PHYSICAL REVIEW B VOLUME 18, NUMBER 6 15 SEPTEMBER 1978

Calculation of the formation volume of vacancies in solids

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(Received 12 October 1977; revised manuscript received 21 March 1978)

By considering the creation of a vacancy as an isothermal and isobaric process the Gibbs formation energy g^f can be expressed as $g^f = CB\Omega$, where B is the isothermal bulk modulus and Ω the mean volume per atom. In former publications a method was proposed in which C was assumed constant. It led to explicit expressions for the formation entropy s^f and enthalpy h^f as functions of T. Extending this method to the formation volume v^f and to the parameters $\beta^f = (1/v^f)(\partial v^f/\partial T)_P$ and $\kappa^f = -(1/v^f)(\partial v^f/\partial P)_T$ explicit relations with the pressure and temperature derivatives of the bulk properties B and β (the volume thermal-expansion coefficient) are derived. The main results can be summarized as follows. (i) The parameters v^f, β^f, and κ^f are found to depend on P and T but in a different way than the bulk properties Ω, β, and κ. (ii) The volume v^f consists of two terms $v_h^f = (\partial h^f/\partial P)_T$ and $v_s^f = -T(\partial s^f/\partial P)_T$. At high temperatures the term v_s^f is never negligible in comparison to v_h^f. (iii) The thermal-expansion coefficient of v_h^f is approximately equal to $-\beta$ whereas that of v_s^f is positive and one order of magnitude larger. In order to check the reliability of the proposed method numerical values of v^f were calculated by using elastic data. In all types of solids investigated close agreement with experiment was found. The calculated values of κ^f and β^f, for alkali halides, agree with the corresponding values that can be extracted from the curvature of the plots of conductivity and diffusion versus pressure at various temperature. The same holds true for tracer experiments on Na and Cd.

I. INTRODUCTION

Zener[1] first indicated that the production of a vacancy should be considered as an isothermal isobaric process; in metals he found it to be correlated to the thermal variation of the shear modulus, e.g., to an anharmonic effect.[2,3] Holder and Granato[4] extended Zener's ideas to various solids. The importance of anharmonic effects was later stressed by Flynn,[5] and by Gilder and Lazarus[6] who mentioned that they could possibly be the cause of the curvature of the Arrhenius plots.

In this paper we present an anharmonic model which has already been found[7] of value for calculating the unexpectedly high formation entropy s^f of certain solids. It considers the creation of a vacancy as an isothermal isobaric process and presumes that the Gibbs formation energy g^f (per vacancy) can be expressed[7] as $g^f = CB\Omega$, where B is the isothermal bulk modulus and Ω is the mean volume per atom. The difficulty is that C may depend on T and P. To a first approximation, we have assumed in this model that C is independent of P and T but does contain "information" for the type of defect created. This leads to expressions for the parameters that are necessary for the study of the variation of ionic conductivity (σ) and the diffusion coefficient (D) under pressure. These expressions have been quantitatively evaluated and found to agree with experimental results. It is an astonishing fact that this single assumption is sufficient, without using any adjustable parameters, to explain a large variety of effects, many of which have been previously described as "strange."

II. FORMATION PARAMETERS

The formation volume v^f per defect is defined

$$v^f = \left(\frac{\partial g^f}{\partial P}\right)_T = \left(\frac{\partial h^f}{\partial P}\right)_T - T\left(\frac{\partial s^f}{\partial P}\right)_T , \tag{1}$$

where h^f is the corresponding formation enthalpy. Due to the fact that there is no thermodynamical restriction as to the temperature and pressure dependence of g^f, the formation volume can depend on P and T as well. Equation (1) shows that v^f has two contributions

$$v^f = v_h^f + v_s^f , \tag{2}$$

where

$$v_h^f = \left(\frac{\partial h^f}{\partial P}\right)_T \tag{3}$$

and

$$v_s^f = -T\left(\frac{\partial s^f}{\partial P}\right)_T . \tag{4}$$

Whenever the function $g^f(P,T)$ is known we can get $v^f(P,T)$ from Eq. (1) and thus

$$v_s^f = T\left(\frac{\partial v^f}{\partial T}\right)_P , \tag{5}$$

because $(\partial v^f/\partial T)_P = -(\partial s^f/\partial P)_T$. By bearing in mind Eq. (2) we can now find v_h^f:

$$v_h^f = v^f - T\left(\frac{\partial v^f}{\partial T}\right)_P . \tag{6}$$

The thermal-expansion coefficient β^f and the compressibility κ^f of the formation volume are defined by

$$\beta^f = \frac{1}{v^f}\left(\frac{\partial v^f}{\partial T}\right)_P \tag{7}$$

and

$$\kappa^f = -\frac{1}{v^f}\left(\frac{\partial v^f}{\partial P}\right)_T . \tag{8}$$

By integrating Eqs. (7) and (8) we get

$$v^f = v_0^f \exp\int_0^T \beta^f \, dT \tag{9}$$

and

$$v^f = v^f(0) \exp\int_0^P - \kappa^f \, dP , \tag{10}$$

where v_0^f and $v^f(0)$ denote the formation volume at $T = 0$ °K and $P = 0$, respectively. The two exponentials can be referred to as the temperature, respectively, pressure, correction factor of the formation volume. In the analysis of experimental results it is usually assumed[8] that v^f does not depend on P and T and hence that $\kappa^f = 0$ and $\beta^f = 0$, whereas in the theoretical treatments[9, 10] β^f and κ^f are usually assumed to be equal to the bulk thermal-expansion coefficient β and to the bulk compressibility κ. We now define the following coefficients:

$$\beta_h^f = \frac{1}{v_h^f}\left(\frac{\partial v_h^f}{\partial T}\right)_P , \tag{11}$$

$$\beta_s^f = \frac{1}{v_s^f}\left(\frac{\partial v_s^f}{\partial T}\right)_P . \tag{12}$$

We will now discuss the consequences of taking the parameters of the formation volume equal to the bulk parameters. (i) Even if β^f were equal to β, Eq. (9) reveals that the volume v^f, at a temperature near to the melting point T_M, exceeds v_0^f by an amount 10%–20% (the total expansion $\exp\int_0^{T_M} \times \beta dT$) depends roughly on the category of solids under discussion). Therefore calculations made for $T = 0$ °K must not be directly compared to the experimental v^f values obtained, usually, at very high temperatures. In Sec. III we shall show that $\beta^f > \beta$, therefore it is clear that v^f calculations made for $T = 0$ have to give much smaller values than the experimental ones. (ii) Even if κ^f were equal to κ, the formation volume v^f depends on pressure; then Eq. (10) becomes

$$\begin{aligned} v^f &= v^f(0)\exp\left(\int_0^P - \kappa \, dP\right) \\ &= v^f(0)\exp\left(\int_0^P - \frac{dP}{B}\right). \end{aligned} \tag{13}$$

Let us take as a characteristic example Rb. It has (at room temperature) $B = 25$ kbar.[11, 12] The usual measurements, under pressure, are made in the region 0–10 kbar. Taking into account that B depends on P through relation

$$B = B(0) + \left(\frac{\partial B}{\partial P}\right)_T P + \frac{1}{2}\left(\frac{\partial^2 B}{\partial P^2}\right)_T P^2 ,$$

and using the experimental values[11, 12] $(\partial B/\partial P)_T = 4.12$ and $\partial^2 B/\partial P^2 = -0.1655$ kbar^{-1}, the exponential at 10 kbar becomes 1/1.3. Therefore we conclude that even if κ^f were equal to κ, an experiment on Rb made in the usual region of pressures will not give the correct $v^f(0)$ value, if the "correction factor" is neglected. This factor has usually been disregarded *a priori* in the analysis of experimental results.[8] In Sec. III we shall show that the compressibility κ^f of the formation volume exceeds the bulk compressibility κ and hence the correction factor is much larger (up to 2 or more in some cases), so that its omission can not be allowed.

III. CALCULATION OF VACANCY FORMATION PARAMETERS

When a vacancy is formed, g^f can be set into the form (see Sec. I)

$$g^f = CB\Omega \tag{14}$$

where C is assumed to be independent of temperature and pressure. At $T = 0$ °K, the energy g^f becomes equal to the formation enthalpy h_0^f and hence Eq. (14) at $T = 0$ °K gives

$$C = h_0^f / B_0 \Omega_0 , \tag{15}$$

where the subscript 0 denotes the corresponding values at absolute zero. By inserting the value of C, given by Eq. (15), into Eq. (14) we get

$$g^f = \left(h_0^f / B_0 \Omega_0\right) B\Omega \tag{16}$$

or

$$g^f = \left(h_0^f / B_0\right) B \exp\int_0^T \beta dT . \tag{17}$$

The value of h_0^f can be extracted[7] from the experimental value $h_{\rm expt}^f$ through the relation

$$h_0^f = h_{\rm expt}^f B_0 / B_0^{\rm SL} , \tag{18}$$

where $B_0^{\rm SL}$ is the intercept of the extension of the linear part (straight line) of the graph $B = f(T)$ with the vertical axis.

A. Vacancy formation volume

The vacancy formation volume is found by differentiating Eq. (14) with respect to pressure

$$v^f = C\left(\frac{\partial B}{\partial P}\bigg|_T + B\frac{\partial \Omega}{\partial P}\bigg|_T\right).$$

The isothermal bulk modulus is, by definition, $B = -\Omega\partial P/\partial\Omega$ (T = const) and hence we get

$$v^f = C\left(\frac{\partial B}{\partial P} - 1\right)\Omega \tag{19}$$

or

$$v^f = \frac{h^f_\Omega}{B_0}\left(\frac{\partial B}{\partial P} - 1\right)\exp\int_P^T \beta dT\,. \tag{20}$$

Equation (19) shows that v^f depends on P and T like the term $(\partial B/\partial P - 1)\Omega$, because both $\partial B/\partial P$ and Ω depend on P and T. This discussion reveals that v^f is never proportional exclusively to the volume Ω but also to $(\partial B/\partial P - 1)$, so that a stronger variation of v^f with P, T is expected in comparison with the variation of Ω on, P, T. This prediction has been experimentally[13] well confirmed.

In the harmonic approximation $\partial B/\partial P = 0$, $\Omega = \Omega_0$, $\beta = 0$ and hence Eq. (19) gives $v^f = -C\Omega_0$. This result contradicts the experimental data.

B. Thermal-expansion coefficient β^f and the compressibility κ^f of the formation volume

The thermal-expansion coefficient β^f and the compressibility κ^f of the formation volume can be calculated by inserting Eq. (19) into Eqs. (7) and (8); we finally get

$$\beta^f = \beta + \frac{\partial^2 B/\partial P\partial T}{\partial B/\partial P - 1} \tag{21}$$

and

$$\kappa^f = \kappa - \frac{\partial^2 B/\partial P^2}{\partial B/\partial P - 1}\,. \tag{22}$$

These equations permit the evaluation of the vacancy properties β^f and κ^f through properties of the bulk material. Experiments[11, 12, 14] have shown that $\partial^2 B/\partial P\partial T > 0$ and $\partial^2 B/\partial P^2 < 0$; therefore Eqs. (21) and (22) reveal that $\beta^f > \beta$, $\kappa^f > \kappa$ (23). All these inequalities become equalities only in solids showing lower order anharmonicity.[15]

C. Bounds of the ratio κ^f/κ at $P = 0$

Equation (22) can be written in the form

$$\frac{\kappa^f}{\kappa} = 1 - \frac{B(\partial^2 B/\partial P^2)}{\partial B/\partial P - 1}\,. \tag{24}$$

It is a striking characteristic of inorganic crystalline solids[16] that despite a several thousandfold variation of B the dimensionless quantity $\partial B/\partial P$ remains within narrow bounds between 4 and 8 (at $P = 0$); the bounds become narrower for solids belonging to a given category. As for the other dimensionless quantity $-B(\partial^2 B/\partial P^2)$ it has also been found to be bounded. For metals Grover, Getting, and Kennedy[11] and later Dunn[12] found it be approximately equal to $\partial B/\partial P$ thus giving for the bounds 4 and 8. For rare-gas solids[16] (RGS) the bounds of $-B(\partial^2 B/\partial P^2)$ are 4 and 15. In alkali halides Spetzler *et al.*[14] found that $-B(\partial^2 B/\partial P^2)$ exceeds $\partial B/\partial P$ by a factor 2–3.

Inserting these results into Eq. (24) one gets for κ^f/κ the bounds 2.14–2.33 in the case of metals. In the case of RGS the bounds are 1.5–3.5 or, according to the experiments of Anderson and Swenson,[17] 1.2–3.5. Finally, for alkali halides, the bounds are between 3 and 9 (or 3 and 5 if some extremely deviating results are disregarded). Materials following a Lennard-Jones potential[16] have $\partial B/\partial P = 8$ and $-B(\partial^2 B/\partial P^2) = 15$ thus giving the precise value $\kappa^f/\kappa = 3.14$.

D. Temperature dependence of β^f

All experiments[14] up to now showed that $\partial B/\partial P$ increases almost linearly with T, and thus its temperature derivative is practically a constant C_i. Therefore Eq. (21) can be written

$$\beta^f - \beta = C_i\Big/\left(\frac{\partial B}{\partial P}\bigg|_{T=0} - 1 + C_i T\right). \tag{25}$$

In materials for which the first term of the right side of Eq. (21) is much smaller than the second one, we get $\beta \ll \beta^f$; then Eq. (25) simplifies in a manner showing that β^f is a decreasing hyperbolic function of T. Thus measurements restricted to a narrow temperature range should give β^f values that are approximately proportional to $1/T$. This effect can only be checked in the case of Zn,[18] and Cd,[19] because only for these materials diffusion plots for various pressures and temperatures exist. From these experiments Gilder and Lazarus[6] come to the conclusion that β^f is proportional to $1/T$ for all metals in agreement with the present theory.

E. Static and vibrational contribution to the formation volume

By inserting Eq. (19) into Eq. (5) we get

$$v^f_s = T\,\frac{h^f_\Omega}{B_0}\left[\frac{\partial^2 B}{\partial T\partial P} + \beta\left(\frac{\partial B}{\partial P} - 1\right)\right]\exp\int_0^T \beta dT\,. \tag{26}$$

Note that at $T = 0$ this term becomes zero as e pected. By subtracting the above v_s^f value from Eq. (20) we finally get

$$v_h^f = v^f - v_s^f = \frac{h_0^f}{B_0}\left((1-T\beta)\frac{\partial B}{\partial P} + T\beta - T\frac{\partial^2 B}{\partial T \partial P} - 1\right) \times \exp\int_0^T \beta dT \quad . \tag{27}$$

Equations (26) and (27) permit the direct evaluation of the two terms of v^f; they contain only experimental quantities, if we remember Eq. (18).

By dividing Eq. (26) by (27) the enthalpy h_0^f vanishes so that the ratio v_s^f/v_h^f contains only bulk properties without any vacancy parameters; it is hence a property of the lattice independent of the type of defect. In order to estimate the reliability of the lattice-statics (LS) technique, which disregards v_s^f, we evaluate below the error committed by this ommision in two examples of real (anharmonic) solids. (a) Sodium: by using the expansivity values of Adlhart *et al.*[20] and the elastic data of Grover, Getting, and Kennedy[11] and that given by Dunn,[12] the ratio v_s^f/v_h^f at $T = 300$ °K is found to be 20%. Near the melting point this ratio becomes appreciably larger. (b) Sodium chloride: by using the expansivity values of Srivastava and Merchant[21] and the elastic data of Spetzler *et al.*[14] the ratio v_s^f/v_h^f is found to be 17%, 47%, and 90% at 300, 700, and 1000 °K, respectively. Thus, according to the present model, it is questionable if the values of v_h^f for $T = 0$ °K deduced by the LS technique should be compared with the v^f values (i.e., $v_h^f + v_s^f$) obtained experimentally. We feel that this might explain (at least, partially) the continuous disagreement[22,23] between experiment and theory as far as the v^f values are concerned.

F. Temperature variation of v_s^f and v_h^f

Inserting the necessary values[24] for NaCl at 600 and 700 °K we obtain for v_s^f 20.9 and 25.4 Å^3 and for v_h^f 55.5 and 54.0 Å^3, respectively; hence an increase of temperature by 17% gives a variation for v_s^f and v_h^f of 21% and −3%. A comparison of each term with a corresponding experimental value is not possible due to the lack of h^f and s^f values under pressure. The approximate proportionality of v_s^f with T, found above, has been observed in Cd and Zn. Actually, Buescher *et al.*[19] found for this temperature difference that $-T(\partial s^f/\partial P)_T$, i.e., v_s^f of Cd increases exactly by 17% and that a change of $(\partial h/\partial P)_T$, i.e., v_h^f is not detectable. A similar behavior was found by Chhabildas and Gilder[18] for Zn in the region between 573 and 673 °K.

According to the Eqs. (11) and (12) the above values of v_s^f and v_h^f of NaCl found for 600 and 700 °K give for β_s^f and β_h^f the mean values 19×10^{-4} and -3×10^{-4} K^{-1}. Comparing to the value of the bulk expansivity β one sees that β_h^f is of the order of $-\beta$ while β_s^f exceeds it by one order of magnitude. The measurements for Zn give $\beta_s^f/\beta = 15$.[18]

G. Migration and activation parameters

The Gibbs energy g^m for the migration process can be assumed to be a sum of electrostatic and dilatation work.[25–27] In the case of metals, due to their high dielectric constant, only the second contribution is of importance. Arguments similar to those proposed for the formation process lead to

$$g^m \approx c\,B\Omega \ , \tag{28}$$

where c is a constant that can be set equal to $h_0^m/B_0\Omega_0$, and h_0^m is the migration enthalpy at absolute zero. Therefore the activation Gibbs energy in metals can be written

$$g^{\mathrm{act}} = g^f + g^m \approx (C + c)B\Omega \ . \tag{29}$$

In this case we have

$$C + c \approx (h_0^f + h_0^m)/B_0\Omega_0 = h_0^{\mathrm{act}}/B_0\Omega_0 \ . \tag{30}$$

A theory for activation parameters can now be developed in the same way as for formation parameters.

IV. EXPLANATION OF VARIOUS EXPERIMENTAL RESULTS

In the following we shall proceed to the numerical application of our formulas (20)–(22) for v^f, β^f, and κ^f. Although this application can be done for a large number of solids, we present here only those examples for which the current theories fail to give an explanation.

A. Alkali halides with NaCl structure

Table I contains the experimental quantities required for the calculation for NaCl, KCl and KBr; we selected these materials because for them precise experiments under pressure exist with various techniques, i.e., conductivity under pressure,[13] tracer diffusion under pressure[28] and x-ray diffuse scattering from the defect displacement field.[29,30] Where question marks are inserted no experimental values are available. In Table I we give the calculated values of $v^f(0)$, $\beta^f(0)$, and $\kappa^f(0)$ for certain temperatures. In the following these results will be compared to the experimental results. Especially for $v^f(0)$, as already discussed in Sec. II, a direct comparison is allowed only to low pressure experiments.

B. NaCl

Yoon and Lazarus,[13] using conductivity techniques under pressure, reported a value $v^f = 55 \pm 9$

TABLE I. Various properties of Schottky defects in alkali halides at $P=0$.

	T (°K)	$B\equiv 1/\kappa$ (kbar)	$\left.\frac{\partial B}{\partial P}\right\|_{P=0}$	$\left.\frac{\partial^2 B}{\partial P^2}\right\|_{P=0}$ (10^{-2} kbar^{-1})	β (10^{-4} K^{-1})	$\frac{\partial}{\partial T}\left(\frac{\partial B}{\partial P}\right)$ (10^{-4} K^{-1})	B_0^{SL} (kbar)	h^f (eV)	$v^f(0)$ (cm^3/mole)	$\beta^f(0)$ (10^{-4} K^{-1})	$\kappa^f(0)$ (10^{-2} kbar^{-1})
NaCl	300	237[a]	5.35[a]	−8.0[b]	1.17[c]	15.7[b]	270[d]	2.44[e]	39.4[f]	4.78	2.26
NaCl	936	135.4[b]	6.35[b]	−9.6[b]	2.10[c]	15.7[g]	270[d]	2.44[e]	53.6[f]	5.04	2.52
KCl	300	181[h]	5.34[h]	−10.4[i]	1.05[c]	?	203[j]	2.50[e]	53.0[k]	?	2.96
KBr	300	148.6[h]	5.38[h]	−12.8[i]	1.17[l]	?	180[j]	2.37[m]	57.3[k]	?	3.60

[a] H. Spetzler, C. G. Sammis, and R. J. O'Connell, J. Phys. Chem. Solids 33, 1727 (1972).

[b] By using the values of Ref. a (linear extrapolation and interpolation).

[c] K. K. Srivastava and H. D. Merchant, J. Phys. Chem. Solids 34, 2069 (1973).

[d] H. B. Huntington, in *The Elastic Constants of Crystals* (Academic, New York 1958).

[e] M. Beniere, M. Chemla, and F. Beniere, J. Phys. Chem. Solids 37, 525 (1976).

[f] The values of the integral $\exp(\int_0^T \beta dT)$ used are 1.05 and 1.15 for $T=300$ and $T=936$ °K, respectively.

[g] By linear extrapolation of the curve $\partial B/\partial P$ vs T of Ref. a.

[h] H. H. Demarest, J. Phys. Chem. Solids 35, 1393 (1974).

[i] With the approximation that the value of $\partial^2 B/\partial P^2$ in KCl and KBr depends on $(1/B)$ $(\partial B/\partial P)$ with the same constant as in NaCl.

[j] A. S. Barker, Jr. and A. J. Sievers, Rev. Mod. Phys. Suppl. 2, 47, 114 (1975).

[k] By using $\exp(\int_0^{\mathrm{RT}} \beta dT)=1.03$.

[l] P. P. M. Meincke and G. M. Graham, Can. J. Phys. 43, 1853 (1965).

[m] J. H. Crawford and L. Slifkin, *Point Defects in Solids* (Plenum, New York, 1972), p. 135.

cm^3/mole obtained by using the low-pressure data at high T (the v^f value in cm^3/mole is simply the v^f per defect multiplied by the Avogadro number N). The necessary consideration of migration effects was taken from the high-pressure data (>1 kbar) at low T. It might have been better to consider this effect from the lower pressures. The difference, however, is surely covered by the large experimental error which they reported. Their v^f value is in nice agreement with our value 53.6 cm^3/mole calculated for the same temperature range.

Later Martin, Lazarus, and Mitchell,[28] with tracer techniques, reported at 936 °K an activation volume $v^{\mathrm{act}}=\frac{1}{2}v^f+v^m=35$ cm^3/mole, which, by using the migration volume value of Yoon and Lazarus,[13] gives $v^f\approx 56$ cm^3/mole ±10%. This second experimental result is also in agreement with our value of 53.6 cm^3/mole. In Table I we note that the $v^f(0)$ value for $T=300$ °K is larger than the molar volume (~27 cm^3/mole) by 45%. At $T=0$ °K this difference is around 30%. In the same table we note that although β^f increases with T, the ratio β^f/β decreases and consistently exceeds unity, which is a sign that the formation volume increases faster with T than the bulk volume. This effect has actually been noted in Ref. 13 in the form of an increase of $kT\,|\partial \ln\sigma/\partial P|$ with T.

An experimental value of β^f can be extracted from the paper by Martin *et al.*[28] as follows: For low pressures the activation volume at 936 and 1004 °K are 35 cm^3/mole and 38 cm^3/mole, respectively, with an accuracy of 10%. Assuming that the activation volume has the same temperature dependence as v^f, these two values correspond to a mean thermal expansion coefficient $\beta^f=12.6^{+35.5}_{-16.4}\times 10^{-4}$ °K^{-1}. The values calculated from Eq. (21) for these temperatures are 5.04×10^{-4}, respectively, 5.07×10^{-4} °K^{-1}; they agree with the experimental mean value within the experimental error.

In another column the calculated values of $\kappa^f(0)$ are inserted. We see that it increases with temperature, a behavior similar to that of κ. From the same table one easily obtains that κ^f/κ will be consistently higher than unity. Equation (22) predicts a pressure dependence of v^f and therefore a bending of the plot $\ln D$ vs P. Its observation is expected at a value of P for which the correction factor deviates from unity by more than 10%, which is the experimental error. The values of κ^f and the correction factor have been calculated from Eq. (22) for 1004 and 936 °K and are given in Table II. The data necessary for the calculation are taken from linear extrapolations of the values $B=f(T)$, $\partial B/\partial P=f(T)$ as given in Ref. a of Table I. It is only beyond 3 kbar that the correction factor deviates from unity by more than 10%, thus showing that curvature should be detectable only from there on.

We will now compare our results with the available experiments. The isothermal $\ln\sigma$ vs P plots of Yoon and Lazarus[13] for the intrinsic conductivity are almost linear up to 3 kbar, but from there on

TABLE II. Pressure correction factors for NaCl.

	$T=936\,^\circ\mathrm{K}$		$T=1004\,^\circ\mathrm{K}$	
P (kbar)	κ^f (10^{-2} kbar^{-1})	$\exp\left(\int_0^P \kappa^f dP\right)$	κ^f (10^{-2} kbar^{-1})	$\exp\left(\int_0^P \kappa^f dP\right)$
0	2.5	1	2.6	1
2	2.6	1.05	2.7	1.05
3	2.7	1.08	2.8	1.08
4	2.8	1.11	2.9	1.12
6	3.0	1.18	3.1	1.19

show a detectable curvature as predicted with the present model. Similarly, in tracer experiments Martin *et al.*[28] found a bending of the $\ln D$ vs P plot for 936 and 1004 °K at the same pressure. As to the absolute values of κ^f at 1004 °K, Ref. 28 gives for $kT|\partial \ln D/\partial P|$ at low pressures and near 6 kbar the values 38 and 26 cm^3/mole (±10%). Assuming that the compressibilities of the formation and migration volumes are equal, the above values imply an average compressibility $\kappa_{\mathrm{expt}}=5.26^{+2.1}_{-3.0}\times 10^{-2}$ kbar^{-1}. The calculated values in Table II are in agreement with this value within the error bars.

C. KCl

For this material certain data are lacking so that in Table I only the formation volume and the compressibility are given. At 300 °K Eq. (20) gives $v^f(0)=53$ cm^3/mole. It is obvious that at high temperatures, at which the measurements of activation volume are made, our v^f value must be higher. Unfortunately the value of $\partial B/\partial P$ at high T is not known and hence the exact calculation of v^f for high T cannot be done. However, it must exceed the value at 300 °K by at least a factor $\exp(\int_{\mathrm{RT}}^{\sim T_M} \beta dT)\approx 1.12$, and hence it must be a little higher than $53\times 1.12\approx 59.3$ cm^3/mole in agreement with the experimental value[13] 61 ± 9 cm^3/mole. From Table I we easily obtain that $\kappa^f>\kappa$, and hence a curvature is predicted which has been actually observed.[13]

D. KBr

Table I shows that at $T=300\,^\circ\mathrm{K}$ the value of $v^f(0)$ is 57.3 cm^3/mole; by following the same considerations as in KCl, we can estimate that at high T it must be somewhat higher than $57.3\times 1.12\approx 64.3$ cm^3/mole. The experimental value[13] is 54 ± 9 cm^3/mole, i.e., a few percent lower than our value; this small disagreement was not expected due to the following reason. At $T=300\,^\circ\mathrm{K}$ the κ^f value of KBr is appreciably higher than that in NaCl and hence the correction factor $\exp(\int_0^P \kappa dP)$ is greater. This means that the curvature in the plot $\ln\sigma$ vs P starts to become prominent at lower pressures than in NaCl. The experimental points[13] in the $\ln\sigma$-vs-P plot of KBr at 625.5 °C confirm this prediction because near 3 kbar they already lie higher than the straight line drawn through the lower pressure data. However these points have been included by Yoon and Lazarus,[13] in the fitting of their curve and therefore [see Eq. (10)] their value 54 ± 9 cm^3/mole must be a little smaller than the actual value of $v^f(0)$.

E. Metals

1. *Potassium*

It has a high compressibility and therefore large values of κ^f are anticipated. Table III contains the necessary quantities for the determination of κ^f values at $T=300\,^\circ\mathrm{K}$ for various pressures. They exceed κ by a factor of 2.34, at $P=0$, which rises to 5.9 at $P=10$ kbar. The large absolute values of κ^f give a large correction factor (up to 2.2 at $P=10$ kbar). This allows the prediction that the $\ln D$ vs P curve will show a very strong curvature. Experiments carried out by Kohler and Ruoff[31] for pressures up to 1 kbar have found no curvature within the experimental error of 10%. This does not disagree with the prediction given above because the pressure correction factor at 1 kbar is 1.07 and cannot give an observable curvature.

In the literature[32] the experimental $(\partial B/\partial P)_{\mathrm{RT}}$ value, for $P=0$, varies between 3.65 and 3.98, whereas the expansivity term $\exp(\int_0^{\mathrm{RT}} \beta dT)$ is 1.055 and $B_0^{\mathrm{SL}}=38.5$ kbar. Taking also into account that h^f_{exp} is[33, 34] ~ 0.40 eV, Eqs. (18) and (20) show that $v^f(0)$ lies between 0.6 and 0.69Ω, while the experimental v^f value is[31] 0.55Ω ±10%. This small difference might be due to the same reason discussed later for sodium.

2. *Sodium*

Diederich and Trivisonno[35] reported the value $B(0)=65$ kbar at 195 °K while Grover *et al.*[11] gave

TABLE III. Defect parameters of potassium at room temperature.

P (kbar)	B [a] (kbar)	$\frac{\partial B}{\partial P}$ [a]	$\frac{\partial^2 B}{\partial P^2}$ [a] (kbar^{-1})	κ^f (10^{-2} kbar^{-1})	$\frac{\kappa^f}{\kappa}$	$\exp\left(\int_0^P \kappa^f dP\right)$
0	31.0	3.93	−0.1268	7.55	2.34	1
2	38.6	3.68		7.32	2.83	1.16
4	45.7	3.42		7.43	3.40	1.35
6	52.3	3.17		7.76	4.06	1.57
8	58.4	2.92		8.32	4.86	1.84
10	64.0	2.66		9.20	5.89	2.19

[a] $B = 31 + 3.93P - (0.1268/2)P^2$; B, P in kbar; see R. Grover, I. C. Getting, and G. C. Kennedy, Phys. Rev. B 7, 567 (1973); also K. J. Dunn, *ibid.* 12, 3497 (1975).

$B(0) = 59.9$ kbar at room temperature. A linear interpolation for 288 °K gives 60.5 kbar. Similarly $\partial B/\partial P$ and $\partial^2 B/\partial P^2$ as function of pressure can be found from a linear interpolation of Dunn's values[12] at 0 °K and 300 °K. Equation (22) gives for κ^f at 288 °K values which lie between 3.72×10^{-2} and 3.85×10^{-2} kbar^{-1} which coincides with the experimental value[6] $(3.3 \pm 0.5) \times 10^{-2}$ kbar^{-1}. By graphical integration the pressure correction factor reaches the value 1.46 at 10 kbar. Mundy's curved isothermal plot[8] ln$D$ vs P at 288 °K actually turns into a straight line if the ordinate is multiplied with $\exp(\int_0^P -\kappa^f dP)$. Therefore the curvature can be sufficiently explained from a large correction factor without having to assume a second defect mechanism.

The formation volume $v^f(0)$ for 288 °K is calculated to be $14^{+1.4}_{-1.2}$ cm^3/mole from Eqs. (18) and (20) by inserting $h^f_{\text{expt}} = 0.354 \pm 0.025$ eV,[36] $B_0^{SL} = 76$ kbar,[35] and $\partial B/\partial P = 4.05$.[11, 12] Using alternate[37, 38] values of $\partial B/\partial P$ one obtains 12 and 12.3 cm^3/mole.

These values are higher than the value 11.1 ± 0.2 cm^3/mole reported by Gilder and Lazarus who analyzed Mundy's experimental data at 288 °K. This difference was expected because the value $h^f_{\text{expt}} = 0.354$ eV was deduced from dilation experiments at high temperatures, whereas the value at 288 °K would be needed; the curved diffusion plot of Mundy when explained in the frame of a single type of defect[6] actually shows a decrease of h for low temperatures.

The $\beta^f(0)$ value is calculated from Eq. (21) to be 5.2×10^{-4} K^{-1} when one uses Dunn's values, or 7×10^{-4} K^{-1} when using Wallace's value[39] at $T = 0$ °K. An experimental value of β^f that could be representative of 288 °K is not available. A combination of isotherms at 288 and 365 °K gives a considerably higher value[6] which just reflects the increasing effect of anharmonicity near the melting point.

3. Lead

Equation (20) gives for the formation volume $v^f(0) = 0.35\Omega$ at room temperature by using $B_0 = 488$ kbar,[40] $\partial B/\partial P = 6.84$,[41] and $h^f_{\text{exp}} = 0.5$ eV.[42] Experimentally only a total activation volume is available; we will proceed to its calculation in the frame of the present model. By differentiating Eq. (29) and using $h^{\text{act}} = 1.1$ eV,[43, 44] we get $v^{\text{act}} = 0.75\Omega$ which lies between the experimental values $0.64\Omega \pm 10\%$ and 0.77Ω reported by Hudson and Hoffman[44] and Nachtrieb *et al.*,[43] respectively.

4. Al, Cu, Au, Ag

Values of the formation volume can be calculated only for low temperatures because to the best of our knowledge no measurements for $\partial B/\partial P$ at high temperatures exist. Inserting room temperature values[45-47] into Eq. (20) we find that $v^f(0)$ lies in the region $(0.3-0.5)\Omega$. For higher temperatures the expansivity term $\exp(\int_0^{\sim T_M} \beta dT)$ will give an increase of at least 10%. A further increase of v^f is anticipated due to the temperature dependence of $\partial B/\partial P$. Reliable experimental v^f values are usually extracted from the high-temperature region; they lie[48] between 0.5 and 0.7Ω and therefore are not inconsistent with our predictions.

In contrast to alkali metals, these fcc metals (and Pb) do not show a curvature of their isothermal ln$D$ vs P plots. Although, as mentioned, values of $\partial B/\partial P$ at high temperatures are not available a justification of this lack of curvature is possible. In the example of aluminum, B_0 is 880 kbar; it decreases up to the melting point by approximately[49] 20% thus giving 700 kbar. As has been previously shown, the lower bound of $\kappa^f(0)| \kappa(0)$ is 2.14 so that $\kappa^f(0)$ cannot be larger than $2.14/700 = 3 \times 10^{-3}$ kbar^{-1}. The pressure correction factor $\exp(\int_0^P \kappa^f \, dP)$ at 10 kbar is therefore at most 1.03 so that under error limits of 10% the curvature is not detectable. A detection would need an extension to pressures about 40 kbar. For the other elements mentioned, similar considerations are valid; still higher pressures for the appearance of the curvature are required.

5. Cd

Although the applicability of the present method in respect to the formation entropy has only been tested for cubic materials,[7] it can be checked in respect to v^{act} and κ^{act} for a hexagonal metal. Suitable data are available only for Cd. We use[50] $B_0 = 630$ kbar and $h^{\text{act}} = 0.86$ and 0.9 eV for the c axis and basal plane, respectively.[19] The pressure derivative of B can be found only for the adiabatic bulk modulus; by using the Anderson Gruneisen constant $\delta = 4.2$ given by Rao[50] and the relation $\delta = \partial B/\partial P - 1$, a value $\partial B/\partial P = 5.2$ is obtained. Equation (20) gives for room temperature the activation volumes 5.6 and 5.9 cm^3/mole, respectively. Experiments have been carried out by Buescher, Gilder, and Shea[19] at higher temperatures. Assuming that their formula can be extended down to 300 °K, one obtains $v^{\text{act}} = 4.4 \pm 1.4$ cm^3/mole, which is in agreement with our value within experimental errors. The same authors reported that within their accuracy the activation volume is independent of pressure and gave for the compressibility an upper limit $\kappa^{\text{act}} = 6 \times 10^{-3}$ kbar^{-1}. Taking into account the published[11] elastic data and the considerations of Dunn[12] we get $-\partial^2 B/\partial P^2 = 8.4 \times 10^{-3}$ kbar^{-1} and hence Eq. (22) gives for the compressibility of the activation volume 3.6×10^{-3} kbar^{-1}; this value is within the upper limit determined by experiments. The resulting value of the correction factor $\exp(\int_0^P \kappa^{\text{act}} dP)$, for pressures up to 8 kbar, is around 1.03 thus explaining why a curvature was not detectable.[19]

V. CONCLUSIONS

The most important conclusions of the present paper are given below. They are based on general thermodynamical considerations, which lead to the relation $g^f = CB\Omega$ and on the approximation that C is pressure and temperature independent.

(i) The usual assumption that the formation volume is temperature and pressure independent (which is equivalent to $\kappa^f = 0$ and $\beta^f = 0$) is not valid even in the case of a harmonic solid. The volume v^f depends on temperature and pressure through the (correction) factors $\exp(\int_0^T \beta^f dT)$ and $\exp(\int_0^P \kappa^f dP)$.

(ii) The existence of a curvature in the plots $\ln D$ vs P and $\ln\sigma$ vs P is not a guarantee that a multiple mechanism occurs. The curvature in the plots of $\ln D$ or $\ln\sigma$ vs P can be explained from the deviation of the correction factor $\exp(\int_0^P \kappa^f dP)$ from unity.

(iii) The present method gives not only a temperature derivative of g^f (i.e., s^f) but also a pressure derivative (i.e., v^f) that are in close agreement with the experimental results for various categories of solids. This agreement strengthens the validity of our assumption that $C = \text{const}$.

(iv) The coefficients β^f and κ^f have been expressed through bulk properties. It has been shown that the inequalities $\beta^f > \beta$ and $\kappa^f > \kappa$ are due to higher order anharmonicity. The values of the correction factors which are calculated from bulk properties only can describe well the temperature and pressure variation of the isothermal plots $\ln D$ or $\ln\sigma$ vs P for alkali halides and some metals.

(v) At high T the term v_s^f is a significant contribution to v^f; therefore the usual calculations made by lattice statics techniques at $T = 0$ cannot lead to v^f values comparable to those obtained experimentally at high T. The rapid increase of v^f with temperature is mainly due to the fact that β_s^f exceeds β by one order of magnitude.

The fact that the values of s^f, v^f, β^f, and κ^f calculated by the present method are in agreement with experiments on various categories of solids possibly means that the assumption $C = \text{const}$ might correspond to an inherent property of solids.

ACKNOWLEDGMENTS

One of us (P.V.) would like to express his sincere thanks to Dr. A. B. Lidiard for keeping him informed on the recent work at Harwell and Professor L. M. Slifkin and Professor A. Seeger for useful suggestions through correspondence.

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