T_{tr}^{(w)} = (w - \lambda x_*)/\ln(\nu/\nu_*); \; T_{tr}^{(s)} = (w - \lambda/2)/(1 + \ln\nu) \qquad (12)$$

where $x_* = 2 - \sqrt{2}$, $\nu_* \equiv x_*^2/(1 - x_*)$, and therefore numerically $\nu_* = 2(\sqrt{2} - 1)$.

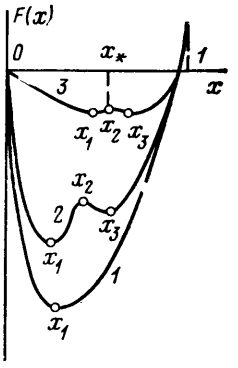


Figure 5. Idealised plots of F against x for different x and T: *1*) the equation of state has one solution, *2*) and *3*) the equation of state has three solutions $\{x_1, x_2, x_3\}$.

A full analysis of the variation of x with temperature for different values of the parameters of the system is given in Refs.28 and 29. Let us examine the main conclusions (Fig.6).

Firstly, gradual and continuous disordering of the initial sublattice with increase of T is possible, as in ordinary ionic crystals (Fig.6*a*), or a relatively slight discontinuity may occur, accompanied by a small jump in x (weak transition, Fig.6*b*).

Secondly, we can have a large jump from a state with a small x to a state with $x \cong 1$ (Fig.6*c*). As the temperature is increased still further the crystal remains in this state, or x may even decrease (compare Figs.6*a* and 6*c*). Physically, a decrease of x with increase of T implies that the state $x_3 > x_\infty$ is created and maintained if sufficiently strong interactions are present ($\lambda > 0$). As the temperature increases, the interaction is effectively "diluted", and at $\lambda/T \to 0$ the "defect gas" becomes ideal. Accordingly, in the state shown in Fig.6*c* the concentration of defects decreases as T increases, approaching (from above) the value $x = x_\infty$.

Thirdly, the system can show two successive transitions (Figs.6*d* and 6*e*). In the former case the second transition does not bring the crystal out of the superionic state,

whereas in the latter case we observe two genetically related phase transitions (bitransitions).

Lastly, the parameters of the system can be such ($\lambda > 2w$) that even at $T = 0$ the crystal is in the state with $x \cong 1$ (Figs. 6*f*, 6*g*, and 6*h*). In this case x decreases as T increases. We note that in the special case of $N_1 = N_2$ (see Ref. 23) double transitions cannot occur, and the temperature of the single transition in such a symmetrical system is given, irrespective of the magnitude of the jump in x, by the expression

$$T_{tr}^{sym} = (w - \lambda/2)/\ln \nu \ .$$

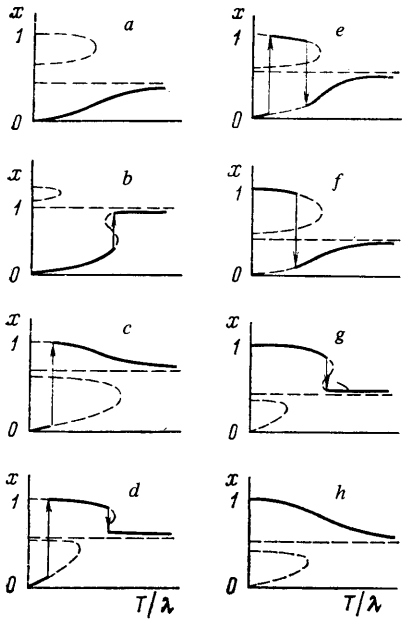


Figure 6. Idealised plots of the possible solutions of the equation of state and of the transitions between solutions: the full lines are realisable situations, the arrows are transitions between these situations.

The case of a collective interaction energy varying arbitrarily but monotonically with the defect concentration is discussed in Refs. 51 and 52, and more complex energy structures of the lattice points and of the interstitial sites are discussed in Refs. 31 and 53. In particular, in the presence of a small concentration of impurities ($c_{imp} = N_{imp}/N_2 \ll 1$) giving rise to interstitials with a different energy structure, the temperature of the strong transition is given[53] by the expression

$$T_{tr}^{(s,imp)} = T_{tr}^{(s)}[1 + c_{imp}/(\ln \nu + 1)] \ , \qquad (13)$$

where $T_{tr}^{(s)}$ is defined by Eqn. (12).

The dependence of the transition temperature T_{tr} on the pressure P is described by the Clausius–Clapeyron equation: $dT_{tr}/dP = (V - V')/(S - S')$, where V, V', S, and S' are the specific volumes and entropies of the states between which the transition is taking place. If the transition is strong the change in specific volume is $\nu_0 N_2$, where ν_0 is the "free volume" of formation of one defect.

Assuming that the contribution of the polymorphic change to the thermodynamics of the transition is relatively minor, and using the expressions given above for $E(n)$ and $T_{tr}^{(s)}$, we obtain[54]

$$\frac{dT_{tr}^{(s)}}{dP} = \frac{N_2|v_0|T_{tr}^{(s)}}{w - \lambda/2} = \frac{N_2|v_0|}{1 + \ln \nu} \ . \qquad (14)$$

If the vibration frequencies ω_1 and ω_2 of the ions in interstitial positions and in lattice sites [which determine the parameter ν, see Eqns. (2) and (4)] have similar pressure dependences, the denominator of Eqn. (14) is independent of P, and the function $T_{tr}^{(s)}(P)$ can be treated as the sum of a linear and a quadratic term in P, since ν_0 varies linearly with P.

A model similar to the above has been used in Refs. 55 and 32 in a detailed analysis of weak transitions for particular values of the parameter N_1/N_2.

Attempts to apply scale invariance (scaling) concepts[56,57] to phase transitions in solid electrolytes are described in Refs. 58 and 59.

Spatially inhomogeneous regions (domains) in single crystals of solid electrolytes with structural disorder have been observed experimentally[36–39], and the theoretical possibility of thermodynamically stable inhomogeneities in solid electrolytes has been examined in detail[39,60].

3. Comparison of the Thermodynamic Theory of Disorder with Experiment

Theoretical models can be used to calculate the transition temperatures and the specific heats ΔC of the disorder, and these can be compared with experimental values. However, in order to find the excess specific heat associated with intrinsic disorder we must subtract from the measured value the specific heat of the defect-free crystal: this is usually done by choosing a particular model to describe the vibrational spectrum[61].

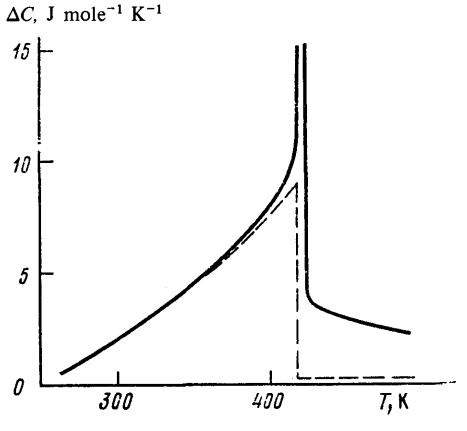


Figure 7. Experimental (full line) and theoretical (broken line) specific heat curves for the disorder in Ag_2S.[30]

The first attempt at interpreting experimental data[61] on the specific heat of superionic $RbAg_4I_5$ near the phase transition at $T_{tr}^{(s)} = 122$ K by the theoretical formulae which allow for defect interactions (see previous Section) is

described in Ref. 27. The same approach was later applied[30] to superionic crystals of AgI, $RbAg_4I_5$, Ag_2S, and others. As an example, the theoretical and the experimental ΔC curve for Ag_2S are compared in Fig. 7. The agreement is satisfactory for the low-temperature regions of the $\Delta C(T)$ curves, but above the transition temperature we note a substantial discrepancy, due no doubt to the polymorphic transition which takes place at the same time as the disorder transformation and for which no allowance is made in the calculation[62]. By comparing data on the excess specific heat of $RbAg_4I_5$ with calculations by a combined disorder and polymorphic transformation model a satisfactory description of the $\Delta C(T)$ curve has been obtained for $T > T_{tr}$ as well as for $T < T_{tr}$.

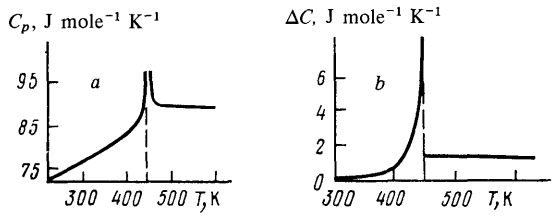


Figure 8. (*a*) Experimental plot of the full specific heat C_p, and (*b*) calculated plot of the specific heat of disordering ΔC in AgI.[34]

In Fig. 8 (taken from Ref. 34) we show some results on the excess specific heat of AgI, and in Fig. 9 we show a similar plot for Ag_2Se. The results were interpreted by the polymorphic transition model, using formula (10); the agreement between theory and experiment (for reasonable values of the adjustable parameters) is gratifying.

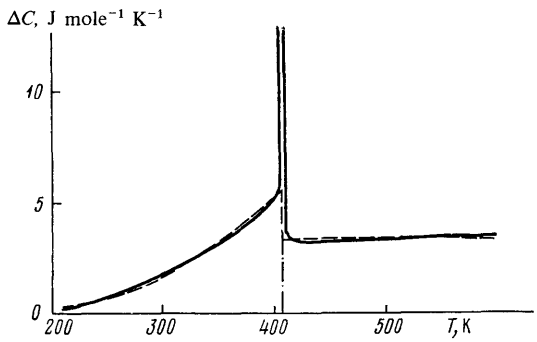


Figure 9. Experimental (full line) and theoretical (broken line) curves for the specific heat of disordering in Ag_2Se.[63]

Anomalies in the temperature dependence $\sigma(T)$ of the ionic conductivity of $RbAg_4I_5$ near the phase transition at $T = 209$ K (a "weak" transition) have been reported[64]. Measurements of the conductivity jump led to values of the thermodynamic parameters ($w = 5.6 \times 10^{-2}$ eV and $\lambda = 9.6 \times 10^{-2}$ eV) close to those previously calculated from specific heat data for the same compound but in a different temperature region ($w = 6 \times 10^{-2}$ eV and $\lambda = 10^{-1}$ eV).

Data[65] on the ionic conductivity of high-temperature solid electrolytes with the fluorite structure (CaF_2, SrF_2, $SrCl_2$) were compared[25,32] with theoretical models of disorder, and satisfactory agreement was obtained.

The dependence of the ionic conductivity of Na_2WO_4 crystals on temperature suggests[66] the existence of two (very close) phase transitions of the first kind accompanied by an increase and by a decrease in ionic conductivity respectively. This behaviour is consistent with the theoretically predicted bitransitions (see Fig. 6*e*). Further experimental evidence of the possible existence of bitransitions was obtained in a study[67] of the temperature dependence of Raman scattering in the solid electrolyte $Ag_{26}I_{18}W_4O_{16}$.

Calculations of the effect of impurities on the thermodynamics of disorder yield a qualitative explanation of changes in transition temperature along a series of isomorphous compounds (in particular, $RbAg_4I_5$, $K_{3/4}Rb_{1/4}$. $.Ag_4I_5$, and KAg_4I_5). Treating the K^+ ions as an impurity, we can calculate the transition temperatures by formula (13): the agreement between theory and experiment (see below) is satisfactory:

Compound	$RbAg_4I_5$	$K_{3/4}Rb_{1/4}Ag_4I_5$	KAg_4I_5
T_{tr}, K (exper)	122	134	137
T_{tr}, K (calc)	122	135.5	140

Experiments on the effect of pressure P on the phase transition temperature T_{tr} in solid electrolytes are reported in Ref. 68. For the compound AgI the function $T_{tr}(P)$ is accurately described by a straight-line dependence corresponding to a decrease in volume of the crystal by ~5.6% during the transition from the low-temperature to the high-temperature phase. In the case of the solid electrolyte $RbAg_4I_5$ we must retain the quadratic terms in P to describe the $T_{tr}(P)$ relationship. We note that the parameters needed to apply formula (14) are not yet known with sufficient precision.

III. BEHAVIOUR OF SOLID ELECTROLYTES IN AN EXTERNAL FIELD. TRANSPORT PHENOMENA

Transport phenomena can be treated by different approaches: one of them (the macroscopic approach) relies on the phenomenological equations of the thermodynamics of irreversible processes, the other (microscopic) relies on concrete microscopic models of the process of interest. The first approach requires very little detail, the properties of the system being described by the phenomenological parameters inserted into the theory. In the present state of development of kinetic models of homogeneous and heterogeneous charge transfer processes in solid electrolytes the phenomenological description offers the best (and sometimes the only) approach.

The electro-diffusion equations applied to transport phenomena in liquid electrolytes and in ionic crystals are based essentially on this phenomenological approach. The same equations (in most cases, unmodified) have been used also to describe the transport of current carriers in solid electrolytes[2-5]. However, solid electrolytes have a number of specific features which are ignored in the standard description, though they may play an important role. The present review is aimed specifically at those features.

The second approach, which should relate the phenomenologically chosen coefficients to the microstructural details and to the dynamic characteristics of the microscopic processes, is still in the formulation stage.

Some aspects of the study of micro-processes and some of the results obtained will be discussed in the following Section.

For relatively small deviations from equilibrium the transport properties of a system are closely related to its thermodynamic properties. Hence, in the phenomenological approach the flows of components (charge carriers) are proportional to the gradients of their electrochemical potentials, which can be obtained from the expression for the free energy F of the system.

For a solid electrolyte with structural disorder and exposed to an external electric field we can write, using the concepts discussed in previous Sections,

$$F(n_1, n_2) = E_1 n_1 + E_2(N_2 - n_2) + e\varphi(n_1 - n_2) - \\ - T \ln \left\{ \frac{N_1!}{(N_1 - n_1)!\, n_1!} \frac{N_2!}{(N_2 - n_2)!\, n_2!} \right\} , \quad (15)$$

where n_1 and n_2 are the concentrations of interstitial ions and of vacancies, E_1 and E_2 are the energies needed to force the ion into an interstitial and to remove it from a lattice site ($E_2 - E_1 = w$), and ϕ is the potential due to the electric field in the crystal. The quantities n_1, n_2, and ϕ usually depend on the spatial coordinates. In Eqn.(15) the terms which allow for changes in the vibrational frequencies due to disorder (vibrational terms) have been omitted to simplify the treatment, and collective interactions have been assumed to have a negligible effect ($\lambda = 0$). The expressions for the electrochemical potentials $\mu_{1,2} = \partial F/\partial n_{1,2}$ of the interstitial ions and of the vacancies are

$$\mu_1 = E_1 + e\varphi + T \ln[n_1/(N_1 - n_1)] \\ \mu_2 = -E_2 - e\varphi + T \ln[n_2/(N_2 - n_2)] . \quad (16)$$

Eqns.(16) can be used to describe both the equilibrium properties of a solid electrolyte in an electric field and the transport phenomena.

1. Equilibrium States in an Electric Field

The concentration distributions of interstitial ions and of vacancies n_1 and n_2 corresponding to thermodynamic equilibrium can be calculated from the conditions of constant chemical potentials and of "chemical equilibrium" ($\mu_1 + \mu_2 = 0$). From (16) we have

$$n_1 = n_0/[\gamma_1 + (1 - \gamma_1)\exp\psi]; \quad n_2 = n_0/[\gamma_2 + (1 - \gamma_2)\exp(-\psi)] . \quad (17)$$

In these expressions $\psi \equiv e\phi/T$, and $\gamma_{1,2} \equiv n_0/N_{1,2}$, where n_0 is the equilibrium concentration of defects in the absence of the electric field, given§ by Eqn.(3). In the limit of $\gamma_1 = \gamma_2 = 0$ Eqn.(17) reduces to the standard Boltzmann distribution: $n_{1,2} = n_0 \exp(\pm\psi)$. However, in the general case the concentrations $n_{1,2}$ are described by distributions of the Fermi type, and at the limit of $\psi \to \pm\infty$ the concentrations n_1 and n_2 reach their maximum allowed values N_1 and N_2. This result demonstrates the lattice saturation effect[69]: the concentrations of interstitial ions and vacancies have an upper limit defined by the specific properties of the crystal. In the simplest case the lattice saturation effect is due to purely structural limitations (the fact that the number of positions available to the ions in the crystal lattice is finite). In the more general case the effect reflects also the interparticle interactions, and the limiting value of $n_{1,2}$ is defined by the appropriate $n_{1,2}^{\max}$ value (rather than by $N_{1,2}$), which is a characteristic parameter of the crystal.

§If the neglected terms associated with the entropy of formation of individual defects are retained in (15) and (16) the expressions (17) are unchanged, and the frequency factor χ occurs only in the equation for n_0.

It is interesting to consider the behaviour of $n_{1,2}$ and ϕ near the interface with allowance for the screening effect on the external field due to the redistribution of the charged particles. Within the self-consistent field approximation the potential distribution is given by an equation of the form

$$d^2\varphi/dz^2 = -\frac{4\pi}{\varepsilon_0} e[n_1(\varphi) - n_2(\varphi)] , \quad (18)$$

where z is the coordinate along the axis at right angles to the planar interface, ε_0 is the static dielectric constant of the crystal, and $e > 0$ is the electronic charge. Inserting into Eqn.(18) the Boltzmann distribution for $n_{1,2}$ we arrive at the standard self-consistent equation of the Gouy–Chapman and Debye–Hückel theories[70]. Integration of (18) after using (17) gives the electric field distribution $d\phi/dz$ and the integral charge Q_e of the surface (diffusion) layer. By differentiating the expression for Q_e with respect to potential we obtain the differential capacity C [70] of the diffusion layer:

$$-\frac{d\psi'}{dz} = \varkappa \operatorname{sgn}(\psi') \left[\frac{1}{\gamma_1} \ln \frac{n_0}{n_1} e^{-\psi'} + \frac{1}{\gamma_2} \ln \frac{n_0}{n_2} e^{\psi'} \right] \quad (19)$$

$$C = \frac{C_0}{2} \frac{\operatorname{sgn}\psi' \,[(n_1 - n_2)/n_0]}{\left[\gamma_1^{-1} \ln \frac{n_0}{n_1} e^{-\psi'} + \gamma_2^{-1} \ln \frac{n_0}{n_2} e^{\psi'} \right]^{1/2}} \quad (20)$$

where ψ' is the value of the potential ψ at the edge of the diffusion layer, $\varkappa \equiv (8\pi e^2 n_0/\varepsilon_0 T)^{1/2}$, (where $\varkappa^{-1}$ is the Gouy or Debye length), $C_0 \equiv \varepsilon_0 \varkappa/4\pi$, $\operatorname{sgn}(\psi') = 1$ for $\psi' > 0$ and $\operatorname{sgn}(\psi') = -1$ for $\psi' < 0$, and the $n_{1,2}$ values are given by Eqn.(17) with $\psi = \psi'$.

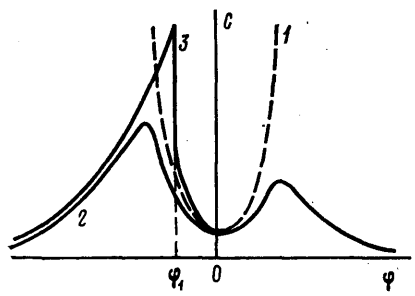


Figure 10. Plots of the diffusion layer capacitance against potential: *1*) $\gamma_1 = \gamma_2 = 0$, *2*) $1 > \gamma_2 > \gamma_1 > 0$, *3*) $\lambda_1 > 0$, $\lambda_2 = \lambda_{12} = 0$, $1 > \lambda_2 > \lambda_1 > 0$.

For $\gamma_1 \to 0$ and $\gamma_2 \to 0$ we obtain from Eqn.(20) $C = C_0 \cosh(\psi'/2)$, which corresponds to the capacity of the diffuse part of the double layer in liquid electrolytes (curve *1* of Fig.10). In the more general case the lattice saturation effect produces two asymmetric maxima in the $C(\psi)$ curve, and far from these maxima (for $|\psi| \to \infty$) we have $C = C_0/(\gamma_{1,2}|\psi|)^{1/2}$ [69] (see curve *2* of Fig.10). A formula similar to (20) is given in Ref.71 for the special case of $\gamma_1 = \gamma_2$. The unipolar model (in which charges of one sign only are redistributed in the field) corresponds to the limit $\gamma_2 = 1$ (or $\gamma_1 = 1$) in Eqns.(19) and (20). Expressions following from (19) and (20) in this model are given in Ref.72.

Thus, because of the lattice saturation effect the capacity of the diffuse part of the double layer in solid electrolytes is quite different from the analogous capacity in liquid

electrolyte systems. We should stress that the experimentally measured capacity is not determined only by the capacitance of the diffusion layer. The surface layer of the crystal may have properties different from those of the bulk (in particular, the energies of defect formation may be different). The influence of the surface layer on the distribution of space charge at the boundary between an ionic crystal and a vacuum is discussed in Refs.73 and 3.

To describe the boundary between a solid electrolyte and a metal we must also allow for the contribution from the fixed part of the double layer (the Helmholtz layer), as in the case of the boundary between a liquid electrolyte and a metal[70]. The effect of the Helmholtz layer, and detailed models of the two surface layers of ions in an ionic crystal, are fully described in Ref.3. We shall not dwell on the expressions obtained for the overall capacity: they are cumbersome, and they contain many parameters which have to be determined experimentally.

A novel effect, associated with the appearance of collective interactions in a crystal exposed to an electric field, is discussed in Ref.74. This effect consists in the stepwise, field-induced generation of disorder. It can be described mathematically as follows[74,75]. The chemical potentials $\mu_{1,2}$ corrected for collective interactions are given by the following expressions [instead of Eqn.(16)]:

$$\mu_1 = E_1 + e\varphi + T\ln n_1/(N_1 - n_1) - T\ln Z_1 - \lambda_1 n_1/N_2 - \lambda_{12} n_2/N_2$$
$$\mu_2 = -E_2 - e\varphi + T\ln n_2/(N_2 - n_2) + T\ln Z_2 - \lambda_2 n_2/N_2 - \lambda_{12} n_1/N_2 \quad (21)$$

In these expressions λ_1, λ_2, and λ_{12} describe respectively the interactions between interstitial ions, the interactions between vacancies, and the interactions between the two types of defect (with $\lambda = \lambda_1 + \lambda_2 + 2\lambda_{12}$); $Z_{1,2}$ are the vibrational partition functions of the ions in interstitials and in lattice sites (with $\chi = Z_1/Z_2$). As a result we obtain from (21) a system of two meshing equations for the dimensionless concentrations $x_{1,2} = n_{1,2}/N_2$ which is parametrically dependent on ϕ and on $x_0 = n_0/N_2$, where n_0 is the value of $n_1 = n_2$ in the absence of an electric field (depending on the difference $E_1 - E_2$ and on the ratio Z_1/Z_2).

The solution of this system over a given range of ϕ values is not unique, and this gives the possibility of phase transitions. The following physical explanation may be suggested. The field causes a redistribution of the charged particles, and the concentration of particles of one kind in the surface layer is increased. The collective interaction energy is itself a function of the concentrations of both kinds of particle. Since a high enough contribution from collective interactions can lead to phase transition, the field can also initiate phase transitions by varying the concentrations of interacting components. In particular, for one of the simplest cases ($\lambda_2 = \lambda_{12} = 0$, $\lambda_1 > 0$, $N_1 = N_2$) we obtain¶ from Eqn.(21)

$$\frac{x_1}{1-x_1} = \frac{x_0}{1-x_0}\exp\left[\frac{\lambda_1(x_1 - x_0) - e\varphi}{T}\right];$$
$$\frac{x_2}{1-x_2} = \frac{x_0}{1-x_0}\exp\left[\frac{e\varphi}{T}\right]. \quad (22)$$

Evidently, when $\lambda_1 > 4T$ the $x_1(\phi)$ curve has an S-shaped portion (see Fig.11), and therefore a change in ϕ must produce a discontinuous jump in x_1. The transition potential ϕ_1 and the discontinuity Δ_1 in the concentration x_1 at the transition are found to be[74]

$$e\varphi_1 = -T\ln(1-x_0)/x_0 + \lambda_1(1/2 - x_0) \quad (23)$$

$$(1+\Delta_1)/(1-\Delta_1) = \exp(\lambda_1\Delta_1/T). \quad (24)$$

¶The case of $\lambda_1 = \lambda_{12} = 0$, $\lambda_2 > 0$ can be treated in a similar way.

In other words, if the potential ϕ varies with the spatial coordinate we obtain a discontinuous change in the concentration x_1 by an amount Δ_1 at the coordinate for which $\phi = \phi_1$. Transitions of this type can give rise to an anomalous charge distribution in the surface layer. By using Eqn.(18) and the solution (22) it can be shown[74] that at high enough potentials an anomalous region of thickness z_* and properties different from those of the bulk material is formed near the surface (see Fig.12). Under these conditions the surface layer can be either enriched or depleted of interstitial ions, depending on the value of x_0, or of vacancies (in the case of $\lambda_1 = 0$, $\lambda_2 > 0$).

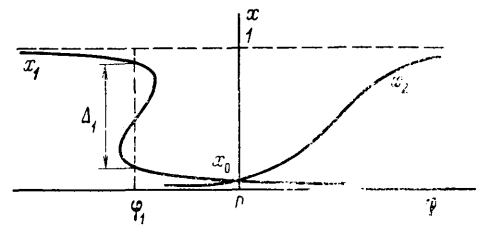


Figure 11. Plots of $x_1(\phi)$ and $x_2(\phi)$ for $\lambda_1 > 4T$ and $\lambda_2 = \lambda_{12} = 0$.

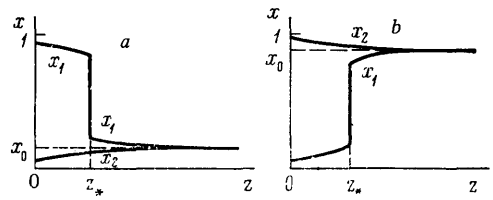


Figure 12. Distribution of x_1 and x_2 in the near-surface region for $\lambda_1 > 4T$ and $\lambda_2 = \lambda_{12} = 0$: (*a*) $x_0 \ll 1$, (*b*) $x_0 \cong 1$.

This effect (the production of a surface layer with anomalous properties whose thickness can be controlled by an applied potential) should be found in all physicochemical processes sensitive to charge distributions near phase boundaries. In particular, if the collective interactions play an important role, and the field can initiate a phase transition, the capacity of the diffusion layer changes suddenly when the transition potential ϕ_1 is reached (curve 3 of Fig.10). The effect can be observed also in studies of ionic surface conductivity, of optical properties of surfaces, and of the current–voltage characteristics of various interfaces (see below). We should stress that surface disorder induced by an electric field may occur also when thermal transitions are excluded by the values of the crystal parameters.

In addition to the surface disorder discussed in Ref.74, an external electric field applied to a crystal can induce disorder (and hence a jump in ionic conductivity) within the volume of the crystal. The theory of discontinuities in bulk ionic conductivity induced by an electric field was developed in Ref.76, and the first experimental data on this effect were reported in Ref.77.

2. Phenomenological Transport Equations

We shall now examine a solid electrolyte with structural disorder whose conductivity is caused by interstitial cations and cation vacancies. There is no difficulty in principle in generalising the discussion to more complex systems. According to the basic principles of irreversible thermodynamics the flows of components (i) can be expressed as[78,79]

$$i_{1,2} = \mp \frac{eD_{1,2}}{T} n_{1,2}(1 - n_{1,2}/n_{1,2}^{\max}) \nabla\mu_{1,2} \ , \qquad (25)$$

where the subscripts 1, 2 refer to interstitial cations and to vacancies, and $D_{1,2}$ are the diffusion coefficients, related to the mobilities $u_{1,2}$ by the Nernst–Einstein relationship $eD_{1,2}/T = u_{1,2}$. Using Eqn.(16) we obtain

$$i_{1,2} = \mp eD_{1,2}[\nabla n_{1,2} \mp eu_{1,2}n_{1,2}(1 - n_{1,2}/n_{1,2}^{\max}) \nabla\varphi] \ . \qquad (26)$$

In the region of $n_{1,2} \ll n_{1,2}^{\max}$ (where the lattice saturation effect is absent) the expressions (26) are indistinguishable from the standard expressions for the currents in systems with low carrier concentrations. Allowing for lattice saturation involves a modification to the transport equations[78,79].

In the absence of current the interstitial ions and the vacancies are in thermodynamic equilibrium†. The flow of current (in general) perturbs the equilibrium. Hence, terms describing the generation–recombination (i.e. the relaxation) processes of the carriers must be included in the transport equations. Thus, the full system of equations for calculating the distribution of the three quantities n_1, n_2, and the potential $\psi \equiv e\phi/T$ is

$$\frac{\partial n_1}{\partial t} = D_1 \frac{\partial}{\partial x}\left[\frac{dn_1}{dx} + n_1 \left(\frac{n_1^{\max}}{n_1^{\max} - n_1}\right)^{-1} \frac{d\psi}{dx}\right] + q(n_1, n_2, \psi) \qquad (27)$$

$$\frac{\partial n_2}{\partial t} = D_2 \frac{\partial}{\partial x}\left[\frac{dn_2}{dx} - n_2 \left(\frac{n_2^{\max}}{n_2^{\max} - n_2}\right)^{-1} \frac{d\psi}{dx}\right] + q(n_1, n_2, \psi) \qquad (28)$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi e^2}{\varepsilon_0 T}(n_1 - n_2) \ . \qquad (29)$$

The relaxation processes in the system are described by the function $q(n_1, n_2, \psi)$. In particular, starting from the law of mass action, and allowing for the lattice saturation effect, we arrive at

$$q = -k_1 n_1 n_2 + k_2 (n_1^{\max} - n_1)(n_2^{\max} - n_2) \ ,$$

where $k_{1,2}$ are the rate constants for the recombination and the generation of the carriers. Under steady-state conditions (i.e. $\partial n_{1,2}/\partial t = 0$) the continuity of the total current ($i = i_1 + i_2$) follows from Eqns.(27) and (28).

The above system of non-linear equations is very complex and can only be solved by approximate methods. One of these methods, used in the solution of electro-diffusion problems in liquid electrolytes, is the boundary layer method[80–83], which relies on the fact that the problem includes a small parameter.

The size of the cell L is usually many orders of magnitude greater than the Gouy (or Debye) screening length κ^{-1}, and therefore we can (as in the case of liquid electrolytes) separate the space charge region of thickness l (comparable to κ^{-1}) from the region of electrical neutrality of thickness L, the size ratio of the two regions being $l/L \ll 1$.

In the electrically neutral region $n_1 = n_2$, and the system of three equations (27)–(29) reduces to the two equations (27) and (28) for the two unknowns $n_1 = n_2$ and ψ. Conversely, in the space charge region we can ignore those equations, and confine our analysis to Eqn.(29), by assuming that in this region the n_1 and n_2 concentration distributions are not perturbed by the flow of current. A detailed discussion of this type of problem is given in Ref.81. The equality $n_1 = n_2$ also allows the expression for q to be linearised to $q = (n_0 - n_1)/\tau$, where n_0 is the equilibrium concentration defined by Eqn.(3), and

$$\tau^{-1} \equiv 2k_1 n_0 + k_2[(n_1^{\max} - n_0) + (n_2^{\max} - n_0)]$$

is the reciprocal relaxation time, independent of $n_{1,2}$. Introducing the relaxation length $l_\tau \equiv (D\tau)^{1/2}$, where D is the smaller of the two values D_1 and D_2, we find that different relative values of L, l_τ, and l give rise to different cases, in which the behaviour of the system is qualitatively different:

1) $l_\tau \leqslant l \ll 1$, the fast relaxation case#;
2) $l \ll L \ll l_\tau$, the slow relaxation case;
3) $l \ll l_\tau \ll L$, the intermediate case.

We must stress that, although the above discussion has been aimed specifically at transport and relaxation processes involving carriers of two kinds, the limitation was not implicit in the use of separate electro-neutrality and space charge regions, or in the calculation of generation–recombination effects. In more complex systems several relaxation processes may be taking place simultaneously, and their role has to be analysed specifically for each particular case. Such an analysis is essential in studies of alternating-current processes in solid electrolytes, for example. Theoretical studies of this type are still insufficiently developed[2–5].

From Eqns.(30) and (31) the limiting current $i_{\lim}$ can be calculated directly. In the case of liquid electrolytes $i_{\lim}$ is determined under stationary conditions with only one type of current carrier (n_1, say), so that $n_1(L) = n_2(L) = n_0$, and at the electrode $n_1(0) = 0$. For the same conditions in solid electrolytes (assuming $q = 0$) we obtain[78,82,83]

$$i_{\lim} = i_D[(\gamma_1 + \gamma_2)/\gamma_2 + (\gamma_1 - \gamma_2)\ln(1 - \gamma_2)/\gamma_2^2] \ , \qquad (30)$$

where $i_D \equiv eD_1 n_0/L$. In the limit of $\gamma_{1,2} \to 0$ Eqn.(30) reduces to $i_{\lim} = 2i_D$, the familiar expression for a binary liquid electrolyte[70]. In general we see from Eqn.(30) that $i_{\lim} > 2i_D$, i.e. the lattice saturation effect increases $i_{\lim}$.

We note that allowance for relaxation processes in the linear approximation does not alter the general form of Eqn.(30) for $i_{\lim}$, and only involves re-normalisation of the i_D value.

An effect closely associated with transport phenomena is the development of a potential difference $\Delta\phi$ under open circuit by the application of a temperature difference ΔT between the electrodes. The thermo-electric power θ is defined as the limit

$$\lim_{\Delta T \to 0} \frac{\Delta\varphi}{\Delta T} = \theta \ .$$

If carriers of one kind only are mobile the parameter θ can be expressed, from the basic principles of the thermodynamics of irreversible processes, by the equation

$$\nabla\tilde{\mu} = \theta \nabla T \ ,$$

†The equilibrium concentrations under these conditions are defined by the condition $\mu_1 + \mu_2 = 0$ [see Eqn.(17)].

#In this case l_τ may differ from $(D\tau)^{1/2}$.

where $\tilde{\mu}$ is the electrochemical potential of the mobile carriers. The quantity $\theta = \theta_{hom} + \theta_{het}$ is divided into a homogeneous component $\theta_{hom} = -Q/Te$, where Q is the heat of transport of the ion§, and a heterogeneous component θ_{het}, associated with the temperature dependence of the contact potential differences at the interfaces. If the current is carried by singly charged cations, and local equilibrium is established at the phase boundaries, we can assume that the component θ_{het} is independent of T [84] and write

$$\theta = -Q/Te + \text{const} \ .$$

Experimental determination of Q from the slope of the linear (θ, T^{-1}) plot yields values close to the activation energy for conduction of the mobile ions. This conclusion is consistent with calculations by the microscopic approach[85-87] (see Section IV).

From measured values of θ we can calculate the thermodynamic characteristics w and λ of the crystal, discussed in Section II. These values are found to agree with those obtained from measurements of the excess specific heat of the disordering process[63].

3. Transport Through a Phase Boundary

Theoretical descriptions of electrode processes are dependent on a correct model of the mechanism by which the current carriers are discharged at the phase boundary. In general, the partial currents i_1 and i_2 at the electrode depend on the carrier concentrations n_1 and n_2 at the discharge plane, and also on the electrode potential ϕ_0 and on the structure of the region adjacent to the electrode. The exact form of the kinetic relationship $i_{1,2} = i_{1,2}(n_1, n_2, \phi_0)$ is largely determined by the chosen microscopic model. The mathematical expressions describing the electrode process can also be used as boundary conditions for the phenomenological transport equations.

A detailed theory of ionic discharge phenomena at a phase boundary, including a solid electrolyte, is not yet available. It is reasonable, therefore, to apply to our system the general model of the slow discharge theory[70], developed for the boundary between a liquid electrolyte and a metal. However, the equations of this theory need some modification. When corrected for the lattice saturation effect and for the contribution of both interstitial ions (cations) and vacancies to the electrode process, the slow-discharge equations for the currents i_1 and i_2 at the electrode–solid electrolyte interface become

$$i_1 = i_{10}\left[\frac{n_1^{max} - n_1}{n_1^{max} - n_1^e}\exp(\beta_1\eta) - \frac{n_1}{n_1^e}\exp(-\alpha_1\eta)\right] \qquad (31)$$

$$i_2 = i_{20}\left[\frac{n_2}{n_2^e}\exp(\beta_2\eta) - \frac{n_2^{max} - n_2}{n_2^{max} - n_2^e}\exp(-\alpha_2\eta)\right] \ . \qquad (32)$$

In these expressions i_{10} and i_{20} are the exchange currents of interstitial cations and cation vacancies respectively, η is the overvoltage ($\eta \equiv (\psi^0 - \psi^0_e) - (\psi' - \psi'_e)$, where ψ^0 and ψ' are the potentials in T/e units of the electrode surface and of the discharge plane¶ of the ions, $n^e_{1,2}(\psi'_e)$ are the equilibrium values (at $\eta = 0$, or $i_1 = i_2 = 0$) of the surface concentrations $n_{1,2}(\psi')$ which appear in (31) and (32); $\alpha_{1,2}$ and $\beta_{1,2}$ are the transport numbers for the cations and the vacancies ($\alpha_{1,2} + \beta_{1,2} = 1$). The presence of two different exchange currents (for ions and for vacancies) in Eqns.(31) and (32) with a common value of η follows from the principle of detailed balancing. Eqns.(31) and (32) can be used, with (27)–(29), to calculate the polarisation current–voltage characteristics of the system.

If the stationary currents are not large ($i_{1,2} < i_D$) we find that apart from their dependence on the relaxation characteristics (the relative values of l, l_τ, and L) the polarisation curves have similar shapes†, determined by Eqns.(31) and (32) with $n_{1,2}$ and $n^e_{1,2}$ values given by Eqn.(17) and η given by the equation

$$\psi^0 - \psi' = \frac{\varepsilon_0 d}{\varepsilon}\frac{d\psi}{dx}$$

(where d and ε are the thickness and the dielectric constant of the Helmholtz layer). This expression, which is used in the theory of the double layer[70], follows from the condition of continuity of the electrical induction at the phase boundary. An analysis of the system leads to the following conclusions:

1. In the low overvoltage region ($|\eta| \ll 1$) we find an ohmic portion $i = R^{-1}(\phi^0 - \phi^0_e)$, and the resistance of the reaction $R = T/e(i_{10} + i_{20})$ depends on the sum of the exchange currents.

2. In the "intermediate" overvoltage region Tafel's law is obeyed, and at fairly high overvoltages a new law sets in as a result of the lattice saturation effect. In particular, if $i_{10} \gg i_{20}$ and $\psi^0 > 0$ we have[88]

$$\ln i/i_{10} = \beta_1\psi^0 + a, \quad \psi^0 < \psi^0_* \qquad (33)$$

$$\ln i/i_{10} = \beta_1\delta(\psi^0/\gamma_2)^{1/2} + b, \quad \psi^0 > \psi^0_* \qquad (34)$$

where a and b are constants independent of ψ^0, $\delta = \varkappa d\varepsilon_0/\varepsilon$, and the potential ψ^0_* of the transition between the laws (33) and (34) is given by

$$\psi^0_* = \ln(\gamma_2)^{-1} + \delta\left(\frac{1}{\gamma_2}\ln 2\right)^{1/2} \ .$$

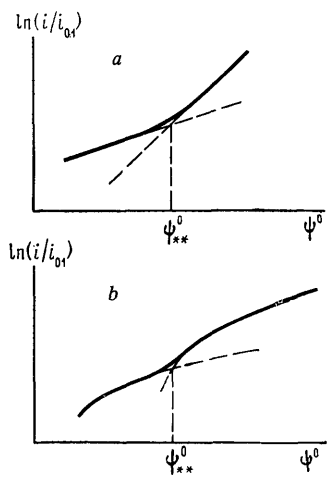


Figure 13. Transitions between different kinetic discharge regimes: (*a*) regimes corresponding to Eqn.(33), (*b*) to Eqn.(34).

§The component θ_{hom} is associated with the cross-over $L_{12} = L_{21}$ coefficient of the phenomenological transport equations of irreversible thermodynamics.

¶This plane is usually identified with the boundary of the diffusion layer (see Section III).

†In the limit of $\tau \to 0$ their shape is the same even for currents $i > i_D$.

3. A transition between different electrochemical reaction regimes is possible: from the discharge of interstitial ions ($i_1 \gg i_2$) to the discharge of ionic vacancies ($i_2 \gg i_1$), or *vice-versa*[82]. The transition may be between current–voltage characteristics of the Tafel type [Eqn.(33)] or of the type of Eqn.(34) (see Fig.13). The potentials of the transitions between regimes (ψ^0_{**}) are given (for $\psi^0 > \psi^0_e > 0$) by the expressions

$$\psi^0_{**} = \psi^0_e + (\beta_2 - \beta_1)^{-1} \ln (i_{10}/i_{20}) \quad (35)$$

$$(\psi^0_{**})^{1/2} = (\psi_e{}^0)^{1/2} + (\beta_2 - \beta_1)^{-1} \gamma_2^{1/2} \delta^{-1} \ln (i_{10}/i_{20}) \quad (36)$$

If the full current i in the system is comparable to i_D the polarisation curves suffer a radical change of shape in the slow relaxation case. The method of calculation and some special cases are discussed in Ref.82.

The polarisation curves may be affected by field-induced phase transitions in the near-surface layer of the solid electrolyte (see Section III). This effect has been shown[89] to lead to a stepwise region ("jump") in the current–voltage characteristic of the system, the potential and the amplitude of the jump being determined by the parameters used above to define the thermodynamic and kinetic properties of the crystal.

The most important of the time-dependent solutions of the transport equations (in relation to studies of electrode processes and of the bulk properties of the system) are those describing the response of the system to small harmonic perturbations. In this case an approximate analytical solution of the system of non-linear equations in partial differentials can be obtained by changing to a system of ordinary linear equations: this change is justified if the amplitude of the harmonic signal is small enough. The method of investigating these systems by studying the relationship between a small harmonic signal and the voltage has been called the impedance method. The application of the impedance method to electrochemical systems is discussed in detail in Ref.90. Within the framework of this method the electrochemical cell is replaced by its corresponding equivalent circuit, in which each element relates to one particular process in the system. The choice of equivalent circuit is not unique, in general. Calculations of the impedance of solid electrolyte cells for different assumed models are described in several papers (see, for example, Refs.91–94).

IV. BASIS OF THE MICROSCOPIC APPROACH. PHYSICAL METHODS OF INVESTIGATION

In this Section we shall examine two groups of problems: 1) some aspects of the microscopic description of ionic transport processes in solid electrolytes, which have been developed in recent years, and 2) the theoretical foundations of the physical methods used experimentally both to justify the choice of microscopic models and to obtain numerical values of the characteristic parameters of the crystals.

The theory of microscopic processes in solid electrolytes is still far behind the stage of development of the theory of transport processes in normal solids. This explains the proliferation of different (and often incompatible) models proposed by various authors. Similarly, the physical methods so far applied to the study of microscopic processes in solid electrolytes have failed, on the whole, to make full use of their implicit possibilities, only a small proportion of the experimental techniques to solid-state physics having been brought to bear.

We shall therefore selectively aim our discussion at those concepts and methods whose value has already been convincingly demonstrated.

1. Microscopic Models of Transport Phenomena

Published theoretical treatments of transport phenomena in superionic crystals by the microscopic approach can be arbitrarily classified into a number of groups.

Many of the papers describe calculations of the diffusion coefficients and mobilities of point defects (interstitial ions or vacancies) under the influence of an externally applied potential. Some of the earlier models have relied on the quasi-free ion concept, analogous to the Sommerfeld–Drude–Lorentz approach to electronic transport phenomena in metals[95,96]. Armstrong and coworkers[97] applied the expressions of the theory of rate processes to a model of thermally activated translation jumps. In this type of calculation the conductivity is expressed, in accordance with experimental data, as $\sigma = \sigma_0 \exp(-E_a/T)$, where the physical significance of σ_0 and that of the activation energy E_a are different in different models. The E_a values for most of the "good" solid electrolytes are relatively small, and similar (~0.1 eV), but the range of σ_0 values extends over several orders of magnitude. Various explanations of this phenomenon have been proposed[98–103] (failure of the simple models when applied to the calculation of the frequency of "attempted jumps" between potential wells, failure to allow for cooperative motion, etc.).

Several papers have dealt with the microscopic calculation of the relationship between the diffusion coefficient and the mobility of the ions allowing for the correlation effects which cause deviations from the Nernst–Einstein relation[104–108].

In another group of papers the properties of the superionic crystal are calculated analytically from a model Hamiltonian[103,109–114]. Some of the earlier attempts[99,100] tried to describe the collective interactions of interstitial ions in superionic crystals by exactly the procedure applied to the electrons in an ordinary ionic crystal (the polaron model). This approach has the advantage of bringing to bear on the problem the well tried mathematical framework of polaron theory. The concept of small polarons was introduced to explain the Hall effect in solid electrolytes[115].

The lattice gas model[85,86,116] is similar to the approach used by Mahan[100]: it assumes the existence of particles described in the secondary quantisation formalism by anti-commutating generation and annihilation operators. The anti-commutation arises because a lattice site (or an interstitial) can be either empty or occupied by a single particle. The Hamiltonian for the sum over the lattice sites includes terms describing the interactions with nearest neighbours, jump terms, and in some treatments terms describing the interaction with phonons. This model has been used[85] in the one-dimensional form to calculate the transport heat Q of the ion, which defines the homogeneous part of the thermo-electric power (see Section III). At relatively low temperatures the parameter Q is found[85] to coincide with the activation energy for conduction E_a, as in the case of non-interacting particles; a three-dimensional treatment of the problem has also been given[86], with allowance for the interaction of the mobile ions with phonons. This interaction causes a small difference between the quantities Q and E_a ($Q < E_a$) due to the energy of formation of the polaron.

Yet another group of papers relies on computer calculations. In the early work of this type[117–119] the interionic interaction potentials were used to calculate the "potential contour" maps for the mobile ions in the crystal and hence

the activation energies, the crystallographic directions of highest ionic conductivity, etc. The energetics of both "shallow" and "deep" levels for ions, their numbers, and their relative position in space have been calculated for specific crystals[120]. This approach helps to determine, in particular, what proportion of the ions is involved in transport phenomena.

Lastly, some of the most recent publications on the theory of solid electrolytes have used the molecular dynamics method (a new method of studying systems of many particles[121]). The development of the molecular dynamics method was made possible by the availability of advanced computer techniques: the method is based on mathematical modelling of the motion of an ensemble of particles subjected to given interaction laws. Numerical solutions of the equations of motion yield the dynamic trajectories of the particles and hence, by applying the ergodic hypothesis, the mean values of the dynamic variables can be obtained. For example, an ensemble consisting of a large number of Ag^+ and I^- ions contained in a cube with periodic boundary conditions has been analysed in this way[122]. From the interaction potentials, whose parameters were chosen from the known ionic radii of Ag^+ and I^-, from the crystal structure of α-AgI, and from diffraction data, the motion of the Ag^+ ions was calculated directly. From results of this type the diffusion coefficient D of the Ag^+ ions (say) can be obtained directly, using the general definition

$$\lim_{t\to\infty}\langle r^2(t)\rangle = 6Dt + \text{const}\ ,$$

where $\langle r^2(t)\rangle$ is the mean-square displacement calculated by the molecular dynamics method#. Similar calculations give the correlation functions of the velocities (u) of the ions: $\langle u(t)u(0)\rangle$. The behaviour of these functions for different values of t characterises the frequency dependence of the conductivity $\sigma(\omega)$. Thus the parameters of the kinetic processes can be expressed through the initial micropotentials of the ionic interactions, which are obtained from independent data.

The molecular dynamics method has been used in studies of the properties of the following solid electrolytes: AgI,[123-127] CuI,[125] CaF_2,[127,128] $SrCl_2$,[129] and γ-Al_2O_3.[79] The characteristics of the superionic crystals which have been calculated include $\sigma(\omega)$, the distribution of the concentration of mobile ions, the diffusion coefficients, and the displacement of the ions in the rigid sublattice. In every case the agreement between calculation and experiment was good. The results also confirm the existence of phase transitions in many solid electrolytes.

2. Interaction with Electromagnetic Radiation

By virtue of its interaction with the individual particles and with the collective excitations present in the crystal, a beam of electromagnetic radiation passing through a solid electrolyte experiences both elastic and inelastic (i.e. accompanied by frequency changes) scattering processes. The inelastic scattering processes are most intimately connected with the microscopic characteristics of the crystal§.

#The result, $D = 2.5 \times 10^{-9}$ m^2 s^{-1}, is close to the value measured experimentally.

§These processes are also called Mandel'shtam–Raman–Brillouin scattering.

The intensity I_R of inelastically scattered radiation of frequency ω is given by the dissipative fluctuation theorem[130] as

$$I_R = A\varepsilon''/[1-\exp(-\hbar\omega/T)]\ , \qquad (37)$$

where $\varepsilon''(\omega)$ is the imaginary part of the complex dielectric constant $\varepsilon(\omega)$, and the quantity A is proportional to the square of the matrix element of the corresponding quantum-mechanical transition. The form of the denominator of Eqn.(37) stems from the fact that the quanta of electromagnetic radiation obey Bose–Einstein statistics.

The frequency-dependent conductivity $\sigma(\omega)$, which describes [like $\varepsilon''(\omega)$] the dissipative processes in the system, is related to ε'' by the expression

$$4\pi\sigma(\omega)/\omega = \varepsilon''(\omega)\ . \qquad (38)$$

If the frequency of the radiation is such that $\hbar\omega \ll T$, and the parameter A is weakly dependent on ω, it follows from (37) and (38) that $\sigma(\omega) \propto \omega^2 I_R$. The last expression shows that the inelastic scattering spectra contain direct information on the microscopic details of the conduction mechanism. Furthermore, independent determinations of the function $\varepsilon''(\omega)$, for example from infrared absorption and reflection data, can also be directly related to the frequency dependence of the conductivity $\sigma(\omega)$. Measurements of this type, using procedures which have become well established in solid-state physics (including dispersion expressions), have been applied to a large number of superionic crystals[131-161].

In one of the simplest models the function $\varepsilon(\omega)$ can be found by examining the frequency of a damped harmonic oscillator in an external electric field E:

$$\ddot{x} + \gamma\dot{x}\omega_0^2 x = zeE/m\ , \qquad (39)$$

where x, Ze, and m are the coordinate, the charge, and the mass (reduced) of the vibrating ion, ω_0 is the vibration frequency in the crystal lattice, and γ is the damping (dissipation) constant. Putting $E = E_0\exp(-i\omega t)$, where $i \equiv \sqrt{-1}$ is the imaginary unit, we can easily calculate from (39) the induced dipole moment $p = ezx$ and hence the polarisability $\alpha(\omega)$ of the system (since $p = \alpha E$). The function $\varepsilon(\omega)$ is then obtained by the formula $\varepsilon(\omega) = \varepsilon_\infty + 4\pi\alpha n$, where n is the number of vibrating ions which scatter radiation per unit volume, and ε_∞ is the value of $\varepsilon(\omega)$ in the limit of $\omega \to \infty$ (in an even more simplified model $\varepsilon_\infty = 1$). The resulting expression for $\varepsilon(\omega)$ is

$$\varepsilon(\omega) = \varepsilon_\infty + S\omega_0^2/(\omega_0^2 - \omega^2 - i\omega\gamma)\ , \qquad (40)$$

where S is a dimensionless constant [according to (39), $S = 4\pi z^2 \cdot e^2 n/m\omega_0^2$]. The function $\varepsilon''(\omega)$, according to Eqn.(40), is given by

$$\varepsilon''(\omega) = S\omega_0^2\omega\gamma/[(\omega_0^2-\omega^2)^2 + (\omega\gamma)^2]\ . \qquad (41)$$

The absorption spectra corresponding to Eqn.(41) should be characteristically bell-shaped (Lorentzian distribution). In spite of its simplicity, the starting model is found to be effective up to frequencies in the infrared region, and the inelastic scattering spectra of many solid electrolytes can be described satisfactorily by Eqns.(37) and (41).[131,133,135]

A direct generalisation of Eqn.(40), applicable to descriptions of the properties of ionic crystals in the infrared spectral region, can be written as

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{S_j\omega_{0j}^2}{\omega_{0j}^2 - \omega^2 - i\omega\gamma}\ , \qquad (42)$$

where S_j is the dimensionless oscillator strength for mode j, which characterises the contribution of this mode to the static ($\omega = 0$) dielectric constant: $\sum_j S_j = \varepsilon_\infty - \varepsilon(0)$. The

absorption spectrum corresponding to Eqn.(42) is a set of peaks of the type described by Eqn.(41), usually overlapping.

The specific property of solid electrolytes is the presence of disorder in one of the crystal sublattices, which can manifest itself in a variety of effects associated with the interaction of radiation with matter: different ions, as a result of differences in their coordination, will have different vibration frequencies, and perturbations in the periodicity of the lattice will affect the selection rules, causing distortions in the optical spectra.

Temperature-induced phase transitions in solid electrolytes can also affect the probabilities of optical excitation of different frequencies. This effect is mathematically equivalent to a change in the parameter S_j, i.e. to a variation of the height of the corresponding peaks. If the symmetry of the crystal lattice is changed as a result of the phase transition, the selection rules for optical transitions will also be changed, causing individual peaks in the absorption spectrum to disappear (or appear). These effects have been very convincingly demonstrated experimentally[156,162,163].

Some attempts have been made to generalise the harmonic oscillator ensemble model in a slightly different direction by allowing for the specific features of the motion of ions in solid electrolytes. In particular, a model of an oscillator with a "finite memory" has been proposed[164]: according to this model the force acting on the ion at time t depends on the velocity $\dot{x}$ of the ion at some previous time. Mathematically this assumption involves replacing the term $\omega_0^2 x$ in Eqn.(39) by $\omega_0^2 \int_{-\infty}^{t} M(t-t')\dot{x}(t')dt'$, where $M(t-t')$ is the "memory function". If this function is chosen as

$$M(t-t') = \exp[-(t-t')/\tau_c],$$

where τ_c is the correlation time, in the case of a harmonic signal [$\propto\exp(-i\omega t)$] the above integral is directly calculable, and the final solution is obtained simply by replacing ω_0^2 by $\omega_0^2 i\omega/(i\omega - \tau_c^{-1})$ in Eqn.(40). In this case the conductivity is given by the expression

$$\sigma(\omega) = \frac{z^2e^2n}{m}\,\frac{\tau_c^{-1}(\omega_0^2-\omega^2+\gamma\tau_c^{-1})+\omega^2(\tau_c^{-1}+\gamma)}{(\omega_0^2-\omega^2+\gamma\tau_c^{-1})^2+\omega^2(\tau_c^{-1}+\gamma)^2}\,. \qquad (43)$$

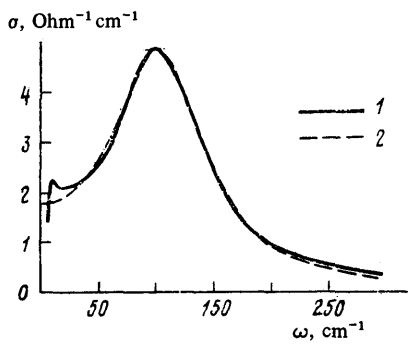


Figure 14. Frequency dependence of the conductivity [$\sigma(\omega)$] for α-AgI at 453 K:[164] *1*) experimental, *2*) calculated by formula (43).

The $\sigma(\omega)$ function calculated by Eqn.(43) for α-AgI with a suitable choice of parameters agrees very well with experiment for $\omega > 20$ cm^{-1} (see Fig.14).

The physical significance of the time τ_c is clear: for $\omega \ll \tau_c^{-1}$ the role of the electric field consists mainly in initiating the diffusional motion of the ion (the term proportional to ω_0^2 is small); conversely, for $\omega \gg \tau_c^{-1}$ the vibrational motion becomes predominant. According to Brüesch and coworkers[164] the characteristic τ_c^{-1} frequency of the transition between these two regimes is ~50 cm^{-1} (~1.5×10^{12} Hz). This value agrees well with that calculated by the formula $\tau_c^{-1} \cong (r_0^2/6D_1)^{-1}$, where r_0 is the distance between potential minima and D_1 is the diffusion coefficient of the interstitial ions.

The frequency dependence $\sigma(\omega)$ in α-AgI at relatively low frequencies ($\omega < 20$ cm^{-1})¶ has been explained[165,166] by allowing for the dependence of the motion of the ion in an alternating field upon the polarisation of the rigid sublattice, using a formalism similar to the above. A system of oppositely charged, interacting ions of two kinds has been discussed[166] by assuming that the ions of one kind can diffuse while those of the other kind are rigidly bound. The solution of the system of two equations obtained shows an apparent change in mass of the diffusion ions with frequency, since the polarisation of the medium (caused by interaction with other ions) either "succeeds" in following their motion or "fails" to do so[166]. Detailed microscopic studies of these phenomena are described in Ref.79.

Correlation effects resulting from the mutual interactions of the mobile ions are discussed in Refs.167–177.

3. Neutron Scattering

The neutron scattering method occupies a special place in the study of the properties of solid electrolytes, because the de Broglie wavelength of thermal neutrons is comparable to the interatomic distances found in typical crystals. At the same time (and unlike X-rays of the same wavelength) these neutrons have an energy comparable to the phonon energy of the crystal. Therefore, valuable information on the vibrational spectrum of the solid can be obtained by measuring the energy spectrum of the scattered neutrons.

Thermal neutrons are scattered by a crystal at a large number of lattice centres simultaneously, and therefore interference of the scattered waves is possible. The part of the scattered radiation affected by interference is called coherent scattering. In addition, different centres can scatter neutrons independently of each other, giving rise to incoherent scattering.

The scattering of neutrons by a system of many interacting particles is directly related to the behaviour of the space- and time-dependent pair correlation function $G(\mathbf{r}, t)$. The differential scattering cross-section within the solid angle $d\Omega$ and the energy range of scattered neutrons $d\mathscr{E} = \hbar d\omega$ can be expressed as

$$\frac{d^2\sigma}{d\Omega d\mathscr{E}} = \frac{a^2}{\hbar}\frac{k}{k_0}S(\varkappa,\omega)\,, \qquad (44)$$

where $S(\kappa, \omega)$ is the Fourier transform of the correlation function $G(\mathbf{r}, t)$ (the dynamic structure factor), $\kappa = \mathbf{k} - \mathbf{k}_0$ (where $\mathbf{k}_0$ and $\mathbf{k}$ are the wave vectors of the incident and of the scattered neutron), the frequencies ω are expressed in terms of the energy changes $\hbar\omega = \hbar^2(k_0^2 - k^2)/2m$ (where m is the mass of the electron), and a is the scattering length.

¶However, we should note that according to Gebhardt and coworkers[154] the conductivity of α-AgI at frequencies between 8×10^9 and 4×10^{10} Hz is described by a simple expression of the Drude type.

Inelastic coherent scattering processes are the most interesting in studies of the dynamic properties of a crystal lattice. Scattering is assumed to take place on nuclei located at lattice sites with a time-dependent displacement determined by the lattice vibrations. The correlation function (for single-phonon scattering) allows for the energy and momentum conservation laws:

$$\hbar^2(k^2-k_0^2)/2m=\hbar\omega_j(\mathbf{q}); \quad \mathbf{k}-\mathbf{k}_0=2\pi\mathbf{b}+\mathbf{q}\,, \qquad (45)$$

where $\mathbf{q}$ is the wave vector of the phonon, $\mathbf{b}$ is the reciprocal lattice vector, and $\omega_j(\mathbf{q})$ is the frequency of the j-th branch of the normal vibration to which the phonon is assigned. By measuring the one-phonon scattering cross-section of the neutrons we can determine the dispersion laws $\omega = \omega_j(\mathbf{q})$ which characterise the phonon spectrum of the crystal.

Phonon spectra have been obtained experimentally for the following series of solid electrolytes: AgI,[178-181] Ag_3SI and Ag_3SBr,[182] $RbAg_4I_5$,[180,181] BaF_2,[183-185] $SrCl_2$,[183-185] PbF_2,[185,186] Li_2SO_4,[187] $LiAlSiO_4$,[188] and β-Al_2O_3.[189,190] Special attention was paid to the spectral changes accompanying the transition of the superionic crystals into the disordered phase[178,179,182,191]. A study of the dispersion curves of silver iodide at different temperatures[178,191] revealed the loss of one low-energy optical mode during the $\beta \to \alpha$ structural phase transition. This is explained[178] by assuming that a relatively small amount of energy is expended in the rearrangement of the rigid (iodide) anion sublattice attending the transition to the superionic state. Similar results were obtained for the superionic conductors Ag_3SI and Ag_3SBr.[182]

Neutron scattering has been used also to study the behaviour of ions in disordered phases of superionic crystals. A study[96,181] of the quasi-elastic scattering of cold neutrons in the α-phase of AgI may be taken as an example. The experimental results were interpreted on the assumption that scattering occurs exclusively on the silver cations†. The following microscopic model was adopted[96] to calculate the correlation function. The ions take part in two independent types of motion: translational, and local. The translational motion of the ion is described by the hopping mechanism: the particle resides in a fixed position for a time τ_0, after which it jumps (in a time τ_1') to a point a distance l_0 away. The local motion of the ion is treated as the random ("Brownian") motion of particles in some limited regions ("cavities") of the crystal, defined by the geometry of the iodine sublattice.

The best agreement between calculated and experimental curves is obtained for the following values of the parameters: $\tau_0 = 7.5 \times 10^{-12}$ s, $\tau_1' = 16.5 \times 10^{-12}$ s, $l_0 = 5$ Å. The diffusion coefficient of the silver cations D can be calculated by the formula $D = l_0^2/6(\tau_0 + \tau_1')$. Inserting the above values of the parameters we find $D \cong 1.75 \times 10^{-9}$ m^2 s^{-1}, in good agreement with the experimental value $D_{\text{exper}} \cong 2 \times 10^{-9}$ m^2 s^{-1}. Detailed studies of the quasi-elastic neutron scattering spectra of α-AgI single crystals[181] have revealed a strong anisotropy in the motion of the Ag^+ ions#.

†The scattering cross-section of iodine is much smaller than that of silver.

#According to Cava and coworkers[192] the average jump length of the cations is $l = 1.79$ Å, but this value is inconsistent with the present result. This problem is examined specifically in Ref. 193.

To conclude this Section we note that the crystal structure of disordered phases in superionic crystals has been studied not only by the quasi-elastic scattering of neutrons, but also by diffuse neutron and X-ray scattering (X-ray and neutron diffraction).[192-211] For example, neutron diffraction experiments with α-Ag_2S have shown[197] that the silver cations are not localised in fixed positions, but behave as a "lattice liquid". The inelastic neutron scattering spectra of $RbAg_4I_5$ are interpreted[103] in terms of a model of the Brownian motion of the diffusing Ag^+ ions in a sinusoidal potential field.

4. Magnetic Resonance

Under NMR conditions, which are highly relevant in studies of superionic crystals[212,213], the system of nuclear spins interacts with an external magnetic field H_0; furthermore, the spins also interact among themselves and with the "lattice".

Let us examine the behaviour of the integral magnetic moment M of a large number of spins (magnetic moments) at a temperature T. Let the external field H_0 be directed along the z axis. In general, the component M_z of the vector M may differ from its equilibrium value M_0, corresponding to a constant field H_0, owing to the fluctuations of the local magnetic field within the crystal. Under these conditions the approach to equilibrium as a result of the interaction of the system of spins with the crystal lattice (in particular, with the phonons) obeys the phenomenological expression (Bloch equation) [214]

$$dM_z/dt=-(M_z-M_0)/T_1\,, \qquad (46)$$

where T_1 has been called the spin–lattice relaxation time.

In discussions of relaxation processes in solid electrolytes the local magnetic field is usually assumed to be produced by the fluctuating magnetic fields of the mobile ions. The time characteristics of the local fields are described in general by the time-dependent pair correlation function $G(t)$, which usually decreases exponentially by the law $\exp(-t/\tau_1)$, where τ_1 is the "relaxation" time of the correlation. Since the nature of the fluctuations changes with temperature, the quantity τ_1 is a function of temperature, and can be expressed as $\tau_1 = \tau_{10}\exp(E_a^*/T)$, where E_a^* is an activation energy and the constant τ_{10} is formally defined as the value of τ_1 at $T \to \infty$.

The relaxation time T_1 is related to τ_1 by the expression[214]

$$\frac{1}{T_1} = B\frac{\tau_1}{1+\omega_0^2\tau_1^2}\,, \qquad (47)$$

where $\omega_0 \equiv \gamma g H_0$ is the precession frequency of the spin in the magnetic field H_0 (the Larmor frequency) and B is a quantity independent of ω_0 and τ_1 and proportional to the intensity of the local magnetic field.

The temperature dependence of the spin–lattice relaxation time T_1 has been studied experimentally at both low and relatively high temperatures in a series of solid electrolytes[215-224]. The activation energies E_a^* obtained from these data by Eqn. (47) for the low-temperature phases of some superionic crystals are satisfactorily consistent with the E_a values calculated from the temperature dependence of the ionic conductivity:

Crystal	PbF_2	$LiAlSiO_4$	CuI
E_a^*, eV	0.7 [217]	0.8 [215]	0.5 [218]
E_a, eV	0.7 [225]	0.7 [226]	0.6 [227]

This agreement between the two sets of activation energy is not surprising, since the transport processes in the low-temperature region occur by jumps of individual ions

between different positions in the crystal. Under these conditions the time τ_1 can be identified with the time between jumps. This agreement is a powerful argument in favour of the validity of the postulates on which these models are based.

Measurements at relatively higher temperatures in the disordered phase (superionic state) have shown that the relaxation rate T_1^{-1} decreases exponentially as the temperature increases[98,219,221]. For $\omega_0\tau_1 \ll 1$, and assuming that the local field (and therefore also the parameter B) is proportional to the concentration of mobile particles $n(T)$, we obtain from (47)

$$T_1^{-1} \propto n(T)\tau_1(T)\,. \qquad (48)$$

In the light of Eqn.(48) the experimental results are readily explained by noting that the quantity $n(T)$ is only weakly dependent on temperature, as discussed in Section II. Thus, the qualitative statements on the "molten" state of one of the sublattices in solid electrolytes[217,218] are experimentally confirmed.

The NMR method has been used in structural studies of superionic conductors, since the local symmetry and the coordination of ions taking part in the transport process can be determined from the NMR spectra of nuclei with a quadrupole moment[228-233]. The method has been found convenient also in studies of phase transitions, especially in $RbAg_4I_5$ [234] and in $Li_{14}Zn(GeO_4)_4$.[235]

However, some results of NMR studies on solid electrolytes are not easily interpreted within the model of independent motion of ions[215,219-221]. These observations suggest the need for many-particle concepts (in particular, allowance for ion correlations) in the description of the transport properties of superionic crystals.

The effect of disorder in one sublattice on the ESR spectra has been demonstrated in solid electrolytes containing paramagnetic ions[236-238]. The ESR method has been used also to study the distribution of impurity ions in superionic crystals[239-243].

* * *

Our analysis of theoretical and experimental results has shown that considerable progress has been made in recent years in understanding the physical basis of the phenomena in solid electrolytes, though many important and interesting problems still await a solution. The set of problems associated with the superionic conduction phenomenon has now been clearly formulated as a self-contained and quite extensive scientific discipline.

The thermodynamics of superionic conduction are closely associated with those of other solid-state phenomena which have been more fully investigated (disorder in alloys, in solid solutions, and in ferroelectrics). We should stress that some of the theoretical results discussed in this review (in particular, the possible existence of bitransitions, and the stimulation of polymorphic transformations in crystalline structures by the presence of disorder in one of the sublattices) are directly relevant to a much wider range of materials.

The discontinuous change in ionic conductivity induced by an external electric field may be found to have practical as well as purely scientific interest.

Ionic transport phenomena in solid electrolytes have a number of specific features whose study offers a better understanding of the analogous phenomena in liquid electrolytes on the one hand and in "normal" ionic crystals on the other hand. We can expect the present intensive studies of the structural, thermodynamic, and kinetic properties of solid electrolytes to lead to a far more detailed knowledge of the behaviour of these materials.

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