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Structural Aspects of Anomalously Fast Ionic Conductivity in Solids

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Conditions for anomalously fast ionic conductivity in solids are derived from the mechanism for interstitial diffusion. It is shown that the presence of more than the equivalent number of sites for one of the constituents is not a sufficient explanation for the anomalously fast diffusion. Some suggestions are made for the development of an approximate description of the anomalously fast diffusion.

1. Introduction

Anomalously fast migration of ions in solids is of interest for solid state batteries and solid electrolytes (*1–7*). Specific conductivities of 0.1 Ω^{-1} cm^{-1} are necessary for many applications. Presently only a limited group of silver compounds have these conductivities at ambient temperature (*3*). The selection of materials with high ionic conductivity could benefit from the understanding of the diffusion mechanism. However, the available theoretical interpretations (*8–14*) are not useful for the purpose of materials selection.

The theories using a liquid sub-lattice to explain the high ionic conductivity are very vague (*17*). They do not lead to a relationship between materials properties and fast diffusion. The free-ion model (*14*) gives a more detailed description of the relationship between some properties depending upon the presence of free ions. However, the reason why free ions should be present in some materials remains obscure.

In many approaches it is suggested that the availability of more than the equivalent number of sites for the mobile ion is already an explanation (*17–18*). In this contribution we want to show that this structural statement is not an explanation, but that it might be a condition for anomalously fast diffusion. First the condition of a low activation energy for the diffusion process is interpreted thermodynamically. Next it is shown that the structural statement does not necessarily mean that the thermodynamic condition is fulfilled. Additional assumptions are required in order to arrive at an adequate description of the process of anomalously fast diffusion.

2. Conditions for Normal and Anomalous Diffusion

The normal diffusion process in solids generally takes place by means of some defect mechanism, like the vacancy-, interstitial-, interstitialcy-, etc. mechanism (*15, 16*). We limit this discussion to the interstitial mechanism. The incomplete description presented in this section deviates somewhat from the conventional one in order to establish the prerequisites for the description of the anomalous process.

When the interstitial mechanism prevails, the conductivity will be proportional to the concentration of the diffusion-ready atoms (ions) X_i.

The following assumptions are used:

(1) during the diffusion process the formation process

$$V_i + X_X \leftrightarrows V_X + X_i \qquad (1)$$

($X_X = X$ atoms (ions) on normal X-sites, $V_X =$ vacancy on X-site, $V_i =$ interstitial site) remains in equilibrium. Thus the diffusion process of X_i is slow compared to the formation process. The standard Gibbs free energy change of process (1) is $\Delta G_i{}^0$;

(2) $[X_i] \ll [X_X]$;

(3) Once the ion is present in the interstitial position 2, its move to interstitial positions 3, 4 etc. leads to energetically and symmetrically equivalent positions (see Fig. 1);

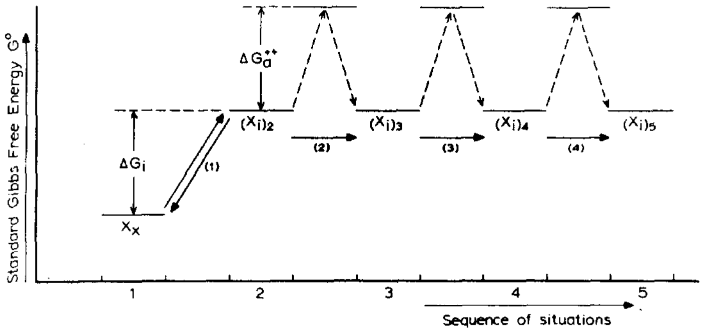

FIG. 1. Standard Gibbs free energies of subsequent situations during interstitial diffusion. The influence of concentration and field gradients is not included. (1), (2), etc. are diffusion steps; 1, 2, 3, etc. are situations.

(4) The diffusion process (2), (3), etc. (see Fig. 1) are assumed to pass through an activated state, characterized by an activation Gibbs free energy ΔG_a^{++}.

The conductivity can be shown to be proportional to the following factors

$$\sigma \propto [X_i]\exp(-\Delta G_a^{++}/kT)$$
$$= [X_X]\exp(-\Delta G_i/2kT)\exp(-\Delta G_a^{++}/kT) \quad (2)$$

The other factors occurring in the complete description are not important in this discussion.

Generally, more complicated processes and situations can occur. See, for example, Fig. 2 where the first step passes through an activated state and where situations 2, 3, 4, etc. are not energetically equivalent. Using the situations and processes indicated in Fig. 2, we can formulate three conditions which must be fulfilled for the interstitial diffusion process in order to lead to anomalously fast diffusion:

(1) Process (1) which brings the lattice atoms into the diffusion ready position, must have ΔG_i small, preferably zero;

(2) The subsequent processes (2), (3), etc. must lead to situations with standard Gibbs free energies equal to that of situation (1);

(3) For all transitions mentioned the activated state must have a small or zero value for ΔG_a^{++}.

Figure 3 represents the case in which the energies of the situations are equal, but where a small activation energy for the processes is still present.

The interpretation of the thermodynamic conditions formulated above leads to some important conclusions. Considering situation 2 in Fig. 3 for a moment as the diffusion-ready situation, it is obvious that $[X_i]_2 = [X_x]_1 = 0.5N_x$ (N_x is concentration of x-sites) when equilibrium between 1 and 2 prevails. Thus one condition for fast diffusion is that *all* atoms (ions) of the major constituent X are diffusion ready. This increases the conductivity with respect to the situation of figure 1 or 2 with many orders of ten. The use of a domain model (see next section) might decrease the concentration of the diffusion-ready ions to 1–10% of the available ions. This still is much larger than in the typical defect type mechanisms.

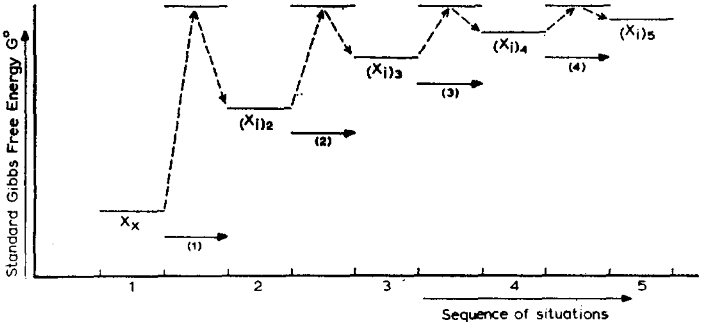

FIG. 2. As Fig. 1: a more complicated series of processes occurs. The increase of the Gibbs free standard energy in situations 2, 3, etc. might be due to an increased distance between the interstitial atom (ion) and the vacancy left behind.

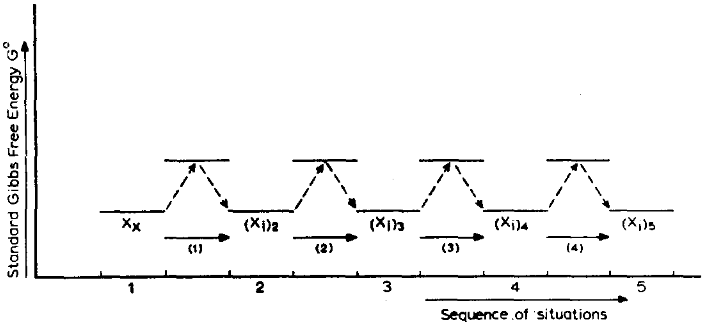

FIG. 3. One of the possible situations during anomalously fast diffusion.

The most obvious way to fulfill condition 1 ($G_1^0 = G_2^0$) and condition 2 ($G_2^0 = G_3^0 = G_4^0$) is to make the situations 1, 2, 3, 4 indistinguishable. This means that each diffusion step transforms each situation (with a large fraction of the atoms or ions X diffusion ready) into an energetically and symmetrically equivalent situation (and thus again a large fraction of all atoms or ions X diffusion ready). Such a process differs fundamentally from the interstitial diffusion process and thus anomalously fast diffusion merits a special theory. The interstitial diffusion mechanism was used to show which changes are necessary to come to anomalously fast diffusion. Once that situation is obtained, the quantities describing the interstitial process cannot be properly used any longer.

3. Structural Aspect of Anomalously Fast Diffusion

It is suggested in the literature (*17, 18*) that the occurrence of anomalously fast diffusion (and thus at least the fulfilment of conditions 1 and 2 in the interpretation given above) is comprehensible when the following structural statement is true. When the unit cell of a crystalline compound contains m equivalent sites whereupon only n atoms (ions) of one of the composing elements occur statistically distributed, the occurrence of anomalously fast diffusion is obvious ($m > n$, both m and n are small, possibly fractional numbers). For example, α-AgI has a body centered structure with 2I$^-$-ions per unit cell. It has 6 sites with a distorted octahedral symmetry per unit cell ($m = 6$), at which 2 Ag$^+$-ions ($n = 2$) must be distributed. (More complicated distributions are considered in the literature quoted.) Although this structural statement generalizes the experimental evidence for a number of materials it is not an explanation for anomalously fast diffusion. This is not only clear when we consider condition 3 (activation energy for the transitions), but even conditions 1 and 2 are not an obvious consequence of the structural statement. The reason is that the structural evidence is based upon X-ray technique, which averages positions in time over vibration modes and over local configurations, when they occur. However, for the diffusion the momentary local configuration is essential and not the average of a number of configurations. Let us assume that the ions are in ordered position in an area of limited size (for α-AgI this might lead to a tetragonal structure locally). Now displacing one ion to another "equivalent" site requires the energy for making an interstitial ion. This energy is much larger than the value found for the activation energy of the anomalously high conduction. Thus condition 1 is not fulfilled.

Since anomalously fast diffusion is found in some of the materials characterized by the structural statement, some other diffusion mechanism must be operative. From the many complex mechanisms we quote the following possibilities:

(1) A cooperative jump of a number of atoms (ions) to the equivalent empty positions. Generally, such a concerted move of many ions is very improbable;

(2) Movement of walls between domains of ordered configurations. In a forthcoming paper (*19*) electrostatic calculations in idealized β-Al_2O_3 will be used to demonstrate that this assumption is attractive for the fulfilment of the thermodynamic condition. Elsewhere, the structural statement will be explored to find favourable structures for anomalously fast diffusion (*20*);

(3) The diffusion process might exist of changes between situations characterized by random

occupation. However, it can be shown that random occupation leads also to the domain description (*20*);

(4) The free-ion model quoted earlier. In a final analysis it is quite well possible that the free-ion model and the domain model with fast moving walls are equivalent descriptions of the same process. Presently, the free ion model is more adapted to relate the properties of known materials, whereas the domain model is more useful for selecting new materials.

Summarizing this contribution it is obvious that the presently available descriptions of anomalously fast diffusion are not useful in the selection of new materials. The condition for anomalously fast diffusion, viz. the low activation energy for the diffusion process, can be formulated thermodynamically. This leads to the statement that for each individual diffusion step the begin- and the end-state are energetically and symmetrically equivalent. This condition is not equivalent to the structural statement, which suggests that the availability of more than the equivalent number of sites for the mobile ion is an explanation for fast diffusion. Although the structural statement might be a necessary condition for anomalously fast diffusion, it is suggested that an additional feature is necessary to fulfill the thermodynamic condition. It is suggested that this feature might be the occurrence of domains. Then diffusion process is the fast movement of domain walls. The structural statement together with the domain description might fulfill the thermodynamic condition.

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