PHYSICAL REVIEW B VOLUME 11, NUMBER 12 15 JUNE 1975

Role of vacancy anharmonicity on non-Arrhenius diffusional behavior*

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(Received 27 January 1975)

Curvature in the Arrhenius plot of self-diffusion, usually attributed to the coexistence of two or more separate mobile defects, is shown to be explainable in terms of a single highly relaxed vacancylike defect, in which the anharmonicity of the lattice modes gives rise to a large thermal-expansion coefficient for the defect. A model based on this approach gives excellent agreement for all cases in which curvature has been observed, as well as for others in which no curvature has been detected.

I. INTRODUCTION

In recent years, there has been an increasing body of evidence to show that self-diffusion in solids is not invariably characterized by strict adherence to the Arrhenius relation,

$$D = D_0 e^{-q/RT}, \tag{1}$$

where the "frequency factor" D_0 and "activation energy" q are constants, independent of temperature. Noticeable departures from this relation have been observed in many cases of "normal" metals, e.g., sodium,[1] potassium,[2] and silver,[3] as well as in the well-known "anomalous" refractory metals such as β-titanium[4] and β-zirconium.[5] In many other elements the Arrhenius relation is rigorously obeyed, and no variations of D_0 and q are measurable within fairly small limits of error.

The departures from Arrhenius behavior have frequently been attributed[3,6,7] to the simultaneous or sequential effects of two or more different defects contributing to the elementary diffusional process. Recasting Eq. (1) by the familiar identification of D_0 and q with thermodynamic variables,[8] the temperature dependence of the diffusivity D is given by

$$\begin{aligned} D(T) &= \sum_{i=1}^{N} D_i(T) = \sum_{i=1}^{N} D_{0i} e^{-\Delta h_i/RT} \\ &= \sum_{i=1}^{N} g_i f_i \nu_{0i} a^2 e^{\Delta s_i/R} e^{-\Delta h_i/RT}, \end{aligned} \tag{2}$$

where N is the total number of diffusing defects, a is the lattice parameter, g_i is a geometrical factor determining the jump distance, f_i is the correlation factor, ν_{0i} is the characteristic attack frequency, Δs_i is the activation entropy, Δh_i is the activation enthalpy, and $D_{0i} = g_i f_i \nu_{0i} a^2 e^{\Delta_i/R}$ is the pre-exponential factor of the ith type of defect. The slope of the graph of $\ln D(T)$ vs $1/T$ is the effective enthalpy Δh_{eff} of diffusion; that is,

$$\Delta h_{\text{eff}}(T) = \sum_{i=1}^{N} D_i \Delta h_i \bigg/ \sum_{i=1}^{N} D_i, \tag{3}$$

where $\Delta h_{\text{eff}}(T)$ is obviously a function of the temperature for $\Delta h_i \neq \Delta h_j$.

Accordingly, the departure from Arrhenius behavior is simply explained by including two (or more) separate defects with different enthalpies and entropies, so that D_0 and q can be temperature dependent, while the basic enthalpy and entropy changes associated with formation and motion of each defect are temperature independent. This simplification has the obvious virtue that it greatly eases the task of the theorist who tries to calculate such enthalpy and entropy changes from first principles, since the state of the lattice only at the absolute zero need be considered.

Nature, however, does not necessarily abjure the complexity of an intrinsic temperature dependence, as evidenced by the fact that matter indeed does expand under an increase in temperature. Therefore, there is little reason, *a priori*, to exclude the theoretical possibility that a single (but possibly complex) defect is involved in the diffusion process and that the enthalpy and entropy changes associated with the formation and motion of this defect are inherently temperature dependent. The only thermodynamic requirement is that the temperature dependences of the two relevant parameters be related by

$$\left(\frac{\partial \Delta h}{\partial T}\right)_P = T \left(\frac{\partial \Delta s}{\partial T}\right)_P; \tag{4}$$

both the enthalpy and entropy must be temperature dependent. Since either term in Eq. (4) defines a specific heat, an equivalent statement is that, for non-Arrhenius behavior, there must be a nonzero

TABLE I. Diffusion parameters for a two-defect model and Δc_p for selected metals.

Metal	Δh_1 (kcal/mole)	Δh_2 (kcal/mole)	$\ln D_{01}$	$\ln D_{02}$	T_h (°K)	T_l (°K)	$\langle \Delta c_p \rangle$ (R)
Na	8.5 ± 0.2	11.5 ± 0.5	-5.2	-0.33	370	195	9 ± 2
K	$8.9 \pm$?	$11.2 \pm$?	-3.0	0.0	335	221	$10 \pm$?
Ag	$41.4 \pm$?	$52.0 \pm$?	-2.6	$+1.8$	1228	914	$15 \pm$?
Cu	50.2 ± 0.3	50.2 ± 0.3	-0.25	-0.25	1334	971	0 ± 1
Zn (c axis)	21.9 ± 0.2	21.9 ± 0.2	-2.1	-2.1	691	512	0 ± 1
Zn (a axis)	23.0 ± 0.1	23.0 ± 0.1	-1.8	-1.8	691	512	0 ± 1
β-Ti	$31.2 \pm$?	$60.0 \pm$?	-7.9	$+0.09$	1813	1172	$23 \pm$?
β-Zr	$27.7 \pm$?	$65.2 \pm$?	-9.4	$+0.29$	2020	1174	$22 \pm$?

specific heat Δc_p associated with the formation and motion of the defect. Table I shows values of Δh_i and $\ln D_{0i}$, as well as Δc_p values, needed to explain the behavior for a number of typical cases; only two defects are presumed for the multiple-defect-model approach. Where both defects have the same enthalpies and pre-exponential terms (Cu and Zn), there is no observed departure from Arrhenius behavior, and $\Delta c_p = 0$. In the two-defect models, Δh_1 has commonly been associated with a monovacancy and Δh_2 with a divacancy for the tabulated cases. Thus, the average specific heat of the two-defect system $\langle \Delta c_p \rangle$ presented in Table I is just the difference between Δh_1 and Δh_2 divided by the difference between T_h and T_l—the upper and lower limits of the diffusion-temperature ranges.

Clearly, an explanation in terms of a single defect requires that there be a large $\Delta c_p \gtrsim 10R$. Several attempts have been made to calculate Δc_p for a vacancy,[9-11] giving an upper limit of $0.5R$, far too small to explain the non-Arrhenius behavior. All these calculations, however, have been based on two assumptions: (i) that the thermal coefficient of expansion of the activated vacancy β_v is identical with that of the perfect lattice β_0; and (ii) that the isothermal compressibility of the activated vacancy K_v is the same as for the perfect lattice K_0. Recent precise measurements of the temperature and pressure dependences of the activation volume for diffusion in[12,13] Zn and[14] Cd have, in fact, shown that while $K_v/K_0 \approx 1$, for these two metals, $\beta_v/\beta_0 \approx (\beta_0 T)^{-1} \approx 15$, which is very far from unity. A large value of thermal expansion coefficient for a vacancy, of course, implies a large local-lattice anharmonicity. Thus, not only are the vibrational modes themselves appreciably altered near the defect (needed to explain the entropy of formation of the vacancy), but, apparently, the relative anharmonicity can also be greatly modified. As will be shown in Sec. II, Δc_p for an activated vacancy is given, to a good approximation, by the following expression:

$$\Delta c_p \cong T\beta_0(\Delta V_0/\Omega_0)\gamma_0 c_v^0(2\beta_v/\beta_0 - K_v/K_0), \tag{5}$$

where ΔV_0 is the activation volume of the defect, Ω_0 is the lattice atomic volume, γ_0 is the Grüneisen constant of the perfect lattice, and c_v^0 is the perfect-lattice specific heat at constant volume. By inspection of the last factor on the right-hand side of Eq. (5), it is evident that the experimentally measured values of β_v and K_v can augment the originally estimated value of Δc_p by a large factor. Thus, Δc_p can possibly be as large as $15R$, large enough to make the single-defect description of Arrhenius-plot curvature plausible.

The purpose of this paper is not to rule out the possibility of more than one defect operating in certain observed cases of curvature, but to show that all the observed cases of curvature in the Arrhenius plot of the self-diffusion coefficient of metals can be equally well accounted for by a single vacancylike defect possessing a thermal coefficient of expansion not unlike that found for zinc and cadmium. To test this idea, the metals sodium, potassium, β-titanium, β-zirconium, silver, copper, and zinc were chosen for analysis. Sodium and potassium exhibit significant curvature in their Arrhenius plots and are considered "normal" bcc metals in the sense that their activation energies follow the melting-point rule while their D_0's lie in the range 10^{-1}–10. On the other hand, β-titanium and β-zirconium were chosen because they exhibit extremely large curvature in their Arrhenius plots and are "anomalous" bcc metals in the aforementioned sense. Silver is the only fcc metal for which significant curvature has been observed. The remaining two metals, copper (fcc) and zinc (hcp), show no detectable curvature in their Arrhenius plots and thus serve as "controls." In addition, zinc is the only metal for which β_v is experimentally known among the metals chosen. Although β_v is also experimentally known for cadmium, there are no corresponding precise measurements of $D(T)$ over a sufficiently large temperature range to establish the limits to the validity of the Arrhenius relationship.

II. THEORY

The excess specific heat Δc_p can be evaluated by estimating the change of the "perfect"-lattice specific heats, c_p^0 and c_v^0, on introducing a vacancy into the lattice at zero pressure and constant temperature T. For the state of the crystal before the introduction of the vacancy,

$$c_p^0 = c_v^0 + \beta_0^2 V_0 T / K_0 , \qquad (6)$$

where V_0 is the volume of the crystal at temperature T. The presence of an activated vacancy in the crystal changes c_p^0 by Δc_p^0, c_v^0 by Δc_v^0, and V_0 by ΔV_0. As shown in the Appendix, the differential of Eq. (6) is given by

$$\Delta c_p^0 = \Delta c_v^0 + \beta_0^2 T \Delta V_0 (2\beta_v/\beta_0 - K_v/K_0)/K_0 . \qquad (7)$$

The detailed calculation of Δc_v^0 appears in the Appendix. Briefly, we assume that the Debye density of states, $g_D(\nu)$, for the normal modes of the crystal is adequate to calculate the specific heat at constant volume, with and without the vacancy. Thus, the effect of the vacancy is to perturb g_D by Δg_D, the Debye frequency ν_D by $\Delta \nu_D$, with the production of Z local modes. Under this assumption, Δc_v^0 is found to be very small compared to Δc_p^0:

$$|\Delta c_v^0| \lesssim (\Theta_D/T)^2 R , \qquad (8)$$

where Θ_D is the Debye temperature. Values of $(\Theta_D/T)^2$ vary from a maximum value of 0.3 for sodium to a minimum value of 2×10^{-2} for Zr. The second term of Eq. (7) can be estimated by making use of the Grüneisen relation, $\gamma_0 = \beta_0 \Omega_0 / K_0 c_v^0$, and the experimental result of $\beta_v \simeq T^{-1}$, as indicated by the measurements on zinc and cadmium. Then

$$\Delta c_p^0 \cong -(\Theta_D/T)^2 R + 2(\Delta V_0/\Omega_0)\gamma_0 c_v^0 . \qquad (9)$$

Taking $\Delta V_0/\Omega_0 \approx 0.7$, $\gamma_0 \approx 2$, and $c_v^0 = 3R$ for $T > \Theta_D$, we find $\Delta c_p^0 \approx 9R$. Evidently, Δc_v^0 is at most 3% of Δc_p^0, assuming $K_v/K_0 \ll \beta_v/\beta_0$. Thus, to a good approximation we can write Eq. (9) as

$$\Delta c_p^0 = \left(\frac{\partial \Delta h}{\partial T}\right)_p = \mu_v T , \qquad (10)$$

where

$$\mu_v = 2\beta_v\beta_0 \Delta V_0 / K_0 = 2(\beta_v \Delta V_0)\gamma_0 c_v^0 / \Omega_0 . \qquad (11)$$

For $\beta_v = T^{-1}$, $\Delta V_0 \propto T$. Thus, the product $\beta_v \Delta V_0$ is independent of temperature. Since γ_0 and c_v^0 are, to a good approximation, also independent of temperature, μ_v has only the weak temperature dependence of Ω_0. Excluding the temperature dependence of Ω_0 in μ_v when integrating Eq. (10) with respect to temperature typically changes $\Delta h(T)$ by no more than ~1% (see the Appendix). We therefore treat μ_v as a temperature-independent quantity in integrating Eq. (10) to obtain

$$\Delta h(T) = \Delta h(T_0) + \tfrac{1}{2}\mu_v (T^2 - T_0^2) , \qquad (12)$$

where T_0 is some reference temperature greater than the Debye temperature. Since $(\partial \Delta s/\partial T)_p = T^{-1}(\partial \Delta h/\partial T)_p$, Eq. (12) yields for the activation entropy $\Delta s(T)$,

$$\Delta s(T) = \Delta s(T_0) + \mu_v (T - T_0) . \qquad (13)$$

Rewriting Eq. (1) for a single defect with a temperature-dependent activation enthalpy $\Delta h(T)$ and activation entropy $\Delta s(T)$,

$$D(T) = D_0(T) e^{-\Delta h(T)/RT} , \qquad (14)$$

where

$$D_0(T) = g f \nu_0 a^2 e^{\Delta s(T)/R} . \qquad (15)$$

Substituting Eqs. (12) and (13) in Eq. (14) gives

$$T \ln D(T) = -(q_0/R) + (\ln d_0) T + \tfrac{1}{2}(\mu_v/R) T^2 , \qquad (16)$$

where

$$q_0 = \Delta h(T_0) - \tfrac{1}{2}\mu_v T_0^2 \qquad (17)$$

and

$$\ln d_0 = \ln(g f \nu_0 a^2) + \Delta s(T_0)/R - (\mu_v/R) T_0 . \qquad (18)$$

Then the pre-exponential term $\ln D_0(T)$ is given by

$$\ln D_0(T) = \ln d_0 + (\mu_v/R) T , \qquad (19)$$

and the activation enthalpy $\Delta h(T)$ by

$$\Delta h(T) = q_0 + \tfrac{1}{2}\mu_v T^2 . \qquad (20)$$

The term $\frac{1}{2}(\mu_v/R)T$ is responsible for the curvature in the graph of $\ln D(T)$ vs T^{-1}. The degree of curvature obviously depends on the value of $\frac{1}{2}\mu_v \times \langle T^2 \rangle$ with respect to the "characteristic" enthalpy q_0.

Whether μ_v is really temperature independent depends on the exact nature of β_v. The assumption that the quantity $\beta_v \Delta V_0$ is independent of temperature should therefore be viewed as a first approximation—suggested by the form of β_v for zinc and cadmium—and subject to verification in other cases. In testing the reasonableness of the model we therefore treat q_0, $\ln d_0$, and μ_v as parameters to be determined from fitting the self-diffusion data for a variety of metals to Eq. (16). This permits a comparison of the computer-determined "best" value of μ_v with the value of μ_v determined from the estimation of each of the parameters in Eq. (11). The calculation was performed with the aid of an IBM-360 computer using a linear-multiple-regression program developed at the C.E.A., Fontenay-aux-Roses, France.

III. RESULTS

A. Characteristic enthalpy q_0 and the extreme values of $\Delta h(T)$

The best-fit values of the diffusion parameters appearing in Eq. (16) are shown in Table II for several metals. With the exception of β-titanium and β-zirconium, the characteristic enthalpy q_0 lies reasonably close to the temperature-averaged value of $\Delta h(T)$; from the computer-derived value of the "curvature parameter" $\frac{1}{2}\mu_v\langle T^2\rangle/q_0$ listed in Table II, for all but β-titanium and β-zirconium, $0.8 < q_0/\langle\Delta h(T)\rangle < 1.0$. On the other hand, $q_0/\langle\Delta h(T)\rangle = 0.43$ for β-titanium and 0.26 for β-zirconium; these relatively small values are a result of the elevated temperature range in which bulk diffusion occurs for these metals (see Table I). From the viewpoint of the characteristic enthalpy q_0, β-titanium and β-zirconium appear to be more closely related to bcc sodium and potassium than to fcc silver and copper.

Equation (20) is used to calculate $\Delta h(T_h)$ and $\Delta h(T_l)$: these are listed in Table II. The total uncertainty in the absolute value of $\Delta h(T)$ is the sum of the uncertainties in q_0 and μ_v. However, the uncertainty in the difference between the high- and low-temperature values of $\Delta h(T)$ is due solely to the uncertainty in μ_v, as can be seen from Eq. (20). Thus, for sodium, the change of $\Delta h(T)$ of 2.2 kcal/mole from 195 to 370°K is some ten times greater than the uncertainty of ±0.2 kcal/mole in the enthalpy difference. For potassium, silver, β-titanium, and β-zirconium, this ratio is, respectively, 3, 6, 5, and 26. For these metals, there is obvious curvature in the Arrhenius plot. On the other hand, for zinc and copper the change in enthalpy is of the same order as its uncertainty, and little or no curvature is expected.

B. Characteristic frequency factor d_0 and the extreme values of $D_0(T)$

The computer-derived values of $\ln d_0$ and its uncertainty are presented in Table II. The most precise values of the pre-exponential factor d_0 are found for sodium and β-zirconium—the two metals with the experimental data extending over the largest temperature range. In these two most favorable cases, d_0 is determined to within 50%. Otherwise, it is determined to within one to two orders of magnitude. In spite of these uncertainties, a pattern for the characteristic size of d_0 emerges for the metals considered. For those metals exhibiting very little or no curvature—zinc and copper—the values of d_0 are consistent with those characteristic of "normal" metals; i.e. $10^{-1} < d_0 < 10$. On the other hand, among those metals having significant curvature, d_0 varies from the order of 10^{-3} for potassium to the order of 10^{-11} for β-zirconium and β-titanium.

The factor d_0 is just the temperature-independent part of the actually measured frequency factor $D_0(T)$, as can be seen by inspection of Eq. (19). The calculated values of $D_0(T_h)$ and $D_0(T_1)$ are presented in Table II. Thus, although d_0 is extremely small, except for zinc and copper, the high-temperature value of the frequency factor $D_0(T_h)$ is not too different from that of "normal" metals. The low-temperature frequency factor $D_0(T_1)$ is "normal" for all of the metals except β-titanium and β-zirconium, for which it has the value of the order of 10^{-4}. For all the metals having significant curvature, $D_0(T)$ increases with increasing temperature, well outside of the experimental uncer-

TABLE II. Best-fit diffusion parameters for a single defect having a temperature-dependent enthalpy and entropy of activation for selected metals.

Metal	q_0 (kcal/mole)	$10^6\mu_v$ (kcal/mole °K^2)	$\ln d_0$	$\frac{1}{2}\mu_v\langle T^2\rangle/q_0$	$\Delta h(T_h)$ (kcal/mole)	$\Delta h(T_l)$ (kcal/mole)	$\ln D_0(T_h)$	$\ln D_0(T_1)$
Na	7.8 ± 0.1	45 ± 3	-9.1 ± 0.5	0.24 ± 0.02	10.9 ± 0.3	8.7 ± 0.2	-0.8 ± 0.8	-4.7 ± 0.6
K	8.2 ± 0.3	33 ± 9	-6 ± 1	0.16 ± 0.05	10.0 ± 0.6	9.0 ± 0.4	-1 ± 2	-3 ± 2
Ag	38 ± 1	13 ± 2	-7 ± 1	0.19 ± 0.03	48 ± 2	43 ± 1	$+1 \pm 1$	-1 ± 1
β-Ti	16 ± 3	19 ± 3	-20 ± 2	1.3 ± 0.5	46 ± 6	29 ± 4	-3 ± 4	-9 ± 3
β-Zr	9 ± 1	19 ± 1	-23.0 ± 0.7	2.9 ± 0.4	48 ± 2	22 ± 1	-4 ± 1	-11.7 ± 0.9
Zn (*c* axis)	20 ± 1	10 ± 9	-5 ± 3	0.09 ± 0.09	23 ± 3	21 ± 2	-2 ± 4	-3 ± 4
Zn (*a* axis)	22 ± 2	6 ± 8	-4 ± 3	0.05 ± 0.06	23 ± 3	23 ± 2	-1 ± 4	-2 ± 3
Cu	47 ± 3	5 ± 4	-3 ± 2	0.08 ± 0.07	52 ± 5	50 ± 3	0 ± 4	-1 ± 3

tainty in μ_v; $D_0(T)$ is essentially independent of temperature for zinc and copper.

C. Coefficient of vacancy specific heat μ_v

The computer-calculated values of the coefficient of the vacancy specific heat μ_v are listed in Table II. The smallest and most uncertain values occur for those metals exhibiting the smallest degree of experimentally observed curvature. Nevertheless, for all of the metals considered, $\mu_v \approx 10^{-5}$ kcal/mole °K^2. Since the activation enthalpy varies quadratically with the temperature, this characteristic value of μ_v permits enthalpy changes of the order of between 1–30 kcal/mole, over the temperature range of interest.

IV. DISCUSSION

A. Characteristic size of the coefficient of vacancy specific heat μ_v

The characteristic magnitude found for μ_v can be compared to the theoretical expression for μ_v given by Eq. (11). Taking $\Delta V_0(T)$ proportional to the temperature,

$$\Delta V_0(T) = \delta\Omega_0(T/T_m)\,, \tag{21}$$

where $\delta\Omega_0$ is the activation volume of the defect at the melting point T_m of the solid, and $\gamma_0 = 2$, we obtain

$$\mu_{v(\text{theor})} = 24\times 10^{-3}(\delta/T_m)\ \text{kcal/mole}\ {}^\circ\text{K}^2\,, \tag{22}$$

where δ is the activation volume expressed as a fraction of the atomic volume Ω_0. Experimentally, $0.3 < \delta < 0.8$. Taking $\delta = 0.6$, as an average, and the actual melting temperatures (T_m varies from 335 °K for potassium to 2130 °K for β-zirconium), $8\times 10^{-6} \leqslant \mu_v \leqslant 43\times 10^{-6}$ kcal/mole °K^2. This result is in good agreement with the computer-calculated values of μ_v listed in Table II.

B. Comparison of best-fit value of $\beta_v\Delta V$ with experimentally determined value for zinc and sodium

1. Zinc

Zinc is the only metal considered for which the product $\beta_v \Delta V = (\partial\Delta V/\partial T)$ has been precisely measured.[13] Its value is $(6.4\pm 0.5)\times 10^{-3}$ cm^3/mole °K, independent of crystallographic direction. From Table II, the best-fit values of μ_v for the a and c crystallographic directions in zinc are $\mu_{v(c)} = (10\pm 9)\times 10^{-6}$ kcal/mole °K^2 and $\mu_{v(a)} = (6\pm 8)\times 10^{-6}$ kcal/mole °K^2. In view of the large uncertainties in these quantities, we take the best-fit value of μ_v as $(8\pm 8)\times 10^{-6}$ kcal/mole °K^2, independent of direction. Taking $\gamma_0 = 2$ and $\Omega_0 = 9.2$ cm^3/mole, we obtain $\beta_v\Delta V_0 = (3\pm 3)\times 10^{-3}$ cm^3/mole °K, in agreement with the experimentally measured value.

2. Sodium

The extraction of the quantity $\beta_v\Delta V_0$ from the data of Mundy[1] is more complicated and perhaps more controversial than for zinc. It is more complicated because the isotherms of $\ln D(T,p)$ vs p show curvature in the case of sodium, whereas they are extremely linear in the case of zinc. With the present model of single-defect diffusion, we attribute the curvature to the relatively large compressibility of the sodium vacancy, rather than to the existence of several incompressible defects. If we assume that the isothermal compressibility of the vacancy K_v is independent of the pressure—a reasonable first-order approximation—it is easy to show (see the Appendix) that an isotherm of $\ln D$ vs p has—to second order in p—the form

$$-\ln[D(T,p)/D(T,0)] = [\Delta V_0(T,0)/RT - K_0\gamma_0]p - [\tfrac{1}{2}K_v\Delta V_0(T,0)/RT]p^2\,. \tag{23}$$

For $K_v p \ll 1$, the second term becomes negligible with respect to the first term, and Eq. (23) reduces to the classic case of a linear isotherm. The quantity $\Delta V_0(T,0)$ is just the vacancy-activation volume at atmospheric or zero pressure. A least-squares fit of Eq. (23) to the 14.8 °C and 91.3 °C isotherms of Mundy yields the following values of $K_v(T)$ and $\Delta V_0(T,0)$: at 288 °K, $\Delta V_0 = (11.1\pm 0.2)$ cm^3/mole, $K_v = (33\pm 5)\times 10^{-12}$ cm^2/dyn; at 365 °K, $\Delta V_0 = (13.0\pm 0.2)$ cm^3/mole, $K_v = (51\pm 6)\times 10^{-12}$ cm^2/dyn. Since $K_0(300\ {}^\circ\text{K}) = 15.8\times 10^{-12}$ cm^2/dyn, K_v is some two to three times greater than K_0, depending on the temperature. Fitting $\Delta V_0(T) = AT$ to the above values of $\Delta V_0(T)$ we obtain $A = (\partial\Delta V_0/\partial T)_p = \beta_v\Delta V_0 = (3.7\pm 0.4)\times 10^{-2}$ cm^3/mole °K. The present best-fit value of μ_v (Table II) is just $(45\pm 3)\times 10^{-6}$ kcal/mole °K^2. Substituting this in Eq. (11), and using $\gamma_0 = 1.31$ and $\Omega_0 = 23.9$ cm^3/mole, we obtain $\beta_v\Delta V_0 = (6.9\pm 0.5)\times 10^{-2}$ cm^3/mole °K. Thus, the value of $\beta_v\Delta V_0$ presently calculated is a little less than twice the value deduced from Mundy's high-pressure self-diffusion data. This difference is well outside the limits of uncertainty in each of the quantities. The most obvious explanation is the questionable validity of the assumption that $\beta_v = T^{-1}$ equally well for sodium as for zinc and cadmium. It should be noted that the relation $\beta_v = T^{-1}$ was established for zinc and cadmium in a temperature range where T is two to three times larger than the Debye temperature Θ_D. However, for sodium $\Theta_D = 150$ °K while the diffusion data fall in the temperature range 195–370 °K, $1.3 < T/\Theta_D < 2.5$, so that the high-temperature functional form of β_v may well be different for sodium.

C. Comparison of best-fit value of $\beta_v\Delta V_0$ with estimated values for K, Ag, Cu, β-Ti, and β-Zr

For K, Ag, and Cu either the "creep" or self-diffusion activation volume has been experimentally determined, but the relatively large experimental uncertainty in the activation volume (~10%) does not permit a determination of β_v. Thus, for K, Ag, and Cu, we assume that the experimentally measured values of ΔV_0 are approximately the same as $\Delta V_0(T_m)$. Equation (21) is then differentiated with respect to temperature to yield an estimated value of $\beta_v\Delta V_0$. For β-titanium and β-zirconium, we take $\delta = 0.5$, the value found for β-Ti.[15] The value of $\beta_v\Delta V_0$ is determined from Eq. (11) and the values of μ_v listed in Table II. The relevant physical parameters in Eqs. (11) and (21) and the estimated and best-fit values of $\beta_v\Delta V_0$ are presented in Table III. The best agreement between the estimated and best-fit values of $\beta_v\Delta V_0$ occurs for potassium and β-zirconium for which, within the calculated uncertainties, they are equal. For silver, copper, and β-titanium the difference is greater, indicating that even at high temperatures (with respect to the Debye temperature) there is no guarantee that $\beta_v = T^{-1}$ is universally true. It would appear, in fact, that the functional form of $\beta_v(T)$ is dependent on the particular metal, although worst-case agreement to within a factor of 3 indicates that, regardless of the metal in question, $\langle\beta_v(T)/\beta_0\rangle \gg 1$.

D. Comparison of model diffusion parameters

In the two-defect model, $D(T)$ is controlled by $D_2(T)$ at high temperatures and by $D_1(T)$ at low temperatures: the monovacancy, described by Δh_1 and D_{01}, controls the diffusion process at low temperatures, and the divacancy, described by Δh_2 and D_{02}, dominates at high temperatures. In the single-defect description, the defect is described by $\Delta h(T_l)$ and $D_0(T_l)$ at low temperatures and by $\Delta h(T_h)$ and $D_0(T_h)$ at high temperatures. The relevant quantities from Tables I and II are collected in Table IV to compare the two models. It should be noted that among those metals exhibiting enough curvature to warrant a two-defect analysis, sodium is the only one for which uncertainties in the diffusion parameters of the two defects have been experimentally determined. For potassium and silver, these uncertainties are probably large owing to the insensitivity of the mean-square deviation of the experimental points from the theoretical curve to variations in the values of the four diffusion parameters defining the two exponential functions.[1-3] For β-titanium and β-zirconium, the diffusion parameters and their calculated uncertainties are not uniquely determined, owing to the nature of the graphical-extrapolation technique[4] employed to evaluate the two exponential functions.

It is evident from Table IV that the agreement between the two sets of diffusion parameters for sodium and potassium is excellent, and at least fair for silver. For β-titanium there is excellent agreement between the low- and high-temperature values of D_0, as well as the low-temperature values of the enthalpy. On the other hand, $\Delta h(T_h) = (46 \pm 6)$ kcal/mole while $\Delta h_2 = (60.0 \pm ?)$ kcal/mole. Even if we assume an upper limit of 5 kcal/mole for the uncertainty in Δh_2, it would appear that $\Delta h(T_h) < \Delta h_2$. The sense of this inequality is consistent with the nature of the extrapolation technique used to determine Δh_2; Δh_1 is probably also overestimated, since data do not extend to sufficiently low temperatures due to termination of the β phase. The extrapolated contribution of the low-temperature diffusion process to high temperature is therefore overestimated, the estimated value of $D_{02}e^{-\Delta h_2/RT}$ decreases faster than it should with decreasing temperature, and one derives a value of Δh_2 which is too large. This effect is observed as well for β-zirconium; i.e., $\Delta h_1 > \Delta h(T_l)$ and $\Delta h_2 > \Delta h(T_h)$. In both descriptions, the low-temperature frequency factors are extremely small (~10^{-5}) and roughly equal. On the other hand, $D_{02} > D_0(T_h)$, consistent with the nature of the extrapolation technique.

A full test of the reasonableness of the single-defect description must necessarily include those

TABLE III. Comparison of estimated and best-fit values of $\beta_v\Delta V_0$ for K, Ag, Cu, β-Ti, and β-Zr.

Metal	δ	γ_0 (Ref. 24)	Ω_0 (cm^3/mole)	T_m (°K)	$10^3(\beta_v\Delta V_0)_{\text{est.}}$ (cm^3/mole °K)	$10^3(\beta_v\Delta V_0)_{\text{best-fit}}$ (cm^3/mole °K)
K	0.54	1.37	45.5	336	73 ± 7	91 ± 23
Ag	0.90	2.36	10.3	1234	7.5 ± 0.8	4.7 ± 0.7
Cu	0.91	2.00	7.1	1356	4.8 ± 0.5	1.5 ± 1.2
β-Ti	0.5	1.18	10.7	2073	2.6 ± 0.5	1.4 ± 0.2
β-Zr	0.5	0.83	14.0	2130	3.3 ± 0.6	2.7 ± 0.2

TABLE IV. Comparison of model diffusion parameters.

Metal	$\Delta h(T_l)$ (kcal/mole)	Δh_1 (kcal/mole)	$\ln D_0(T_l)$	$\ln D_{01}$	$\Delta h(T_h)$ (kcal/mole)	Δh_2 (kcal/mole)	$\ln D_0(T_h)$	$\ln D_{02}$
Na	8.7 ± 0.2	8.5 ± 0.2	−4.7 ± 0.6	−5.2 ± 0.1	10.9 ± 0.3	11.5 ± 0.5	−0.8 ± 0.8	−0.33 ± 0.07
K	9.0 ± 0.4	8.9 ± ?	−3 ± 2	3 ± ?	10.0 ± 0.6	11.2 ± ?	−1 ± 2	0 ± ?
Ag	43 ± 1	41.4 ± ?	−1 ± 1	−2.6 ± ?	48 ± 2	52 ± ?	1 ± 1	1.8 ± ?
β-Ti	29 ± 4	31.2 ± ?	−9 ± 3	−7.9 ± ?	46 ± 6	60.0 ± ?	−3 ± 4	0.09 ± ?
β-Zr	22 ± 1	27.7 ± ?	−11.7 ± 0.9	−9.4 ± ?	48 ± 2	65.2 ± ?	−4 ± 1	0.29 ± ?
Zn[a] (c axis)	21 ± 2	21.9 ± 0.2	−3 ± 4	−2.1 ± 0.1	23 ± 3	21.9 ± 0.2	−2 ± 4	−2.1 ± 0.1
Zn[a] (a axis)	23 ± 2	23.0 ± 0.1	−2 ± 3	−1.8 ± 0.1	23 ± 2	23.0 ± 0.1	−1 ± 4	−1.8 ± 0.1
Cu[a]	50 ± 3	50.2 ± 0.3	−1 ± 3	−0.25 ± ?	52 ± 5	50.2 ± 0.3	0 ± 4	−0.25 ± ?

[a] Only one type of defect is assumed to obtain the temperature-independent diffusion parameters.

cases of self-diffusion for which no measurable curvature is observed. A lack of measurable curvature is inevitably related to the precision with which diffusion coefficients can be measured, typically of the order of a few percent. Rearranging Eq. (16):

$$D(T) = D_{\mathrm{SL}}(T)e^{\mu_v(T-T_0)^2/2RT}, \tag{24}$$

where

$$D_{\mathrm{SL}}(T) = D_0(T_0)e^{-\Delta h(T_0)/RT}. \tag{25}$$

$D_{\mathrm{SL}}(T)$ is just a straight-line Arrhenius function tangent to the curved graph, represented by Eq. (24), at the point where $T = T_0$. The case of little curvature corresponds to $\mu_v(T-T_0)^2/2RT \ll 1$. Expanding Eq. (24),

$$D(T) \cong D_{\mathrm{SL}}(T)[1 + \mu_v(T-T_0)^2/2RT]. \tag{26}$$

For $T_0 = (T_h T_l)^{1/2}$,

$$\mu_v(T_h - T_0)^2/2RT_h = \mu_v(T_h^{1/2} - T_l^{1/2})^2/2R.$$

Thus, little or no curvature will be measured when

$$\mu_v(T_h^{1/2} - T_l^{1/2})^2/2R \lesssim \Delta D/D. \tag{27}$$

In the present analysis, $\mu_v = (8 \pm 8) \times 10^{-6}$ kcal/mole °K^2 for zinc. With $T_h = 691$ °K and $T_l = 512$ °K, $\mu_v(T_h^{1/2} - T_l^{1/2})^2/2R = (2 \pm 2) \times 10^{-2}$. Since $\Delta D/D \sim 3 \times 10^{-2}$, the curvature for zinc is masked by the experimental uncertainty in the measurement of D. The same situation holds for copper since the estimated value of $\mu_v = (5 \pm 4) \times 10^{-6}$ kcal/mole °K^2 yields $\mu_v(T_h^{1/2} - T_l^{1/2})^2/2R = (4 \pm 3) \times 10^{-2}$. On the other hand, for sodium, potassium, silver, β-titanium, and β-zirconium, $(3 \pm 1) \times 10^{-2} < \mu_v(T_h^{1/2} - T_l^{1/2})^2/2R < (54 \pm 4) \times 10^{-2}$, consistent with the pronounced curvature experimentally observed for these metals.

E. Isotope effect

The value of the isotope-effect parameter $E = f\Delta K$, which measures the mass dependence of the diffusivity, is an extremely sensitive indicator of the diffusion mechanism. Indeed, the observation that curved Arrhenius plots have, in some cases, been accompanied by a temperature dependent E has given strong support for multiple-defect mechanisms, since the value of the correlation factor f differs markedly for different mechanisms.[1,3,16-19] The factor ΔK, which is a many-body correction term, is generally believed to be relatively insensitive to temperature. Achar[20] has estimated that ΔK changes less than 0.5% in copper over the temperature range of diffusion measurements.

In the usual kinetic model for the diffusion process, the factor ΔK is a measure of the fraction of kinetic energy in the jump direction carried by the diffusing atom or atoms. If the lattice modes are largely harmonic, as usually assumed, there is little coupling between the modes of the jumping atom and those of the surrounding atoms and ΔK is close to unity. On the other hand, if the modes show strong anharmonicity, as would be required to explain a large coefficient of thermal expansion for a vacancy, the mode coupling must be greatly increased and ΔK would, correspondingly, be expected to decrease with increasing temperature. This effect would undoubtedly be more important in bcc than in fcc lattices, since the vacancy volume in the former is already greatly contracted due to inward relaxation of the neighbors. For example, Mundy's data show that the activation volume for self-diffusion in sodium at 290 °K is only 11 cm^3/mole. Since the atomic volume is 24 cm^3/mole, this indicates an inward relaxation of at least 54%. Moreover, Mundy finds that the activation volume increases with increasing temperature, from 11 cm^3/mole at 290°K to 13 cm^3/mole at 390°K. This evidence, cited in support of the vacancy-divacancy model, could equally well support the notion of a single defect with a positive thermal expansion coefficient and a strongly temperature-dependent value of ΔK.

F. Entropic considerations

Both single- and multi-defect models show anomalously low values for the pre-exponential factor D_0 at low temperatures in cases where marked curvature is found in the Arrhenius plot [compare values of $\ln D_{01}$ in Table I and $\ln D_0(T_1)$ in Table II]. Since D_0 [see Eq. (15)] consists of a product of geometrical factors $gf\nu_0 a^2$ and an entropic term $e^{\Delta s(T)/R}$, the order of magnitude of D_0 can be readily estimated and compared to the best-fit values. Taking ν_0 as the order of the Debye frequency, $10^{12}-10^{13}$ Hz, a the lattice parameter, and g and f of order unity, the product of geometrical factors must be of order $10^{-2}-10^{-3}$. Thus, to explain values of D_0 less than this range, the activation entropy $\Delta s(T)$ must be *negative*. The entropic term includes a contribution to the entropy for formation of the defect and one for motion of the defect.

Huntington, Shirn, and Wajda[21] have calculated values for the entropy of formation and motion of a vacancy in copper, and find both to be positive: $\Delta s_f = +1.47$ e.u. and $\Delta s_m = +0.93$ e.u. This result indicates that lattice vibrational frequencies in the vicinity of the defect must be *lowered* both on forming the defect and moving it through the saddle point,[22] at least in copper. A positive value of Δs is clearly required to fit the diffusion data for the great bulk of cases in which no curvature is observed and which D_0 is found to be in the range $10^{-1}-10$. By almost any model, the entropy of formation of a simple monovacancy is expected to be positive if there is little lattice relaxation around the missing atom, since the removal of an atom must result in a lowering of local-lattice frequencies (as well, of course, in disordering of the lattice). The motional entropy, on the other hand, would have a negative contribution from raising the local vibrational frequencies as the diffusing atom crowds through the saddle configuration, offset by a lowering of the over-all frequency spectrum due to relaxation at the surface. The motional entropy, in any event, is expected to be small for a simple monovacancy. Thus, a multi-defect model in which the low-temperature defect is identified with a simple monovacancy with a temperature-independent entropy and enthalpy is not, in fact, consistent with values of D_0 less than $10^{-2}-10^{-3}$.

In the single-defect model, the defect is not presumed to be a simple monovacancy, but a complex defect in which the effect of the missing atom is compensated by large relaxation of several shells of neighbors. The "vacancy," in this sense, is a many-body structure with a small over-all volume of formation but with highly perturbed lattice frequencies and strong local anharmonicity. Such a defect could have a negative entropy for formation and motion, as well as a large thermal expansion coefficient, and could be a more consistent explanation for the "anomalous" results, particularly for the bcc lattice where large relaxations may be anticipated.

V. CONCLUSIONS

It has been shown that the experimentally determined functional form of the large vacancy thermal coefficients of expansion found for zinc and cadmium results in a modified self-diffusion equation which yields intrinsic curvature in the Arrhenius plot of self-diffusion for a single defect. We have shown that the existence of curvature is not guaranteed by a large vacancy thermal coefficient of expansion, since it depends on the upper- and lower-temperature limits of the diffusion range as well as the precision with which the diffusion coefficients are measured.

The temperature-dependent diffusion parameters calculated in the present single-defect model are consistent with those found in multi-defect diffusion models of diffusion. The model predicts the proper degree of curvature for those metals where curvature is measured, and little or no curvature in those cases where curvature is undetected experimentally. All of the known cases of Arrhenius-plot curvature are at least as well explained by a single highly relaxed vacancy endowed with a large thermal coefficient of expansion as by recourse to a group of two or more separate defects, each characterized by temperature-independent diffusion parameters.

ACKNOWLEDGMENTS

One of us (H.M.G.) would particularly like to thank the Centre d'Etudes Nucléaires (C.E.A.), France, for providing an atmosphere that was extremely conducive to the realization of this work. In addition, both authors wish to express their deepest thanks to Dr. Y. Quere and Dr. L. Chhabildas for many helpful discussions, and to Mlle. Sovay for her considerable contribution to the computer calculation.

APPENDIX

A. Calculation of Δc_p^0

The differential operator Δ gives the change in each physical property of the host lattice when a single defect is introduced at zero pressure and constant temperature T. Applying this operator to Eq. (6) yields

$$\begin{aligned}\Delta c_p^0 &= \Delta c_v^0 + T\Delta(\beta_0^2 V_0/K_0) \\ &= \Delta c_v^0 + \beta_0^2 T \Delta V_0 (2V_0 \Delta\beta_0/\beta_0 \Delta V_0 + 1 \\ &\qquad - V_0 \Delta K_0/K_0 \Delta V_0)/K_0 .\end{aligned} \tag{A1}$$

The definition of β_0 is just

$$\beta_0 = V_0^{-1}\left(\frac{\partial V_0}{\partial T}\right)_p . \tag{A2}$$

Operating on Eq. (A2) with Δ we obtain

$$\begin{aligned}\Delta\beta_0 &= \Delta\left[V_0^{-1}\left(\frac{\partial V_0}{\partial T}\right)_p\right] \\ &= -V_0^{-2}\left(\frac{\partial V_0}{\partial T}\right)_p \Delta V_0 + V_0^{-1}\Delta\left(\frac{\partial V_0}{\partial T}\right)_p \\ &= -\beta_0 \Delta V_0/V_0 + V_0^{-1}\left(\frac{\partial \Delta V_0}{\partial T}\right)_p ,\end{aligned}$$

or

$$\Delta\beta_0 = -\frac{\beta_0 \Delta V_0}{V_0} + \frac{\Delta V_0}{V_0}\,\Delta V_0^{-1}\left(\frac{\partial \Delta V_0}{\partial T}\right)_p . \tag{A3}$$

The definition of the intrinsic thermal coefficient of expansion of a vacancy is just

$$\beta_v = \Delta V_0^{-1}\left(\frac{\partial \Delta V_0}{\partial T}\right)_p . \tag{A4}$$

Substituting Eq. (A4) in Eq. (A3) gives for $\Delta\beta_0$

$$\Delta\beta_0 = (\Delta V_0/V_0)(\beta_v - \beta_0) . \tag{A5}$$

The intrinsic isothermal compressibility of a vacancy is given by

$$K_v = -\Delta V_0^{-1}\left(\frac{\partial \Delta V_0}{\partial p}\right)_T . \tag{A6}$$

The isothermal compressibility of the lattice is given by the usual expression

$$K_0 = -V_0^{-1}\left(\frac{\partial V_0}{\partial p}\right)_T . \tag{A7}$$

As the form of Eqs. (A6) and (A7) is mathematically identical to the form of Eqs. (A2) and (A4), by inspection of Eq. (A5) we immediately obtain for ΔK_0

$$\Delta K_0 = (\Delta V_0/V_0)(K_v - K_0) . \tag{A8}$$

Finally, substituting Eqs. (A5) and (A8) in Eq. (A1) yields for Δc_p^0

$$\Delta c_p^0 = \Delta c_v^0 + \beta_0^2 T \Delta V_0 (2\beta_v/\beta_0 - K_v/K_0)/K_0 , \tag{A9}$$

which is just Eq. (7).

B. Calculation of Δc_v^0

In the Debye approximation, the perfect-crystal constant-volume specific heat is given by the usual expression

$$c_v^0 = k\int_0^{\nu_D} f(\nu, T) g_D(\nu)\, d\nu , \tag{A10}$$

where ν is a frequency of the continuum defined by $0 < \nu < \nu_D$, and

$$f(\nu, T) = (h\nu/kT)^2 e^{h\nu/kT}(e^{h\nu/kT} - 1)^{-2} . \tag{A11}$$

The Debye density of states is given by

$$g_D(\nu) = (9N/\nu_D^3)\nu^2 , \tag{A12}$$

where N is the number of atoms in the crystal. Operating on Eq. (A10) with Δ gives, to first order in the differential quantities, the following expression for the vacancy-induced change in the continuous part of c_v^0

$$\begin{aligned}\Delta c_{v(\mathrm{cont})}^0 = k\biggl(& f(\nu_D) g_D(\nu)\Delta\nu_D \\ & + \int_0^{\nu_D + \Delta\nu_D} [f(\nu)\Delta g_D(\nu) + g_D(\nu)\Delta f(\nu)]\, d\nu \biggr) .\end{aligned} \tag{A13}$$

In addition to changing the frequencies in the continuum of states, the vacancy produces localized vibrational modes.[23] If there are z local modes of frequencies ν_l, we can write for the local-mode contribution to the change in c_v^0

$$\Delta c_{v(\mathrm{local})}^0 = k\sum_{\nu_l} (h\nu_l/kT)^2 e^{h\nu_l/kT} - 1)^{-2} . \tag{A14}$$

To evaluate the integrals of Eq. (A13) we need to know $\Delta\nu_D$, as well as the dependence of each frequency shift $\Delta\nu$ on the frequency ν, since Δg_D and Δf are proportional to $\Delta\nu$. We suppose, for simplicity, that

$$\Delta\nu = C\nu , \quad C = \mathrm{const} \tag{A15}$$

consistent with the calculated frequency shifts induced by a light impurity in a one-dimensional chain.[23] Thus, to first order in C

$$\begin{aligned}\Delta g_D(\nu) &= \Delta[(9N/\nu_D^3)\nu^2] = (9N\nu^2/\nu_D^3)(2\Delta\nu/\nu - 3\Delta\nu_D/\nu_D) \\ &= -(9NC/\nu_D^3)\nu^2 .\end{aligned} \tag{A16}$$

In the defect-free crystal the number of modes in the continuum is just $3N$; i.e.,

$$3N = \int_0^{\nu_D} g_D(\nu)\, d\nu . \tag{A17}$$

Introducing the vacancy by operating on Eq. (A17) with **Δ**, we obtain

$$\begin{aligned} -Z &= \Delta\left(\int_0^{\nu_D} g_D(\nu)\, d\nu\right) \\ &= g_D(\nu_D)\Delta\nu_D + \int_0^{\nu_D+\Delta\nu_D} \Delta g_D(\nu)\, d\nu \\ &= (9N/\nu_D)C\nu_D + (-9NC/\nu_D^3)(\tfrac{1}{3}\nu^3)\Big|_0^{\nu_D+\Delta\nu_D} \\ &= 6NC\,, \text{ to first order in } C. \end{aligned} \tag{A18}$$

Thus,

$$C = -Z/6N. \tag{A19}$$

A second-order expansion of Δg_D and Eq. (A18) yields the same value of C for $Z \neq 0$. If there are no local modes ($Z = 0$), the second-order solutions yield $C = 0$, $\frac{2}{11}$, which are, respectively, trivial and physically unacceptable, since we expect that a single vacancy shifts the frequencies by the order of N^{-1}. It would appear, then, that the existence of localized modes is necessary to maintain the assumption that the fractional frequency shift is a constant, independent of frequency.

In the high-temperature limit, series expansions give the following results for $f(\nu, T)$ and $\Delta f(\nu, T)$:

$$f(\nu, T) = 1 - \tfrac{1}{12}(h\nu/kT)^2 \tag{A20}$$

and

$$\Delta f(\nu, T) = -\tfrac{1}{6}(h/kT)^2\nu\Delta\nu = -(\tfrac{1}{6}C)(h\nu/kT)^2 . \tag{A21}$$

Substituting Eqs. (A12), (A16), and (A19)–(A21) in Eq. (A13) then gives the following expression for $\Delta c^0_{v(\text{cont})}$:

$$\Delta c^0_{v(\text{cont})} = -kZ[1 - \tfrac{1}{40}(h\nu_D/kT)^2] . \tag{A22}$$

The local-mode contribution to Δc^0_v is estimated in the following way. Since $\nu_l > \nu_D$, $h\nu_l \ll 1$, so that the high-temperature-limit form of $f(\nu_l, T)$ can be used in Eq. (A14). Thus,

$$\begin{aligned} \Delta c^0_{v(\text{local})} &= k\sum_1^Z [1 - \tfrac{1}{12}(h\nu_l/kT)^2] \\ &= k\left(Z - \tfrac{1}{12}(h\nu_D/kT)^2 \sum_1^Z (\nu_l/\nu_D)^2\right) . \end{aligned} \tag{A23}$$

Since we are only interested in the order of magnitude of Δc^0_v, we will estimate ν_l from the one-dimensional crystal calculation of Montroll and Potts.[23] They found that for a vacancy in a one-dimensional crystal there is only one local mode ($Z = 1$) which is very similar to the pulsation of a bubble. The frequency of this mode is determined in terms of the ratio P between the perfect-lattice central-force constant γ, and the central-force constant γ' with which neighboring atoms on opposite sides of the vacancy are coupled. Specifically, they showed that:

$$\nu_l/\nu_D = \tfrac{1}{2}P(P-1)^{1/2} , \tag{A24}$$

where $P = \gamma'/\gamma > 2$. A reasonable upper limit to P can be calculated with a Morse-type potential of the form

$$U(r) = D(2e^{-3\alpha(r-r_0)} - 3e^{-2\alpha(r-r_0)}) , \tag{A25}$$

where D is the dissociation energy of a pair of atoms, α is a range parameter, r is the separation between two atoms, and r_0 their equilibrium separation. The central-force constant is just the second derivative of $U(r)$. Thus, for the linear crystal,

$$\frac{\gamma'}{\gamma} = \frac{3e^{3\alpha r_0(1-gf)} - 2e^{2\alpha r_0(1-gf)}}{3e^{3\alpha r_0(1-f)} - 2e^{2\alpha r_0(1-f)}} , \tag{A26}$$

where fr_0 is the actual equilibrium separation of atoms in the defect-free chain and gfr_0 is the separation between an atom neighboring the vacancy and its first nearest neighbor. The quantity αr_0 is typically between 3 and 4, so we will use $\alpha r_0 = 3.5$. We further assume that the first nearest neighbors to the vacancy relax by about 5%, so we fix the value of g at 1.05. The ratio γ'/γ is then calculated as a function of f. The maximum value of γ'/γ occurs at $f = 1$, and it equals 2.2. Thus, for $P = 2.2$, Eq. (A24) yields a maximum value of 1.5 for the quantity $(\nu_l/\nu_D)^2$. Then, the value of $\Delta c^0_{v(\text{local})}$ from Eq. (A23) is

$$\Delta c^0_{v(\text{local})} = k[1 - \tfrac{1}{8}(h\nu_D/kT)^2] . \tag{A27}$$

The total value of Δc^0_v is just given by the sum of Eqs. (A22) and (A27):

$$\Delta c^0_{v(\text{total})} = -\tfrac{39}{40}(h\nu_D/kT)^2 k \approx -(\Theta_D/T)^2 k . \tag{A28}$$

Equation (A28) is just the equivalent to Eq. (8).

C. Justification of ignoring temperature dependence of $\Omega_0(T)$ in μ_v

With $\beta_v \Delta V_0$ independent of the temperature, from Eq. (11) we can write for μ_v

$$\mu_v = J/\Omega_0(T) , \tag{A29}$$

J is a constant independent of temperature. Substituting Eq. (A29) in Eq. (10) and integrating with respect to the temperature, we obtain:

$$\begin{aligned} \Delta h(T) &= \Delta h(T_0) + J/\Omega_0(T_0) \int_{T_0}^{T} T\, dT/[1 + \beta_0(T - T_0)] \\ &= \Delta h(T_0) + \tfrac{1}{2}\mu_v(T^2 - T_0^2) - \tfrac{1}{2}\mu_v T_0 \beta_0 (T - T_0)^2 , \end{aligned} \tag{A30}$$

where we have used $\beta_0(T - T_0) \ll 1$ to expand the logarithmic quantities that result from performing the integral appearing in Eq. (A30). The ratio w of the third term to the second term of Eq. (A30) is just

$$w = T_0\beta_0(T - T_0)/(t + T_0). \qquad \text{(A31)}$$

For sodium, $w(\text{Na}) = 1.2\times 10^{-2}$. In the limit of very-high-temperature diffusion, such as for β – Ti, $w(\text{Ti}) = 7.6\times 10^{-3}$. Thus, since the third term of Eq. (A30) is at most 1% of the second term, Eq. (A30) reduces to Eq. (12).

D. Equation of curved isotherm of ln$D$ vs p

We integrate Eq. (A6) with respect to pressure while imposing the condition that K_v is independent of pressure. We obtain

$$\Delta V_0(T,p) = \Delta V_0(T,0)e^{-K_v p}, \qquad \text{(A32)}$$

where $\Delta V_0(T,0)$ is just the activation volume at atmospheric or zero pressure. Applying the thermodynamic relation $\Delta V_0(T,p) = -(\partial\Delta G/\partial p)_T$ to Eqs. (14) and (15) we obtain

$$\Delta V_0(T,p) = -RT\left(\frac{\partial \ln D}{\partial p}\right)_T + RTK_0\gamma_0. \qquad \text{(A33)}$$

Substituting Eq. (A33) in Eq. (A31) and integrating with respect to pressure between the limits $p = 0$ and $p = p$ at constant temperature T yields

$$\ln D(T,0)/D(T,p) = -\Delta V_0(T,0)(e^{-K_v p} - 1)/RTK_v - K_0\gamma_0 p. \qquad \text{(A34)}$$

Expanding $e^{-K_v p}$ to second order in p in Eq. (A34) yields

$$\ln D(T,0)/D(T,p) = -(\Delta V_0/RT - K_0\gamma_0)p + [\tfrac{1}{2}K_v\Delta V_0(T,0)/RT]p^2, \qquad \text{(A35)}$$

which is just Eq. (23).

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*Supported in part by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-1198.

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