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The relationship between experimental and calculated point defect energies

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Résumé. — Nous calculons la dépendance en température pour NaCl et KCl de l'enthalpie de formation h_p d'un défaut Schottky et son énergie de formation à volume constant u_v . Nous utilisons l'approximation quasi-harmonique avec des potentiels inter-ioniques et des méthodes de simulation bien éprouvées. Nous trouvons que h_p augmente avec la température alors que u_v décroît jusqu'à une valeur d'environ 70 % de h_p au point de fusion. Nous examinons les implications de ces résultats en ce qui concerne les termes d'énergie et d'entropie, calculés à partir des données expérimentales.

Abstract. — The temperature dependence of the Schottky defect formation enthalpy, h_p , and of the Schottky formation energy at constant volume, u_v , have been calculated for NaCl and KCl. The quasi-harmonic approximation was used with well-proven lattice simulation methods and interionic potentials. h_p increases with temperature whereas u_v decreases and close to the melting point is approximately 70 % of h_p . The implications of these results for the energy and entropy terms derived from the analysis of experimental transport data are examined.

1. Introduction. — For the more intensely studied simple ionic crystals there have been marked improvements recently in both the reliability and accuracy of experimentally determined defect formation energies. Simultaneous progress in computer simulation methods have made commensurate improvements to the theoretically calculated energy values for the same processes. Recent advances in our understanding of the thermodynamics of point defects [1] have made it possible to set down clearly the relationships between these experimental and calculated values. In certain cases the usual practice of comparing calculated energies directly with the energies deduced from experimental studies may no longer be acceptable. Attention was drawn to an apparent conflict between calculated and experimental defect formation energies by Varotsos and Alexopoulos [2]. So far, however, the quantitative interpretation of conductivity data in terms of a temperature dependent defect formation

energy has been accomplished for only one substance, namely, AgCl [3]. It is the first aim of this paper to make possible an extension of this kind of treatment by calculating the temperature dependence of the Schottky defect formation energies and enthalpies for NaCl and KCl. This work will use the standard thermodynamic relationships governing point defect formation under conditions of constant volume which are appropriate to the static lattice calculations and also under conditions of constant pressure which correspond to the typical experimental situation : these are discussed and collected in our recent study of AgCl [3]. We then examine the implications of these advances for the energy and entropy terms which finally emerge from the analysis of experimental data.

Attention has been focussed on this problem first by the experimental studies of AgCl [4-6]. This work clearly demonstrates that the free energy of Frenkel pair formation as a function of temperature decreases

more rapidly than would be predicted using temperature independent enthalpy and entropy terms. Our successful analysis of this effect [3, 6, 7] using the calculated temperature dependent Frenkel energy at constant volume $u_v(T)$, showed the importance of using the correct thermodynamic expression governing the relationship between defect energies and enthalpies of formation. Thus we have shown that in this material at temperatures close to the melting point the value of h_p , the enthalpy of defect formation at constant pressure, is approximately 50 % higher than that of u_v . We note that whereas the former increases with temperature, the latter decreases — an important point which was omitted from previous attempts to analyse this problem [2].

For the widely-studied alkali metal halides the only attempt to quantify these effects are the estimates given recently by Varotsos and Alexopoulos [8] who claim that for NaCl at its melting point the value of u_v is only about 30 % of h_p . In view of the importance of accurate estimates of these fundamental quantities we have applied the method used in our study of AgCl for a number of widely-studied halide crystals. We use our results to comment on the analysis of experimental transport data for these materials.

2. Calculations. — The temperature dependence of u_v is calculated in the quasi-harmonic approximation using the atomistic simulation methods incorporated in the HADES program [9]. The potentials used were those given previously for these substances [10]. The values of the lattice parameters used in the quasi-harmonic approximation and the sources of these data are given in table I. The resulting calculated values of u_v are also reported in this table.

Table I. — ⁽¹⁾ The lattice distance (anion-cation separation) was calculated by Jacobs and Pantelis [11] from the data of Enck et al. [12]. ⁽²⁾ a for NaCl is calculated from the dilation measurements of Enck and Dommel [13].

Temp./K	KCl			NaCl		
	$a^{(1)}/\text{\AA}$	u_v/eV	h_p/eV	$a^{(2)}/\text{\AA}$	u_v/eV	h_p/eV
300	3.146 8	2.445 9	2.593 5	2.820 1	2.406 6	2.570 4
350	3.152 5	2.421 0	2.598 5	2.825 7	2.378 9	2.576 5
400	3.158 5	2.395 1	2.606 9	2.831 6	2.350 2	2.583 4
450	3.164 7	2.368 0	2.617 9	2.837 7	2.320 6	2.591 1
500	3.171 3	2.339 5	2.631 1	2.844 0	2.290 1	2.599 8
550	3.178 1	2.309 6	2.646 2	2.850 6	2.258 6	2.609 5
600	3.185 1	2.278 3	2.662 9	2.857 4	2.226 3	2.620 4
650	3.192 5	2.245 5	2.681 3	2.864 5	2.192 9	2.632 6
700	3.200 1	2.211 2	2.701 7	2.871 9	2.158 6	2.646 2
750	3.207 9	2.175 4	2.724 2	2.879 5	2.123 3	2.661 6
800	3.216 1	2.138 1	2.748 8	2.887 4	2.086 8	2.678 8
850	3.224 5	2.099 1	2.775 2	2.895 8	2.049 2	2.698 1
900	3.233 2	2.058 5	2.802 5	2.904 6	2.010 5	2.719 9
950	3.242 1	2.016 5	2.828 5	2.913 8	1.970 4	2.744 3
1 000	3.257 4	1.973 2	2.849 8	2.923 5	1.929 0	2.771 8
1 050	—	—	—	2.933 9	1.886 1	2.802 7

To obtain the values of h_p we used the standard thermodynamic relation

$$h_p = u_v + \left(\frac{T\beta_p}{\kappa_T} \right) v_p \quad (1)$$

where β_p is the volume thermal expansion coefficient, κ_T the isothermal compressibility and v_p the increase in volume which occurs when a defect is formed at constant pressure. The results are again reported in table I.

We note that the coefficients of linear expansion for both substances were measured with a dilatometer. Since this measurement includes macroscopic expansion of the lattice due to the formation of Schottky defects the temperature variation of the calculated values of u_v is slightly overestimated at the highest temperatures.

3. Discussion. — Because of their availability and relative simplicity KCl and NaCl have been the subject of a number of recent detailed experimental and theoretical studies. As discussed by Catlow [18] the reliability of modern theoretical estimates of defect energies depends primarily on the short-range potential used to simulate that part of the crystal in which the interactions between the ions are summed explicitly. In this respect four separate recent studies [14-17] using different interionic potentials of varying complexity for KCl and NaCl have produced calculated Schottky defect formation energies which agree to within 10 % for KCl and to better than 5 % for NaCl. Thus for these most ideal of ionic crystals we may have considerable confidence in our calculated defect energies. The other major factor which governs the usefulness of the results given in table I is the ability of the quasi-harmonic approximation to treat the temperature variation of defect formation energies. Our recent study of AgCl indicates that it certainly can. In AgCl the vacancy concentration has been uniquely probed in the elegant experiment of Batra and Slifkin [5]. Their measurements of sodium diffusion are free from the ambiguities which typically obscure the interpretation of transport data in which a number of competing transport mechanisms, perhaps even with temperature dependent activation energies, are superimposed on a defect formation energy. Our calculated values of u_v when combined with a temperature independent entropy s_v accurately reproduced the experimentally determined vacancy concentration over the entire range in which measurements were made [5, 6]. It is reasonable therefore to expect that a similar treatment will work at least as well for KCl and NaCl.

The results in table I show first that u_v and h_p vary with temperature as would be expected. The values of u_v decrease by just over 19 and 21 % respectively for KCl and NaCl from room temperature to close to the melting points of the crystals. The corresponding values of h_p increase by 10 and 9 % over the same ranges. Thus close to the melting points u_v is just less

than 70 % of h_p for both substances. These changes compare with those for AgCl where u_v decreases by more than 18 % over a much shorter temperature range. Even in this latter rather extreme case, where the variation in the free energy of defect formation has been clearly detected and evaluated experimentally, the value of u_v is some 65 % that of h_p close to the melting point.

The implications of results such as these for the usual procedure of comparing experimental defect energies directly with those calculated with the lattice parameter set at its value at absolute zero, has been discussed by Gillan [1]. He has shown that for the specific case of CaF_2 $u_v(0)$ is a reliable estimate of $h_p(T)$ but has pointed out that this will not necessarily be the case in all materials. We now focus attention on another consequence of our present calculations, namely; the extraction of defect parameters from transport data and, in particular, from ionic conductivity measurements taken over a long temperature range. Since the curvature in the high-temperature regions of $\log \sigma T$ vs. $1/T$ curves was first observed a variety of explanations for its existence have been put forward. For KCl and NaCl these have included: contributions from trivacancies [19], cationic and anionic Frenkel defects [20, 21, 22] and more recently temperature-dependent energies of defect formation [21, 22]. Since our calculations show the last of these possibilities to be a reality we may expect it to be a major contributory factor to the observed curvature and as a consequence must re-examine the methods of data analysis used to determine defect parameters from conductivity data.

Since its introduction to this type of problem [23], the use of non-linear least squares analysis, in which the energies and entropies of defect formation and migration are the adjustable parameters by which the minimization is achieved, has been used extensively. When the technique is properly applied, with input from measurements on both pure and doped crystals and, more particularly, when relevant diffusion data can be incorporated [24], then it is believed to produce the most reliable defect parameters available. Since the experiments are done at constant pressure the standard procedure is to partition the defect free energies into enthalpy, h_p , and entropy, s_p , terms. These are the adjustable parameters of the fitting procedure and, in almost all cases, are assumed to be temperature-independent. The essence of the method is that it includes data from the complete temperature range over which the measurements have been made. This is clearly advantageous when, for example, in a divalently doped alkali halide the activation enthalpy for vacancy motion is unambiguously defined in the extrinsic region and this value can in the fitting be simultaneously made compatible with the more complex intrinsic region in which there are several contributing Arrhenius energies. However, this concept obviously breaks down with temperature-depen-

dent enthalpies. The best that can be expected is that some average value of the parameter, presumably depending on the temperature range of the data used for the analysis, will emerge.

This uncertainty in respect of the evaluation of the defect formation energy is further aggravated by its combination with a temperature-independent entropy term in the data analysis. To produce the observed upward curvature in the conductivity curves the free energy of defect formation must decrease with increasing temperature more quickly than would result from the use of temperature-independent terms in the Arrhenius equation. Hence if the energy term increases with temperature, as does h_p , the corresponding entropy term, s_p , must also increase rapidly with temperature to give the desired result. In contrast the calculated internal energy of defect formation at constant volume, u_v , decreases with temperature and evidence from an analysis of conductance data for AgCl in which $u_v(T)$ was incorporated [6], and from theoretical calculations for CaF_2 [24] shows that its associated entropy, s_v , is either constant or changes only very slightly with temperature.

Thus the imposition of a temperature-independent entropy term in the analysis of experimental data adds further uncertainty to the nature of the defect energy term which is determined.

4. Conclusions. — The calculations summarized in this paper have clearly shown that both the temperature dependence of defect energies, and differences between h_p and u_v are of sufficient magnitude that they should not be ignored in detailed analysis of accurate transport data in ionic materials (although we should note that the size of $h_p - u_v$, even at the melting point, is far smaller than recently suggested [8]).

This conclusion raises several problems. The first concerns the manner in which the temperature dependence of defect parameters is to be included when defect energies are deduced from experimental data. For the majority of ionic solids, the high temperature intrinsic regions, in which the effects are most pronounced, are extremely complex due to defect interactions and the presence of several migration mechanisms. It seems therefore to be unlikely that the extent of the temperature variation of the formation energy can be determined reliably from the empirical fitting procedures. A more promising approach is to obtain this variation by calculations of the type described in this paper and whose reliability for the prediction of temperature effects is supported by our study of AgCl [6, 7].

A further problem, already discussed, concerns the interpretation of the defect parameters obtained from empirical fitting procedures which omit the temperature variation of these quantities. The most obvious interpretation of the energy and entropy parameters are as h_p and s_p . However, since these quantities have an explicit dependence on temperature, as in equa-

tion (1), it is not clear that such an interpretation is correct when analyses exclude this dependence.

The final point concerns the comparison between experimental and calculated defect energies. The generally good agreement between calculation and experiment is not compromised by this work. Initially it was necessary to compare the calculated u_v at 0 K with experimental h_p (which is an average over the intrinsic range) because no other experimental results

were available. It is now evident that a more detailed analysis of experiment along the lines of our AgCl work [6, 7] is necessary before a final assessment can be made. It is also clear that such a treatment is not a trivial matter and the first stage in any analysis of conductivity data is still to analyse using a temperature independent h_p . We anticipate that the values of h_p so obtained may exceed the corresponding calculated values of u_v at 0 K by less than about 10 %.

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