is seen to be favorable, but with an important difference in implication. From their data there is no indication that θ_D has yet begun to level off toward a constant value. The present work, however, indicates a leveling off in the neighborhood of 3°K with an approach to a value between 128 and 129°K for $T=0$°K. The average of the ten points below 3.5°K gives $\theta_{KI}=128.3$°K. The value of 3°K is in rough agreement with Blackman's criterion of $\theta_0/50=2.6$°K. Norwood and Briscoe,[2] in a companion paper to this one, describe measurements of the low-temperature elastic constants of KI. Again comparison of the elastic-constant θ with specific-heat θ may be made. They report two values, depending on the method of calculation. Using DeLaunay's tables,[12] they derive $\theta_0=131\pm2$. Using Houston's method[13] as extended by Betts, Bhatia, and Wyman,[14] they get $\theta_0=129\pm2$. The agreement with either is felt to be good.

In light of a recent paper by Ludwig,[15] the agreement may be even better between the data on elastic constants and the specific heat data. He indicates that because of anharmonic terms in the crystal potential which are normally neglected there will generally be a slight difference between the θ_0 derived from data on

elastic constants and that derived from specific heat data. For LiF he reports, as for certain other alkali halides, that this should have the effect of making θ(elastic constants) a percent or two *higher* than θ(specific heat). Barron and Morrison,[16] by another approach, consider the effect of anharmonic terms retained in the frequency distribution functions. They find a slight change in the specific-heat θ.

The present work adds confirmation to the not very extensive body of low-temperature data that the Debye θ's derived by elastic means and by thermal means do substantially agree. It is hoped, further, that this work, coupled with the elastic constants experiments, will contribute to the increasing effort being made to evaluate anharmonic terms and their influence on the physical properties of crystals. More work of this nature is needed to test recent extensions of the simple Debye model.

ACKNOWLEDGMENTS

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Vacancy Pairs in Ionic Crystals

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Equations for the thermal equilibrium concentrations of Schottky vacancies and vacancy pairs are presented; these equations allow for the effects produced by Debye-Hückel screening.

IN the study of lattice defects in ionic crystals and semiconductors the concept of "association" between defects bearing opposite effective charges—as borrowed from the theory of electrolyte solutions—has played a useful role.[1–3] In many applications it is good enough to treat the assembly of defects on the assumption that those pairs of oppositely charged defects which are close together are bound into neutral complexes, while defects at large separations move independently with their full effective charge available for interaction with external fields. It is sometimes desirable, however, to refine this picture and in a previous paper the question of the association between impurity ions

and vacancies in ionic conducting crystals has been discussed in higher approximation.[4] The notion of associated pairs is retained but the unassociated defects are described by the Debye-Hückel theory which takes account of the correlated motion caused by the long-range Coulomb interactions among the defects. The same approach can be used to refine the theory of the formation of Schottky and Frenkel defects.[5,6] This topic was reviewed again recently by Theimer[7] who suggests that these previous calculations are incomplete, in that they neglect the effect of the Debye-Hückel screening on the energies of formation of the defects,

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specifically in that term called the polarization energy.[8] It is the purpose of this note to show that this assertion is wrong and to present correct formulas for the concentrations of Schottky defects and vacancy pairs.

Two distinct approaches to the problem should be noted. The one used previously[4-6] assumes that the energy of a crystal containing defects is made up of two parts, (a) the energies of formation of the defects calculated without regard to one another and (b) their interaction energies—of Coulombic form $q_i q_j / \epsilon r_{ij}$ at large separations although somewhat modified at close distances.[9,10] Now Theimer draws attention to the polarization energy part of the energy of formation of a vacancy: this is one-half the energy which the ion to be removed would have in the field of the surrounding ions if these had the configuration and electric moments appropriate to the vacancy.[8] But the moments on these surrounding ions will be altered by the presence of other vacancies acting as centers of polarization in the lattice. Theimer therefore calculates the average energy of formation of a vacancy by calculating the polarization energy from $P = (1 - 1/\epsilon)D/4\pi$, with D the displacement around a vacancy with its Debye-Hückel screening cloud and not q/r^2 as usual. In doing so he abandons in principle the continuum dielectric model and works instead with a lattice of ions having electric charges and moments dispersed *in vacuo*. This is the second approach to the problem. It is valid provided the electric fields are evaluated as for charges *in vacuo*. In particular this means that in the total energy of the crystal there are (a) energy terms for vacancy formation as evaluated by Theimer and (b) interaction terms between the vacancies which must now be written as $q_i q_j / r_{ij}$ and not as $q_i q_j / \epsilon r_{ij}$ as in the first approach.

On this basis we see that the electrostatic interaction term $U(n_d)$ in Theimer's equation (11) is too small by a factor ϵ. If we correct this and if we generalize the equations to conform to the limitation that two ions, or two vacancies, cannot approach closer than the

lattice spacing then we find that the term $U(n_d)$ cancels with the term coming from the 1 of the $(1 - 1/\epsilon)$ factor in Theimer's $e[\Phi(n_d) - \Phi(0)]$. The remainder is the energy of interaction of the vacancy with its screening cloud as evaluated in the first approach. Thus Theimer's approach consistently applied gives the same result as previously obtained.

To conclude, we present the correct equations describing the thermal equilibrium concentrations of Schottky vacancies and vacancy pairs. The equation for the molar fraction of vacancy pairs, x_p, is unaffected by the accuracy with which we describe the effects of the interactions among the unassociated defects,

$$x_p = z \exp(-g_p/kT), \qquad (1)$$

where g_p is the free energy of formation of a vacancy pair and z is the number of distinct orientations of the pair (6 for NaCl). This equation is exact in so far as we can neglect the small dipolar interactions of the vacancy pairs with one another and with the unassociated defects. The equation for x_u, the molar fraction of unassociated Schottky vacancies, is, in a crystal where anion and cation have equal valency,[11]

$$x_u^2 = \exp\left[\frac{-1}{kT}\left(g - \frac{q^2 \kappa}{\epsilon(1 + \kappa R)}\right)\right]. \qquad (2)$$

Here $\pm q$ is the charge on the vacancies, g is the free energy of formation of an unassociated Schottky pair (evaluated in the absence of other defects), κ is the Debye-Hückel screening constant,

$$\kappa^2 = (8\pi q^2 x_u)/(v \epsilon kT),$$

where v is the molecular volume and R is the distance of closest approach of two unassociated defects. Similar formulas with only minor modifications apply to Frenkel defects and to Schottky defects in crystals where the ions have differing valencies. The relation of Eqs. (1) and (2) to experimental results on ionic conductivity and diffusion has recently been discussed elsewhere.[9,12]

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[11] The correction term given by Spicar should be divided by 2; the error appears also in Seeger's quotation equation (10.8).
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