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Calculation of the sodium vacancy thermal coefficient of expansion

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The method of lattice statics is used to calculate the temperature variation of the vacancy formation volume ΔV of sodium in the range 90–300 K. ΔV is shown to derive its temperature dependence from that of the elastic constants and that of the interionic potential taken from the work of Rasolt and Taylor. The thermal coefficient of expansion of the sodium vacancy is found to be about 15 times greater than that of the perfect lattice at high temperature. This result could play an important role in high-temperature defect measurements and provides at least a partial explanation for the Arrhenius-plot curvature in sodium.

I. INTRODUCTION

In general, assuming a single-defect mechanism, one expects the self-diffusion coefficients $D(T)$ of pure metals to show a T^{-1} exponential behavior; i.e., a plot of $\ln D(T)$ vs T^{-1} (Arrhenius plot) should yield a straight line. However, experimentally, significant curvatures in Arrhenius plots of $D(T)$ are usually found and it is of interest to gain an understanding of the mechanisms behind these curvatures. Clearly, one possible explanation is that more than one defect is involved in the diffusion process. However, an alternative explanation, involving only a single-vacancy mechanism, has been proposed.[1] This requires the enthalpy changes Δh associated with the formation and motion of this defect to be strongly temperature dependent. Consequently the corresponding specific heat $\Delta c_p = (\partial \Delta h/\partial T)_p$ should be large. Now Gilder and Lazarus[1] have shown that, to a good approximation,

$$\Delta c_p \simeq 2TK\beta_0\beta_v \Delta V_D\,, \tag{1}$$

where β_0 and K are, respectively, the thermal coefficient of expansion and the bulk modulus of the perfect lattice. ΔV_D is the vacancy activation volume of self-diffusion related to the thermal coefficient of expansion of the activated vacancy by

$$\beta_v = \Delta V_D^{-1}\left(\frac{\partial \Delta V_D}{\partial T}\right)_p . \tag{2}$$

Hence one can see that a strongly temperature-dependent ΔV_D can lead to a large value of β_v and an appreciable curvature in the Arrhenius plot of $D(T)$. This appears to be the case in zinc[2] and cadmium[3] where the large variations of the activation volumes with temperature can be interpreted as due to large values of β_v ($\sim 15\beta_0$). Accepting that such large values of β_v are plausible, it is entirely possible that the Arrhenius curvature is consistent with the single-vacancy mechanism in the diffusion process. Hence it follows that, before attempting to incorporate other defect processes into an analysis of diffusion, one should assess the magnitude of the effect of the activated vacancy thermal expansion. In this paper we provide an estimate of this effect, not in cadmium or zinc, but in sodium for which it is possible to perform with greater ease, a meaningful calculation.

In sodium we note that the experimental values of $D(T)$ do exhibit an appreciable curvature when displayed on an Arrhenius plot.[4] Unfortunately there are not sufficient data for ΔV_d as a function of temperature to determine β_v precisely. However, the curvature in Mundy's data[4] is consistent with a large value of β_v similar to those found in zinc and cadmium. Hence a numerical estimate of this quantity in sodium will provide a good test of the importance of the vacancy thermal-expansion mechanism in this system and help establish the degree of plausibility for the presence of the same mechanism in other systems.

In order to calculate $\Delta V_D(T)$, and thus β_V, we need to know not only the vacancy formation volume ΔV but also the migration volume ΔV_M:

$$\Delta V_D = \Delta V + \Delta V_M .$$

Generally speaking, ΔV_M is believed to be much smaller than ΔV although it is a poorly defined quantity. Ideally we should include the effect of ΔV_M in our calculations, particularly since its temperature derivative could still be comparable with that of ΔV, but such a calculation is beyond the scope of this paper. Hence we focus our attention on a calculation of the relaxed-vacancy thermal-expansion coefficient,

$$\beta = \Delta V^{-1}\left(\frac{\partial \Delta V}{\partial T}\right)_p . \tag{3}$$

If this quantity turns out to be of about the same magnitude as the values of β_v needed to explain the observed Arrhenius-plot curvature, the vacancy-expansion mechanism will be established as an important contributor to this effect. If, on the other hand, it turns out to be very much smaller, then it is likely that such a mechanism can safely be ignored.

In Sec. II we describe the method of calculation and the interionic potential used. Then in Secs. III and IV we present our results and discuss their implications.

II. CALCULATION OF THE TEMPERATURE VARIATION OF THE VACANCY FORMATION VOLUME

The formation of the vacancy introduces changes in the interatomic interactions in its vicinity, giving rise to the lattice relaxation. Taking the defect itself as the origin of the coordinate system, the position of the atom l having suffered a displacement $\vec{u}(l)$ from its equilibrium site $\vec{r}(l)$ is given by

$$\vec{x}(l)=\vec{r}(l)+\vec{u}(l). \tag{4}$$

The overall response of the crystal will be a uniform expansion by some fraction of an atomic cell, which is referred to as the formation volume ΔV. In the lattice statics method, as proposed by Kanzaki[5] and extensively used by Hardy and coworkers,[6] ΔV can be written

$$\Delta V=\Omega+G/3K. \tag{5}$$

Ω is the atomic volume, K is the bulk modulus, and G is the vacancy dipole moment defined by

$$G=\sum_l n_l G_l. \tag{6}$$

The contribution G_l of an atom in the lth shell comprising n_l atoms is given by

$$G_l=\vec{F}(\vec{x}(l))\cdot\vec{r}(l). \tag{7}$$

The force $\vec{F}(\vec{x}(l))$ on the lth atom due to the defect has to be evaluated at the relaxed positions.

The formulation of lattice statics is strictly valid at zero temperature, and the calculation of the formation volume at elevated temperatures should take into account the effect of lattice vibrations and thermal expansion. But it has been shown, in a previous paper,[7] that the contribution of vibrations to the calculated value of ΔV is negligeable for all metals. Then, if it is assumed that the host atoms interact among themselves through a pairwise potential Φ, the defect potential due to the absence of an atom is just $-\Phi$, in the case of a vacancy. Therefore, the use of an interionic potential taking into account the variation of electronic charge density with lattice parameter or temperature to calculate the forces in Eq. (7) will give a good description of the variation of ΔV with temperature.

For the interionic potential we used that of Rasolt and Taylor[8] recalculated at the electron densities appropriate to the temperatures of interest. These authors have shown that the contributions to the interionic potential beyond second order in perturbation theory can be simulated by a model potential, the parameters of which are determined by the requirement that a linear-response calculation of the charge density of an isolated ion embedded in an infinite electron gas should agree exactly with a full nonlinear calculation of the same quantity. Full details are given in their paper. Using this procedure, accurate phonon dispersion curves can be generated in sodium, as well as other systems,[9] with no parameters adjusted to fit other experimental properties. Also, other thermodynamic properties of sodium are reproduced satisfactorily.[10] Hence this potential should be entirely suitable for our purposes. For all our calculations, the potential was truncated at the eighth neighbor since this procedure has been shown to give rise to negligeable errors.[10,11]

To determine the contribution G_l for each shell, we can either use the exact value of the first derivative of the potential at the relaxed positions of the atoms

$$\Phi_l'(u)=\left.\frac{\partial\Phi(x)}{\partial x}\right|_{x(l)=|\vec{r}(l)+\vec{u}(l)|}, \tag{8}$$

or we can approximate $\Phi_l'(u)$ by means of a Taylor's series expansion in $\vec{u}(l)$. In the first case

$$G_l=\sum_i\frac{x_i(l)r_i(l)}{x(l)}\Phi_l'(u), \tag{9}$$

which reduces to

$$G_l=r(l)\Phi_l'(u) \tag{10}$$

when the displacements are radial. In the second case, we can write

$$F_i(\vec{x}(l))=F_i(\vec{r}(l))+\sum_j u_j(l)\left.\frac{\partial Fi}{\partial x_j(l)}\right|_{\vec{r}(l)}+\cdots. \tag{11}$$

Of course

$$F_i(\vec{r}(l))=r_i(l)\Phi_l'(0)/r(l), \tag{12}$$

thus

$$\left.\frac{\partial F_i}{\partial x_j(l)}\right|_{\vec{r}(l)}=\frac{r_i(l)r_j(l)}{r^2(l)}\left(\Phi_l''(0)-\frac{\Phi_l'(0)}{r(l)}\right)+\frac{\delta_{ij}\Phi_l'(0)}{r(l)}. \tag{13}$$

Substituting Eqs. (12) and (13) in Eq. (7), and neglecting higher-order terms, we obtain

$$G_l=r(l)\Phi_l'(0)+\vec{u}(l)\cdot\vec{r}(l)\Phi_l''(0). \tag{14}$$

We can see from Eq. (14) that a calculation of G_l requires knowledge of the values of the first derivative of the potential, not at the relaxed positions as in the first approach defined by Eqs. (9) and (10), but rather at the equilibrium positions of the ions.

The choice between using Eq. (10) or Eq. (14) for the calculation of G_l will be determined by considering the convergence of the Taylor's expansion used in Eq. (11) and the possibility of calculating the atomic displacements for the different shells.

In the case of sodium, considering the first two shells, one observes that although the first-derivative value of the potential is of the same order of magnitude for the first and the second neighbor, the second-derivative value for the second neighbor is only 7% of its value for the first neighbor. Thus we can expect the use of Eq. (14) to be justified to calculate G_2. On the contrary, G_1 ought to be obtained from Eq. (10), which is appropriate in that case as we know from symmetry considerations, that the displacements of the first neighbors of the vacancy are radial.

In order to calculate the value of G_1 from Eq. (10), we need to know the displacements of the atoms belonging to the first shell; those have been obtained by use of the static Green's function method.[12] The first and second derivatives to the interionic potential are calculated for the lth shell at each temperature or lattice parameter, the force-constant matrix $\underline{\phi}$ is then given by

$$\phi_{\alpha\beta}^{(l)}=\frac{r_\alpha(l)r_\beta(l)}{r(l)^2}\left(\frac{\Phi_l'(0)}{r(l)}-\Phi_l''(0)\right)-\frac{\delta_{\alpha\beta}\Phi_l'(0)}{r(l)}\,. \tag{15}$$

Next the Fourier transform of the matrix $\underline{\phi}$ is calculated. Taking the inverse of $\underline{\phi}$ and then the inverse Fourier transform of $\underline{\phi}^{-1}$, by summing over the allowed values of the wave vector in the Brillouin zone, the lattice Green's function $\underline{\Gamma}$ is readily obtained. Assuming a perturbed space consisting of the nearest neighbors and the vacancy site, the expression for the displacement of the first neighbors may be written[12]

$$u_1(1)=\Phi_1'(0)[\lambda_\Gamma^{-1}-\Phi_1''(0)]^{-1}\,, \tag{16}$$

where λ_Γ is a simple combination of the matrix elements:

$$\begin{aligned}\lambda_\Gamma=\Gamma_{11}^{(0)}-\Gamma_{11}^{(2)}-2\Gamma_{22}^{(2)}-\Gamma_{33}^{(3)}-2\Gamma_{11}^{(3)}\\ -2\Gamma_{12}^{(3)}-\Gamma_{11}^{(5)}-2\Gamma_{23}^{(5)}\,.\end{aligned} \tag{17}$$

To determine the displacements of the atoms of the second to eighth shells, we make use of the value of the elastic field around a symmetric point defect in a cubic anisotropic material[13]

$$\vec{u}(l)\cdot\vec{r}(l)=GP_l/r(l)\,, \tag{18}$$

where P_l is a factor dependent on elastic constant values and orientations of the atoms of the lth shell. In addition, P_l is given by a rather complicated integral expression which is, in general, not reducible to a simple analytical form. Numerical integration is thus required to generate the P_l's appropriate to the present calculation. The validity of using two approximations, namely, Taylor's expansion and elastic-field approximation, in the calculation of the contribution of the non-first-neighbor shells will be justified below in considering their numerical values. Another advantage of making those two approximations is that it is no longer necessary to undertake an explicit calculation of the displacements and potential values for the second to eighth neighbors, because in the determination of G_2 to G_8 an elimination of the displacement $\vec{u}(l)$ occurs between Eqs. (6), (14), and (18). On the contrary the calculation of G_1, from Eq. (10), implies the determination of the displacement $u_1(1)$ from Eq. (16) and then the calculation of the interatomic potential first derivative $\Phi_1'(u)$.

Finally, substituting Eq. (10) for $l=1$ and Eqs. (14) and (18) for $l=2$ to 8 in Eq. (6) yields

$$G=\frac{n_1r_1\Phi_1'(u)+\sum_{l=2}^{8}n_lr(l)\Phi_l'(0)}{1-\sum_{l=2}^{8}n_lP_l\Phi_l''(0)/r(l)}\,, \tag{19}$$

from which a temperature-dependent value of the formation volume of the vacancy can be obtained via Eq. (5), when the temperature dependence of the isothermal elastic constants contributing to K and P_l is known.

III. RESULTS

Using Eq. (15), the force constant matrix $\underline{\Phi}$ has been obtained from the interionic potential calculated for several lattice parameter values or temperatures. The derivation of the temperature-dependent lattice Green's function $\underline{\Gamma}$ required subsequently the inversion of $\underline{\Phi}$ and summation over 85 000 points in the Brillouin zone. The displacement component of the first-neighbor atom then followed from Eq. (17); it was found to be directed inward (in the direction of the vacancy) and its amplitude $u_1(1)$ expressed in unit of the lattice parameter was found to decrease with temperature from 0.041 at 93 K to 0.033 at 296 K.

The non-first-neighbor displacements contribute to the defect strength with the second term in the denominator of Eq. (19); this contribution appeared to be small at all temperatures and of the order of 0.051. This result justifies the approximations of elastic-field displacements and Taylor's series development which have been used to calculate $G_2, \ldots, G_8$.

The isothermal elastic constants of sodium were taken from the data of Martinson[14] and used to calculate $K(T)$ and $P_l(T)$. The experimental data were used in preference to the calculations of Ref. 10 because of the difficulty of generating an accurate representation of the volume-dependent potential which also contributes to the elastic constants.[15,16] We did not extend our calculations to temperatures above 300 K due to the absence of experimental elastic constants above that temperature.

The variation of the formation volume is plotted against temperature in Fig. 1 and shows a rapid increase with temperature. The calculated values, in the range 90–300 K, are in very good agreement with a quadratic best fit of the form

$$\Delta V/\Omega = 0.2733 + 2.235\times 10^{-6} T^2 , \qquad (20)$$

where the contribution of higher order in T can be neglected.

The slope of the $\Delta V(T)$ curve gives the value of the vacancy thermal coefficient of expansion β. We note that

$$\Delta V^{-1}\left(\frac{\partial \Delta V}{\partial T}\right)_p = \Omega^{-1}\left(\frac{\partial \Omega}{\partial T}\right)_p + \left(\frac{\Delta V}{\Omega}\right)^{-1}\left(\frac{\partial(\Delta V/\Omega)}{\partial T}\right)_p . \qquad (21)$$

Combining Eqs. (21), (3), and (20) we find that

$$\beta = \beta_0 + 4.47\times 10^{-6} T/(0.2733 + 2.235\times 10^{-6} T^2) .$$

The values of $\beta(T)$ and $\beta(T)/\beta_0(T)$, as calculated from Eqs. (20) and (21), are illustrated in Fig. 2. β is found to increase with temperature from 1.55 $\times 10^{-3}$ K^{-1} at 93.1 K to 3×10^{-3} K^{-1} at 296.2 K; or in terms of the thermal coefficient of expansion of the perfect lattice β_0, we have $11.7\,\beta_0 < \beta < 14.7\beta_0$ in the same temperature range.

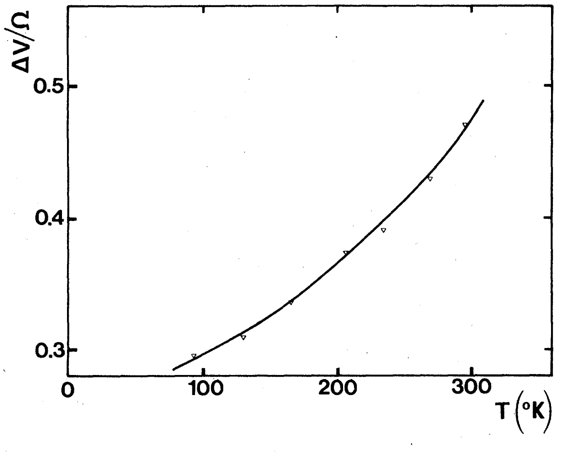

FIG. 1. Variation of the vacancy-formation volume in sodium with temperature.

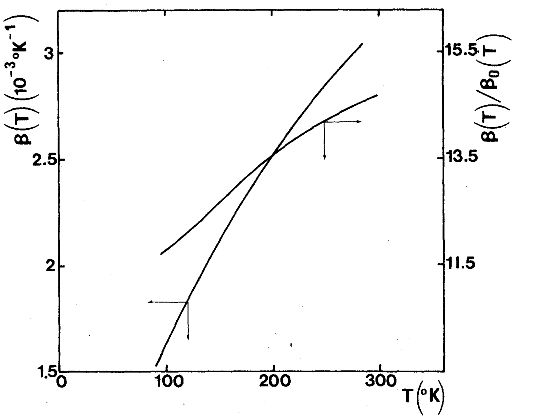

FIG. 2. Variation of the coefficient of vacancy thermal expansion in sodium with temperature.

IV. DISCUSSION

For sodium the self-diffusion activation volume has been experimentally determined[4] at two temperatures, the values being $\Delta V_D = 0.467 \pm 0.008\ \Omega$ at 288 K and $\Delta V_D = 0.540 \pm 0.008\ \Omega$ at 365 K. Therefore, the increase of the calculated formation volume is consistent with the increase of the measured activation volume. In addition, the value of $\Delta V = 0.46\,\Omega$, presently calculated at 288 K, is evidently in good agreement with these measurements.

Our results show that a good description of the first-neighbor displacement is essential in the case of sodium; the value of $u(1)$ obtained by lattice-statics calculation is much larger than the value given by the elastic-field theory, as previously pointed out.[17] At 300 K, if the relaxation of the first neighbors were either neglected or approximated by a value derived from the elastic theory, we would obtain, respectively, the values of 0.91 and 0.87 Ω for ΔV, both of which are two times greater than the presently calculated value.

The large calculated value of thermal-expansion coefficient for a vacancy in sodium, $\beta \simeq 15\beta_0$ at high temperature is of the right order of magnitude to be consistent with the activation volume measurements of Mundy.[4] However, we find an increase of β with increasing temperature in the case of sodium, opposite to the behavior found in zinc. This difference in behavior is not too surprising, inasmuch as $\beta = T^{-1}$ 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, so that the presently calculated values of ΔV fall in the "reduced temperature" range, $0.6 < T/\Theta < 2$. We thus expect ΔV, at low reduced temperature, to decrease and become independent of temperature ($\beta \to 0$ for $T \to 0$ K), consistent with the third law of thermodynamics.

In the temperature range 195–370 K the curvature in the Arrhenius plot of sodium experimental diffusion data implies a change in the vacancy-diffusion enthalpy $\delta\Delta H = 2.2 \pm 0.1$ kcal/mole.[4] Using Eq. (1) and extrapolating our calculations of β to 370 K we obtain a value of $\delta\Delta H = 1.0$ kcal/mole, which is of the same order of magnitude. Since we have ignored the contribution of $(\partial \Delta V_M / \partial T)_p$ to the diffusion enthalpy, the difference between these two numbers should not be regarded as significant. Hence we conclude that it is quite possible that the Arrhenius curvature is entirely due to the thermal expansion of the diffusing vacancy. But in any case it is clear from our calculation that the highly relaxed monovacancies of sodium are endowed with a sufficiently large thermal coefficient of expansion to make an important contribution to the measured Arrhenius-plot curvature. It would appear then that to neglect this effect in an analysis of diffusion data is unrealistic, even when it is assumed that at least two diffusion mechanisms are operative.

In a final comment we note that a change in ΔH of 1 kcal/mole ($\simeq 0.04$ eV) over the temperature range 195–370 K is $\simeq 10\%-15\%$ of the measured formation enthalpy in Na.[18,19] Hence this effect should not be ignored when interpreting these experiments.

In conclusion, it has been shown that the availability of reliable interionic potentials for simple metals makes it possible to undertake temperature-dependent calculations of the vacancy thermal coefficient of expansion.

However, this supposes that for each metal considered there exists an adequate way of handling the problem of convergence that arises from the oscillating nature of the potential. In the case of sodium this problem is, in effect, drastically simplified by the fact that the truncation at the eighth nearest-neighbor site, used by us, had been previously shown to yield all of the phonon and thermodynamical properties of sodium. Although the present results cannot be readily applied to other metals (nonalkaline as well as alkaline), the technique can, provided that a reliable interionic potential that depends on lattice parameter exists and that an adequate means of treating the problem of convergence is readily available. Inasmuch as the present calculation represents the only known first-principle-type calculation of the vacancy coefficient of thermal expansion, it remains to be seen whether the above-mentioned conditions can be satisfied for a wide variety of metals. Considering the order of magnitude of the present result, it is clear that the thermal properties of the vacancies should not be neglected in future studies of thermal dilation and self-diffusion in metals.

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