Self-diffusion in sodium under pressure revisited

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Abstract
The pressure–volume relation in sodium has been measured up to 100 GPa using
high-resolution angle-dispersive synchrotron x-ray diffraction (Hanfland *et al*
2002 *Phys. Rev.* B **65** 184109). In the light of these data, we show that a model
suggested long ago (e.g., Varotsos *et al* 1978 *J. Phys. C: Solid State Phys.* **11**
L305–15) can satisfactorily answer the long-standing question of the variation
of the diffusion coefficient D under pressure P, which resulted in a curved $\ln D$
versus P plot, in the frame of a single operating mechanism (monovacancies).
This is achieved without using *any* adjustable parameters.

Both theoretical [1, 2] and experimental [3–6] studies have shown that Li and Na, which are
considered textbook examples of free electron metals (because of the single s electron in the
valence band), exhibit unexpected complexity at sufficiently high pressures. For example,
the observations of a resistivity increase at high pressures (P) and temperatures (T) and the
discovery [4–6] of superconductivity in Li demonstrated that the alkali metals are not as simple
as we initially thought. Their pressure-induced complexity is attributed [1, 2] to the increased
role of core electrons becoming more appreciable with decreased volume. With the evidence of
a sequence of phases having complex crystal structures at high pressures in Li [3] and Na [7, 8],
these elements have recently attracted a great experimental and theoretical interest. Among
these experimental findings, we shall focus here on the pressure–volume (PV) relation of
Na measured up to 100 GPa in [7] using high-resolution angle-dispersive synchrotron x-ray
diffraction (cf it was found that at 65 GPa Na undergoes a structural phase transition from bcc
to fcc). We shall show here that these accurate experimental measurements also shed light on
the unusual variation of the self-diffusion coefficient (D) in Na upon increasing pressure when
they are combined with an early suggestion [9–11]—called the cBΩ model (see also [12])—
which interconnects point defect parameters with bulk properties. Similar arguments can be
easily extended to Li, but here we shall intentionally prefer to discuss the case of Na since it
has been found [13, 14] to exhibit a more pronounced curvature in the $\ln D$ versus P plot. This
has challenged a large number of publications during the last 35 years.

In Na, simultaneous measurements of the macroscopic thermal expansion and lattice parameters (for a compilation of references, see [12]) demonstrate that vacancies and not interstitials are the dominant intrinsic point defects in thermal equilibrium. The thermodynamic parameters for the defect formation (f) process—designated by g^f, h^f, s^f for the Gibbs energy, enthalpy and entropy, respectively—are defined upon comparing a real (i.e., containing defects) crystal to an *isobaric* ideal (i.e., *not* containing defects) crystal; see [12]. When a single mechanism is operating, the (radiotracer) diffusion coefficient is given by

$$D = \gamma \alpha^2 \nu \exp\left(-\frac{g^{\mathrm{act}}}{kT}\right) \tag{1}$$

where γ (beyond a numerical constant) is the correlation factor ($= 0.727$ for monovacancies in bcc metals like Na), α stands for the lattice constant, g^{act} denotes the Gibbs energy for the activation (act) process and ν the attempt frequency which is of the order of the Debye frequency ν_{D}. In most materials the plot of $\ln D$ versus P (for $T = \mathrm{const}$) is found to be straight line, which means that g^{act} increases linearly upon increasing the pressure (for $T = \mathrm{const}$). In Na, however, this plot is found to deviate strongly from linearity. In particular, isothermal radiotracer measurements at $T = 288$ and 364.3 K for pressures up to ~1 GPa (as well as measurements [15] of the NMR line-width at room temperature and pressures up to 5 GPa) reveal that the quantity $-kT(\mathrm{d} \ln D/\mathrm{d}P)_T$—which gives the defect activation volume υ^{act} (see also below)—continuously decreases upon increasing P. The most popular explanation for this curvature of the $\ln D$ versus P plot was the following (for a compilation of references see [12]): it results from the superposition of two or more diffusion mechanisms, namely the monovacancy–divacancy model (rarely, e.g., see [16], the interstitial has been also suggested as a significant contributor for self-diffusion but at temperatures close to melting). An alternative explanation was forwarded long ago [9–11, 17], as mentioned above, which proposed that this curvature can be described in the frame of a *single* mechanism (i.e., monovacancy) the thermodynamic parameters of which exhibit reasonable *intrinsic* temperature and pressure dependences. These were envisaged within the following model, to which we now turn.

The defect Gibbs energy g^i is interconnected with the bulk properties of the solid through the relation [9–11] (cf a survey of its proof can be found in pages 363–401 of [12]):

$$g^i = c^i B \Omega \tag{2}$$

where B stands for the isothermal bulk modulus, Ω the mean volume per atom and c^i is dimensionless, which can be considered—to the first approximation—independent of temperature and pressure (cf this approximation holds if the ratio $\Delta P/B$—where ΔP refers to the pressure range of our experimentation—is appreciably smaller than unity; otherwise a small correction factor should be also incorporated; see page 126 of [12]). The superscript i in equation (2) refers to the defect process under consideration, i.e., i = f, act, and m stand for the formation, self-diffusion activation and migration, respectively. By differentiating equation (2) in respect to pressure, we find the activation volume $\upsilon^{\mathrm{act}}(= -\mathrm{d}g^{\mathrm{act}}/\mathrm{d}P)_T$ for the diffusion process:

$$\upsilon^{\mathrm{act}} = c^{\mathrm{act}} \Omega \left(\left.\frac{\mathrm{d}B}{\mathrm{d}P}\right|_T - 1\right) \tag{3}$$

which can be alternatively written as

$$\upsilon^{\mathrm{act}} = \frac{g^{\mathrm{act}}}{B} \left(\left.\frac{\mathrm{d}B}{\mathrm{d}P}\right|_T - 1\right). \tag{4}$$

The validity of equation (4) has been checked for the self-diffusion processes in a variety of solids [18, 19] as well as for the indenter penetration into a (ionic) crystal surface [20] (during which transient electric signals are emitted, in a similar fashion to the signals measured [21–23]

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before earthquakes). Furthermore, we note that the above procedure can be also applied to mixed ionic solids since their B-values used in equation (2) can be estimated from the corresponding B-values of the pure constituents [24].

We now proceed to the presentation of our results related to the pressure variation of D in Na. The quantity v^{act} is experimentally determined through the slope of the $\ln D$ versus P plot by means of the procedure mentioned above. It is clear that only if v^{act} is arbitrarily assumed as pressure independent (which is usually adopted in the monovacancy–divacancy model for each of the mechanisms involved) is the $\ln D$ versus P plot expected to be a straight line. However, it is reasonable to consider that, even in the case of a single operating mechanism, v^{act} may vary upon compression. Thus, the curvature of the $\ln D$ versus plot can be described in terms of the compressibility κ^{act} defined as

$$\kappa^{\mathrm{act}} \equiv -(\mathrm{d}\ln v^{\mathrm{act}}/\mathrm{d}P)_T. \tag{5}$$

The data analysis [10, 11, 17] of the plots obtained in the experiment of [13], for $T = 288$ and 364.5 K, indicate that their curvatures can be fully described by the values $\kappa^{\mathrm{act}} = (33 \pm 5) \times 10^{-2}$ GPa^{-1} and $(51 \pm 6) \times 10^{-2}$ GPa^{-1}, respectively (see also page 127 of [12]). Hence, the question arises whether these κ^{ac}-values can be predicted by the cBΩ model. By inserting equation (3) into equation (5), the following relation is obtained [10, 11]:

$$\kappa^{\mathrm{act}} = \frac{1}{B} - B\frac{\mathrm{d}^2 B}{\mathrm{d}P^2}\bigg|_T \left(\frac{\mathrm{d}B}{\mathrm{d}P}\bigg|_T - 1\right)^{-1}. \tag{6}$$

Quite interestingly, this equation reveals that a property of the defect volume (i.e., κ^{act}) can be calculated in terms of the bulk elastic data without the knowledge of any other defect parameter. Let us now consider the elastic data in Na measured at room temperature (RT) by Hanfland *et al* [7]. For fitting the PV data, they used the relation of Holzapfel [25]:

$$P = 3B_0 X^{-n}(1 - X)\exp\{[1.5(\mathrm{d}B_0/\mathrm{d}P) - n + 0.5](1 - X)\}$$
$$\text{with } X = (V/V_0)^{1/3} \quad \text{and} \quad n = 5 \tag{7}$$

where V_0, B_0 are the volume and the bulk modulus, respectively, at a reference pressure (usually ambient pressure). By assigning a relative error of 1.5% at each pressure value, they reported (see their table 1)—by fitting equation (7) to the bcc phase data—the following results at ambient pressure:

$$B_0 = 6.310(80) \text{ GPa} \quad \text{and} \quad (\mathrm{d}B/\mathrm{d}P)_0 = 3.866(20). \tag{8}$$

Concerning the quantity $(\mathrm{d}^2 B/\mathrm{d}P^2)|_T$, it can be determined of course by differentiating equation (7). To simplify the situation, however, we took advantage of the following remark made by Hanfland *et al* [7]: their data can be equally well described (in a least-squares sense) by a Birch (also termed third-order Birch–Murnaghan) equation [26], the corresponding parameter values of which are similar to those obtained for equation (7). The consistency of equation (7) and Birch relations over a wide range of pressure and density can also be seen in figure 6(a) of Hanfland *et al* [7] where they plotted with parallel solid straight lines the correlation between $(\mathrm{d}B_0/\mathrm{d}P)|_T$ and B_0 for these two fits. From the slope of these lines one easily finds (at RT)

$$(\mathrm{d}^2 B/\mathrm{d}P^2)|_T \approx -0.4 \text{ GPa}^{-1}. \tag{9}$$

By inserting equations (8) and (9) into equation (6), we get (at RT)

$$\kappa^{\mathrm{act}} \approx 0.3 \text{ GPa}^{-1}. \tag{10}$$

This value, which we recall was calculated by making use of the bulk elastic data of Hanfland *et al* [7] alone, is in striking agreement with the aforementioned value $\kappa^{\mathrm{act}} \approx (33 \pm 5) \times 10^{-2}$ GPa^{-1} obtained from the analysis of the diffusion data at various pressures, at $T = 288$ K.

Unfortunately, an application of equation (6) to the higher temperature $T = 364.5$ K, at which diffusion data under pressure have been also obtained, cannot be made, because the quantity $(\mathrm{d}^2 B/\mathrm{d}P^2)|_T$ is unknown at that temperature, since the experiment of Hanfland *et al* [7] was carried out solely at RT (which is of course close to $T = 288$ K, thus allowing the aforementioned direct comparison of the experimental κ^{act} value with the one obtained from equation (6)). Upon comparing, at $T = 288$ K, either the experimental or the theoretical value (resulted from equation (6)) of κ^{act} to the bulk compressibility $\kappa = (1/B_0$, where $B_0 = 6.31$ GPa [7]), we find that they have a ratio: $\kappa^{\mathrm{act}}/\kappa \approx 1.9$. In other words, the self-diffusion activation volume decreases on compression with a rate faster than the bulk volume, a point that has been already stressed in [10, 11].

We now turn to the formation volume υ^{f} for which, however, no *direct* experimental determination is yet available. Thus, we shall restrict ourselves here to a comparison of the predictions of the cBΩ model with those obtained from microscopic calculations [27, 28]. Before proceeding, we clarify that in [12] (see page 205) the c^{f}-value for the (mono)vacancy formation process has been calculated as follows: the concentration n/N of (mono)vacancies is given by

$$n/N = \exp(-g^{\mathrm{f}}/kT)$$

and hence—through equation (2) for i = f—we have

$$n/N = \exp(-c^{\mathrm{f}}B\Omega/kT).$$

This equation, when using $T = 370.2$ K (which is close to the melting point $T = 370.9$ K), the values $\Omega = 40.069 \times 10^{-24}$ cm^3, $B = 5.744$ GPa (see table 9.12 of [12]) and the concentration $n/N \approx 7 \times 10^{-14}$ reported in [29] at the melting point, gives the value $c^f = 0.159$. This value, when inserted into the relation $\upsilon^{\mathrm{f}} = c^{\mathrm{f}}\Omega(\frac{\mathrm{d}B}{\mathrm{d}P}|_T - 1)$—similar to equation (3) but applied here to the formation process—leads to (after using the aforementioned value $(\frac{\mathrm{d}B}{\mathrm{d}P})_0 = 3.886$, see equation (8))

$$\upsilon^{\mathrm{f}} \approx 0.46 \, \Omega \tag{11}$$

which is in reasonable agreement with the υ^{f}-value of about 0.5 Ω deduced from the microscopic calculations of [27, 28]. The resulting value in equation (11) decreases upon increasing pressure, in view of the negative sign of $\frac{\mathrm{d}^2 B}{\mathrm{d}P^2}|_T$ discussed above—a behaviour which is similar to the one found also in the microscopic calculations of [27, 28]. The latter calculations also report that the migration volume (determined within the framework of the so-called transition-state theory) is much smaller than υ^{f}, a point which again agrees with an early expectation [10].

In summary, we have used the pressure–volume relation that was recently measured in Na by Hanfland *et al* [7] and led to reliable values of the B_0, $(\mathrm{d}B/\mathrm{d}P)_0$ and $-\frac{\mathrm{d}^2 B}{\mathrm{d}P^2}|_T$ at RT. On the basis of these elastic data alone, we have shown that the cBΩ model suggested long ago [9–12, 18, 19] leads to a diffusion activation volume in Na that decreases rapidly upon increasing pressure and has a compressibility κ^{act} which is in striking agreement with the one deduced from the analysis of diffusion data under pressure. This enables the explanation of the curvature observed in the $\ln D$ versus P plot on the basis of a single operating mechanism, i.e., monovacancies, without any necessity of resorting to multi-mechanism approaches suggested repeatedly during the last 35 years.

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