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Calculation of point defect parameters in diamond

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We show that the most recent values of the defect entropy and the defect enthalpy for the vacancy formation in diamond have a ratio which is comparable to the one predicted by a model suggested three decades ago [P. Varotsos and K. Alexopoulos, Phys. Rev. B **15**, 4111 (1977); **18**, 2683 (1978)]. This model, which interconnects the formation Gibbs energy with the bulk elastic and expansivity data, has been also recently found of value in high T_c superconductors as well as in glass-forming liquids.

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The following interconnection between the Gibbs energy g^f for the defect formation (f) or the Gibbs energy g^m for the defect migration (m) and the bulk properties (i.e., the expansivity and the elastic data) has been suggested long ago,[1,2]

$$g^f = c^f B\Omega \tag{1}$$

and

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

(called $cB\Omega$ model) where B is the isothermal bulk modulus and Ω the mean volume per atom. It has been argued[3] that the values of c^f and c^m are practically *independent* of temperature and pressure. As a consequence, the corresponding Gibbs energy g^{act} for activation (act) processes (when a single mechanism is operating) is given by

$$g^{act} = c^{act} B\Omega, \tag{3}$$

where $c^{act}(=c^f + c^m)$ is also independent of temperature and pressure. [cf. As an example, Eq. (3) enables[4] the calculation of self-diffusion coefficients at any temperature and pressure from a single measurement.] For reasons of brevity, the above relations are jointly written as

$$g^i = c^i B\Omega, \tag{4}$$

where i stands for the corresponding process, i.e., $i = f, m, act$. By differentiating Eq. (4) with respect to either the temperature T for P=const or the pressure P for T=const, we find the following expressions for the defect entropy s^i $\left(=-\frac{dg^i}{dT}\Big|_P\right)$, the defect enthalpy $h^i\left(=g^i - T\frac{dg^i}{dT}\Big|_P\right)$, and the defect volume v^i $\left(=\frac{dg^i}{dP}\Big|_T\right)$:

$$s^i = -c^i\Omega\left(\beta B + \frac{dB}{dT}\bigg|_P\right), \tag{5}$$

$$h^i = c^i\Omega\left(B - T\beta B - T\frac{dB}{dT}\bigg|_P\right), \tag{6}$$

$$v^i = c^i\Omega\left(\frac{dB}{dP}\bigg|_T - 1\right), \tag{7}$$

where β stands for the thermal (volume) expansion coefficient. These relations reveal that the ratios s^i/h^i and v^i/h^i are *solely* governed by the macroscopic properties β, B, $\frac{dB}{dT}\big|_P$, and $\frac{dB}{dP}\big|_T$. This has been checked (for example, see Ref. 5) in a variety of solids, i.e., rare-gas solids, metals and ionic crystals, and the results have been compiled in a monograph.[3] Furthermore, the $cB\Omega$ model enables[3] the determination of the concentration at which the conductivity (σ) and the self-diffusion coefficients (D) maximize when studying mixed alkali halides (solid solutions) [cf. in the latter solids, the B values of the mixed crystal (if they are not experimentally available) can be estimated[6] at various concentrations in terms of the B values of the pure constituents].

Later,[7] the $cB\Omega$ model was found of value to describe experimental results in ionic crystals, which revealed that a time-dependent electric polarization arises (in the *absence* of any external electric field) upon changing the rate of the uniaxial stress or by the indenter penetration into the crystal surface. These experiments led to activation volumes which—although being order(s) of magnitude smaller than those measured in other cases, e.g., in alkali halides—were found to agree[7] with the ratio v^i/h^i predicted from the $cB\Omega$ model. Such experiments have a specific importance because they are closely interrelated[7] with transient electric signals that have been found to precede[8–10] earthquakes (cf. these signals are emitted from the focal region, where a stress accumulation is expected[3] to occur before the earthquake occurrence).

The interconnection between g^i and elastic data has recently attracted a strong interest, in view of a number of challenging findings, chief among of which are the following. First, in type-II superconductors, high critical current densities can be achieved by the presence of high-density defects which will provide suitable pinning centers for the magnetic flux lines (e.g., see Ref. 11 and reference therein). In such a flux-line pinning, point defects can play an important role in cuprates such as $YBa_2Cu_3O_{7-\delta}$ (Y-123) in which the superconducting coherence length is of the order of tens of angstroms. Doping $YBa_2Cu_3O_{7-\delta}$ with alkaline earth elements improve bulk and grain-boundary transport and other properties (e.g., Ref. 12 and references therein). Interestingly, it was found[11] that in the latter superconductors, the formation volume of Schottky defects obeys the behavior predicted by the $cB\Omega$ model. On the other hand, the model does not seem to describe the case when the replacement of Y is made by rare-earth elements. [cf. This is strikingly reminiscent of the early finding[13] that in alkali halides doped with alkaline earth divalent cations, the h^m value for the reorientation process of the electric dipoles formed by a divalent cation and a nearby cation vacancy (taking place through jumps of the cation vacancy neighboring of the divalent impurity) increases upon increasing the ionic radius of the dopants; this is *not* the case, however, for rare-earth divalent dopants. The origin of this striking analogy has not yet been understood.]

Second, when studying the basic characteristics of the liquid-glass transitions, almost all glass-forming liquids (including oxide melts, ionic liquids, metallic liquid alloys, polymers, molecular liquids, or viscous liquids studied by computer simulations) exhibit "universal" features which are not yet well understood.[14] Chief among these features is the fact that the viscosity of glass-forming liquids with few exceptions exhibits a temperature dependence which markedly deviates from the Arrhenius behavior. This has been recently investigated in depth in a series of challenging papers[14–16] which point to the conclusion that the elastic models play a prominent role in the following sense. Following Ref. 16, let us start from the point that viscous liquids could be viewed more as "solids which flow" than as less-viscous liquids such as ambient water; the glass-forming liquids exhibit extremely large viscosity upon approaching the glass transition, thus most molecular motion goes into vibrations, just like in a solid. Only rarely does anything happen in the form of a flow event, a molecular rearrangement (in which the migration barrier is $\gg k_BT$, where k_B stands for the usual Boltzmann constant). These flow events are similar to the point defect motion in solids and, in the frame of the elastic models, the non-Arrhenius behavior of the viscosity is captured by the temperature variation of the elastic constants.

The present study is focused on the investigation of the validity of the $cB\Omega$ model in diamond, which exhibits certain properties that differ significantly from those in the materials mentioned above, e.g., it has a very large Debye temperature, $\Theta_D \approx 2246$ K, making it a "quantum" crystal even at room temperature. Its hardness and abrasive qualities, highly valued in technology, and gem industry are controlled by the large elastic moduli (e.g., see Ref. 17 and references therein). In general, the point defect parameters of diamond are of great interest in diverse fields. For example, in earth sciences its diffusion properties have a specific importance because natural diamonds and their mineral inclusions provide information about the geochemical character and geotherm of the ancient continental lithosphere (e.g., see Ref. 18 and references therein). In particular, the spatial distribution of carbon and nitrogen isotopes in diamond provides information on mantle residence time.[19] Diamonds with long residence at high temperature will gradually lose their initial zoning patterns due to diffusion and hence the diffusion data can constrain the maximum possible age of diamonds. Rare diamonds originating from the mantle transition zone should have developed[19] a length scale of ≈1 mm of isotopic zoning over the age of the Earth (4.5×10^9 years).

A large body of data has been accumulated in diamond during the last few years, which allowed the present study to become possible. First, the B values have been calculated by a general model[20] (relating mechanical and vibrational properties through a combination of first Szigeti and Lyddane-Sachs-Teller relations) up to 1800 K from available Raman measurements.[21–24] The calculated values are in excellent agreement with experimental results[17] up to 1600 K that were based on Brillouin scattering measurements. Second, the vacancy formation enthalpy was calculated to be $h^f = 7.2$ eV by Brenner *et al.*[25] (see their Table 10). Third, by using the self-consistent charge density-functional-based tight-binding method and correcting for the strong finite-size effects, Rauls and Frauenheim[26] achieved in finding that the vacancy formation entropy is $s^f = 2.85k_B$ with a plausible uncertainty which is less than $\pm 0.3k_B$. Finally, the self-diffusion coefficients have been recently[18] measured in a natural diamond at the condition within its field of stability: 10 GPa and 2075–2375 K. An activation enthalpy $h^{act} = 6.8 \pm 1.6$ eV was then reported, which is approximately 30% lower than results predicted from *ab initio* calculations.[27,28]

We now proceed to a numerical check of the $cB\Omega$ model. A combination of Eqs. (5) and (6), for $i=f$, reveals

$$\frac{s^f}{h^f} = - \frac{\beta B + \left.\frac{dB}{dT}\right|_P}{B - T\beta B - T \left.\frac{dB}{dT}\right|_P}. \tag{8}$$

Let us make the calculation for the highest temperature $T = 1600$ K at which, according to Aguado and Baonza,[20] we can rely on the experimental B values. A least-squares fit to a straight line of the B values that are given in Fig. 1 of Ref. 20 as a function of T gives, in the range $T \geq 1200$ K, the value $\frac{dB}{dT}|_P \approx -2.5 \times 10^{-2}$ MPa/K (with a plausible uncertainty of around 10%), while the B value (at 1600 K) is ≈415 GPa. Taking the density from the expression[17] $\rho = 3.513 + 7.4 \times 10^{-6}T - 3.8 \times 10^{-8}T^2 + 7.1 \times 10^{-12}T^3$ as deduced from the thermal-expansion data of Slack and Bartman,[29] we estimate (for $T = 1600$ K) that $\beta \approx 17.26 \times 10^{-6}$ K^{-1}. By inserting these values into Eq. (8), we find

$$\frac{s^f}{h^f} \approx 4 \times 10^{-5} \text{ K}^{-1} \tag{9}$$

(with a plausible uncertainty of around 10%). We now compare this result with the value

$$\frac{s^f}{h^f} = 3.4^{+0.4}_{-0.4} \times 10^{-5} \text{ K}^{-1} \tag{10}$$

deduced when inserting the published parameters $s^f = (2.85 \pm 0.3)k_B$ (from Ref. 26) and $h^f = 7.2$ eV (from Ref. 25) mentioned above. This comparison indicates more or less a satisfactory agreement, if one also considers the uncertainties involved. The agreement becomes even better if one takes into account that, in the light of the aforementioned self-diffusion experimental results which led to $h^{act} (= h^m + h^f) \approx 6.8$ eV, the value of 7.2 eV used in Eq. (10) seems to somewhat overestimate the actual h^f value. Furthermore, we note that the experimental value $h^{act} \approx 6.8$ eV enables the direct determination of v^{act} (for the self diffusion process) as follows: By dividing Eqs. (6) and (7), we immediately find the ratio v^{act}/h^{act}, i.e.,

$$\frac{v^f}{h^f} = \frac{\left.\frac{dB}{dP}\right|_T - 1}{B - T\beta B - T\left.\frac{dB}{dT}\right|_P}. \tag{11}$$

Upon inserting the aforementioned elastic and expansivity data along with the value[30] $\left.\frac{dB}{dP}\right|_T \approx 4$ and then using the value $h^{act} \approx 6.8$ eV, we get $v^{act} \approx 4.4$ cm^3 mol^{-1}. Unfortunately, a comparison of this calculated v^{act} value with an experimental result cannot be made because to the best of our knowledge an experiment toward determining v^{act} (i.e., self-diffusion measurements at various pressures) has not yet been performed.

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