PHYSICAL REVIEW B VOLUME 37, NUMBER 11 15 APRIL 1988-I

Thermodynamic criterion for the analysis of point-defect data in solids

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(Received 23 September 1987)

By using the thermodynamic concept of the existence of two families of vacancy-formation parameters (i.e., under constant *volume* and constant *pressure*), we find a relation which indicates that the formation entropy has to be bounded between two values. These values are determined with the help of the vacancy-formation volume, which is known from pressure experiments. This relation seems to play a decisive role in the check of the self-consistency of the analysis of point-defect data in solids; examples are presented for the cases of alkali halides and metals, and give rise to considerable doubts concerning the validity of the vacancy-divacancy model in metals.

It is accepted today that a real (i.e., containing defects) crystal can be compared either to an *isobaric* ideal (i.e., *not* containing defects) crystal or to an *isochoric* ideal crystal. Therefore the current aspects on the thermodynamics of point defects in solids reveal that there are two families of defect formation (f) parameters[1,2]: the "constant pressure" parameters labeled in the usual way (i.e., h^f, s^f, and v^f for the formation enthalpy, entropy, and volume, respectively) and the "constant-volume" ones labeled with an asterisk, i.e., h^*, s^*, etc. These two families are connected through thermodynamic relations which can be found in a recent review by Varotsos and Alexopoulos.[3]

The two formation entropies s^f and s^* are related with

$$s^f = s^* + v^f \beta B \ , \tag{1}$$

where β denotes the (volume) thermal expansion coefficient and B the isothermal bulk modulus. We clarify that Eq. (1) does *not* involve any approximation and is an alternative form of the thermodynamic relation

$$\left[\frac{\partial g^f}{\partial T}\right]\Bigg|_V = \left[\frac{\partial g^f}{\partial T}\right]\Bigg|_P + \beta B \left[\frac{\partial g^f}{\partial P}\right]\Bigg|_T \ ,$$

where the definitions $s^f \equiv -(\partial g^f/\partial T)|_P$, $s^* \equiv -(\partial g^f/\partial T)|_V$, $v^f \equiv (\partial g/\partial P)|_T$ have been used, and the quantity g^f denotes the usual isobaric Gibbs formation energy.

Upon an isobaric heating of a solid the frequencies vary; various experimental and theoretical results agree that this variation is mainly due to the volume variation; i.e., the frequencies exhibit only a small explicit temperature variation.[4,5] In view of this result and considering the detailed arguments presented in Chaps. 3 and 14 of Ref. 3 we are led to the following conclusions.

(1) The absolute value of s^f is appreciably larger than the absolute value of s^*, i.e.,

$$|s^f| > |s^*| \ . \tag{2}$$

(2) The value of s^* is negative (and in many cases close to zero), i.e.,

$$s^* \leq 0 \ . \tag{3}$$

It should be emphasized that the negative sign of s^* is confirmed by all the recent microscopic calculations carried out for (Schottky defects in) alkali halides[6] and metals.

In most cases the s^f and v^f values are positive; in such cases a combination of the relations (1) and (3) leads to

$$s^f \leq v^f \beta B \ , \tag{4}$$

whereas a combination of (1) and (2) reveals

$$s^f > \tfrac{1}{2} v^f \beta B \ . \tag{5}$$

Therefore the inequalities (4) and (5) indicate that the s^f value is restricted between the bounds

$$\tfrac{1}{2} v^f \beta B < s^f \leq v^f \beta B \ . \tag{6}$$

This relation being of thermodynamic origin should be used as an external constraint in the analysis of point-defect data in solids, e.g., differential dilatometry, self-diffusion, ionic conductivity data, etc. We proceed now to a presentation of its implications to two classes of solids, e.g., alkali halides and fcc metals.

ALKALI HALIDES

We start first with NaCl. For the highest temperature ($T \simeq 766$ K) of the Yamamoto *et al.* measurements[7] we have $\beta \simeq 1.676 \times 10^{-4}$ deg^{-1} and $B = 162.3$ kbar, whereas the pioneering data of Lazarus and co-workers[8,9] indicate that $v^f \simeq 55 \pm 9$ cm^3/mol. By inserting these data into relation (6) we find

$$9k < s^f \leq 18k \ .$$

If we accept the lower value of the formation volume, i.e., $v^f = 55 - 9$ cm^3/mol, then we find $7.5k < s^f \leq 15k$; for the case of $v^f = 55 + 9$ cm^{3}mol, we get $10.5k < s^f \leq 21k$.

Therefore we see that, for Nacl, the lowest s^f value that is allowed from relation (6) is around $7.5k$.

We now turn to the case of KCl, for which Yoon and Lazarus[8] gave $v^f = 61 \pm 9$ cm^3/mol. By considering that, for $T > \Theta_D$, the quantity βB varies only slightly with the temperature,[4,7] we may use the room-temperature values[10-12] $\beta=1.1\times10^{-4}$ deg^{-1} and $B=173.5$ kbar and hence the quantity $v^f\beta B$ is around $(14.1\pm2.1)k$; therefore s^f has to be bounded between

$$(7.1\pm1.1)k < s^f \leq (14.1\pm2.1)k \ .$$

Many papers have been published dealing with the analysis of diffusion and/or ionic conductivity data of NaCl and KCl and some of them[13-15] gave s^f values that lie within the bounds determined above. However, there are others that lead to values [e.g., $s^f\simeq4.2k$ for KCl (Ref. 16)] that strongly violate the lower bound indicated by relation (6). Furthermore, microscopic calculations that lead to s^f values [e.g., $s^f\simeq5.25k$ for KCl (Ref. 6)] lower than $\frac{1}{2}v^f\beta B$ should be reconsidered.

METALS

We first examine the case of Al for which we have[17] (for $T=850$ K) $\beta\simeq1.05\times10^{-4}$ deg^{-1}, $B=617$ kbar, and $\Omega\simeq17.45\times10^{-24}$ cm^3 (where Ω denotes the mean atomic volume) and hence the quantity $\Omega\beta B$ is around $8.2k$. In view of the fact that the self-diffusion activation volume is around[18-20] 0.7Ω we can safely assume that v^f cannot be lower than $v^f=\frac{1}{2}\Omega$; in such a case Eq. (6) indicates that s^f should lie between $2k$ and $4.1k$. However, the differential dilatometry and resistivity measurements on quenched samples [see Fig. 8 of Siegel (Ref. 18)], when they are analyzed in terms of the vacancy-divacancy model, lead to the value $s^f=0.7k$ (for monovacancies) which strongly violates the lower bound of $2k$ determined above. We should stress here the following point: If one accepts the value $s^f=0.7k$ then thermodynamics [i.e., Eq. (1)] implies that $s^*\simeq(s^f-v^f\beta B)=(0.7-4.1)k \simeq -3.4k$ and hence the absolute value of s^* should exceed that of s^f by a factor of 5. Such a result, however, is not physically possible.

We finally turn to the case of Cu for which we have[21] (for $T=1356$ K) $\Omega\simeq12.62\times10^{-24}$ cm^3; $\beta\simeq7.9\times10^{-5}$ deg^{-1}, and $B=102.1$ kbar, whereas the self-diffusion activation volume is around[20] 0.9Ω. Therefore the quantity $\Omega\beta B$ is around $7.4k$; by considering that v^f cannot be lower than 0.6Ω, the relation (6) indicates that s^f has to be higher than $2.2k$. By recalling that the vacancy-divacancy model[19,22] leads to s^f values of around $1k$ we see that this model is not in accordance with thermodynamics. The same result is obtained for Ag and Au. On the other hand, the Gilder-Lazarus model[23] that assumes only a monovacancy mechanism, with a formation enthalpy and entropy increasing with temperature, leads to s^f values that agree with relation (6).

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