The Nature of Lattice Defects in Silver Bromide Crystals

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IT was first pointed out by Frenkel[1] that ionic crystals may have a volume conductivity only if there are free vacancies, or free interstitial ions in the lattice. He also suggested that the presence of these defects may be explained thermodynamically by the fact that the crystal with vacancies or interstitial ions has a higher entropy than a perfect crystal. Schottky and Wagner[2] and others[3] subsequently investigated the possible types of defects that can occur, and, as a result of this work, it is generally agreed that either one of the following two types occur in the monovalent metal halides with the sodium chloride type of lattice.

I (Cf. Fig. 1a). Positive or negative ions, or both, leave regular lattice sites and enter interstitial positions. It is generally assumed that the entropy S, gained by forming n vacancies and n interstitial ions of a given kind in this way is

$$S = kn \log (n/N_n) + kn \log (n/N_i), \quad (1)$$

where N_n is the total number of normal sites and N_i is the number of interstitial sites. For simplicity we shall assume that

$$N_n = N_i \equiv N.$$

From this value of the entropy, it is found that the ratio, r_I, of the number of vacancies of a given kind to the number of normal ions is

$$r_I = n/N = \exp \left[-\epsilon_I''/2kT \right], \quad (2)$$

where ϵ_I' is the energy required to transfer an ion from a lattice position to an interstitial position.

II (Cf. Fig. 1b). Positive and negative ions leave normal sites in equal number and move to the surface. In this case there are an equal number of vacancies of each kind and there are no interstitial atoms. The equation analogous to (2) is

$$r_{II} = n/N = \exp \left[-\epsilon_{II}''/2kT \right], \quad (3)$$

where ϵ_{II}'' is the energy required to move both a positive and a negative ion to the surface.

Detailed computations of Jost and Nehlep[4] seem to show conclusively that $\epsilon_I - \epsilon_{II}$ is positive and of the order of 1 ev for the face-centered alkali halides. Hence defects of type II are far more probable than those of type I in these salts. On the other hand, the same workers have given good semi-quantitative evidence to show that $\epsilon_I - \epsilon_{II}$ probably is negative in AgCl and AgBr because the van der Waals forces between Ag ions and halogen ions are considerably larger than those between alkali metal ions and halogen ions. As a result, they suggest that defects of type I occur more commonly than those of type II in these silver halides.
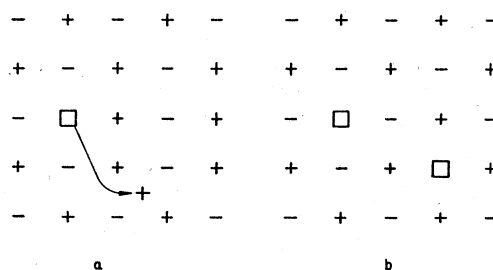

a　　　　　　　　b

FIG. 1. (a) Lattice defect of type I. Ions leave normal lattice sites and enter interstitial sites. The crystal then has vacancies and interstitial ions. In the case illustrated defects for the positive ion lattice are shown. (b) Lattice defect of type II. There are vacancies in both lattices in equal numbers and no interstitial ions. The ions that leave the lattice to form vacancies go to the surface and extend the crystal. The density of the crystal is the same as for a perfect lattice in case I; it is smaller in case II.

Wagner and Beyer[5] claim to have direct experimental evidence supporting Jost and Nehlep's conclusion concerning the type of defects in AgBr. They assume that r is of the order of unity for the liquid salts at the melting point and compute r for the solid at the same temperature by taking the ratio of the ionic conductivity of the solid to that of the liquid, that is

$$r \text{ (solid)} = \sigma \text{ (solid)}/\sigma \text{ (liquid)}. \quad (4)$$

[1] I. Frenkel, Zeits. f. Physik **35**, 652 (1926).

[2] C. Wagner and W. Schottky, Zeits. f. physik. Chemie **B11**, 163 (1930), *et. seq.*

[3] Cf. W. Jost, *Diffusion und Chemische Reaction in Festen Stoffen* (Dresden, 1937).

[4] W. Jost and G. Nehlep, Zeits. f. physik. Chemie **B32**, 1 (1936).

[5] C. Wagner and J. Beyer, Zeits. f. physik. Chemie **B32**, 113 (1936).
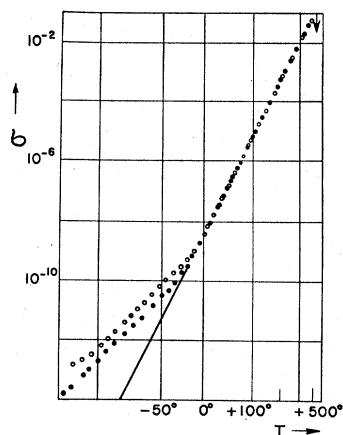
FIG. 2. A log σ versus $1/T$ plot of the conductivity, σ, of AgBr (after Lehfeldt). The slope of the high temperature part of the curve, which is precisely reproducible, corresponds to an activation energy of 0.66 ev. The slope of the low temperature position, which depends on the previous history of the specimen, corresponds to one of about 0.30 ev.

This leads to the value 0.16 for r (solid). They then show that, to within the experimental error of about one percent, the observed density at this temperature is the same as that computed from the x-ray lattice constant measurements under the assumption that each cell is fully occupied. Since this can occur only for a crystal of type I if r actually is 0.16, they conclude that AgBr is of this type.

It seems to the writer that the use of Eq. (4) is not well justified because recent investigations on the structure of liquids show that they possess a large amount of local order. Hence r may be considerably less than unity for the liquid at the melting point. The following alternative method of computing r (solid) at the melting points should be somewhat more reliable.

The conductivity of an ionic crystal may be expressed in the form

$$\sigma = ne\mu, \qquad (5)$$

where n is the number of potentially free ions or vacancies, given by Eqs. (2) or (3) in the present case, e is the ionic charge, and μ is the mobility of these ions. We shall assume that μ has the form

$$\mu = A \exp [-\epsilon'/kT], \qquad (6)$$

where A is practically independent of temperature and ϵ' is the activation energy for motion of the potentially free ions or vacancies. A formal equation could be written for A with the theory of reaction rates, but this is not necessary for the present discussion since we shall be interested only in ϵ'. Eq. (5) may be written in the form

$$\sigma = NeA \exp [-(\tfrac{1}{2}\epsilon''+\epsilon')/kT],$$

using Eqs. (2) or (3) and (6). ϵ'' is one of the energies in case I or II. According to Lehfeldt's[6] measurements of the conductivity of AgBr near the melting point (cf. Fig. 2)

$$(\epsilon''/2+\epsilon') = 0.66 \text{ ev}.$$

The observed slope of the log σ versus $1/T$ curve becomes less steep at low temperature. We shall assume that the high temperature value of r is quenched in this low temperature range so that the slope is determined by ϵ' alone. From the experimental curve we find

$$\epsilon' \cong 0.30 \text{ ev},$$

whence

$$\epsilon''/2 \cong 0.36 \text{ ev}.$$

Placing this in either (2) or (3) we find

$$r \sim \exp [-4.150/T],$$

which is $10^{-2.6} = 0.0025$ at the melting point (410°C). According to this result the influence of the defects on the density in case II would be less than the experimental error. Moreover, if we assume that the relation

$$r \text{ (solid)}/r \text{ (liquid)} = \sigma \text{ (solid)}/\sigma \text{ (liquid)}$$

is valid at the melting point, we find from Wagner and Beyer's results and the preceding estimate of r (solid), that

$$r \text{ (liquid)} \sim 0.015.$$

To summarize, it may be said that value of ϵ'' computed from the observed conductivity indicate that the fraction of defect ions in AgBr is too small to allow a differentiation between types I and II on the basis of present density and x-ray lattice constant measurements

[6] W. Lehfeldt, Zeits. f. Physik 85, 717 (1933).