Cohesive energies of crystals

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We comment on the controversies that seem to exist about the experimental value of the cohesive energy for silicon. We argue that this can be safely taken to be 4.62±0.08 eV/atom. We conclude that, whereas in the case of diamond the cohesive energy predicted by recent variational quantum Monte Carlo pseudopotential calculation is in excellent agreement with experiment, for silicon there remains a discrepancy of 0.19 eV/atom. To clarify these points, we mention briefly some fundamental principles of the measurement of cohesive energies and explain how they can be obtained from the thermodynamic tables.

In a recent paper,[1] Fahy, Wang, and Louie described a variational quantum Monte Carlo (VQMC) pseudopotential approach to the calculation of structural properties of solids, and applied it to the calculation of the cohesive energies of diamond and silicon. In the case of silicon, referring to a number of different sources, they concluded that the available experimental values for the cohesive energy are widely scattered, from 4.55 to 4.90 eV/atom.[2] They suggested that it would be desirable if more accurate determination of the cohesive energy for silicon could resolve this apparent problem.

We have looked closely at the experimental references of Fahy, Wang, and Louie, and discuss our findings by considering three of them.

According to Fahy, Wang, and Louie,[1] Davis, Anthrop, and Searcy[3] obtain 4.70±0.13 eV/atom for the cohesive energy of silicon. However, this is in fact the figure given by Davis, Anthrop, and Searcy[3] as the room-temperature enthalpy of formation for silicon, $\Delta H_{298\text{ K}}$. This is not the cohesive energy, since enthalpy of formation, or heat of sublimation, is, by definition,[4-6] equal to the cohesive energy only at absolute zero of temperature (see the Appendix). Using JANAF thermodynamic tables,[7] we find that $(H_{0\text{ K}}^0 - H_{298.15\text{ K}}^0)_g - (H_{0\text{ K}}^0 - H_{298.15\text{ K}}^0)_{cr}$ amounts to -0.045 eV/atom, where H_T^0 is the standard enthalpy at temperature T, and g and cr refer to the gas and the crystal phase, respectively. Therefore, the experimental cohesive energy for silicon according to Davis, Anthrop, and Searcy is equal to 4.66±0.13 eV/atom. This amount is much the same as the cohesive energy given by Brewer,[8] namely 4.63 eV/atom.

Now we look at the paper by Batdorf and Smits[9] (Ref. 23 of Fahy, Wang, and Louie). Fahy, Wang, and Louie extract the cohesive energy as being 4.55 eV/atom. This is precisely the slope of the pressure on the logarithmic scale versus inverse temperature (Fig. 2 of our Ref. 9), to which Batdorf and Smits refer as the "activation energy of evaporation." This is, as explained in the Appendix, far from being the cohesive energy. It would have been the cohesive energy if the temperatures considered by Batdorf and Smits were low, i.e., around 0 K, and not about 1200 °C–1350 °C. Taking 4.55 eV/atom as the

cohesive energy for silicon neglects the temperature dependence of the enthalpy of formation altogether. In fact, if one uses the JANAF thermodynamic tables,[7] in which the Batdorf and Smits results have been used as one of the sources to calculate the enthalpy of formation for the silicon gas, to obtain the zero-temperature enthalpy of formation (i.e., cohesive energy), one obtains 4.62±0.08 eV/atom. Hence, the Batdorf-Smits measurements give a cohesive energy which is in excellent agreement with the two earlier results mentioned above.

The third paper is by Zmbov, Ames, and Margrave.[10] According to Fahy, Wang, and Louie, the cohesive energy given by these authors should be 4.77±0.13 eV/atom.[2] However, this is, in fact, what Zmbov, Ames, and Margrave call their "best" value for the heat of sublimation of silicon at 298 K, which corresponds (see above) to a cohesive energy of 4.73±0.13 eV/atom, consistent with 4.62±0.08 eV/atom given above.

We emphasize that we attach weight not to any individual experiment but to the careful analysis of all the experimental data (including all those listed in Ref. 1) performed by the authors of the JANAF tables.[7] These authors have employed sophisticated procedures for evaluating the sources of error in each experiment, including internal consistency checks and fitting techniques much superior to, for example, a simple average. Since individual experimental papers use rather diverse values of other thermodynamic quantities to convert their measurements to the standard form, the procedure in the JANAF tables of analyzing the raw data rather than the final values of the enthalpy of formation ($\Delta H_{298\text{ K}}^0$) is much superior.

In summary, we note that the error in the VQMC cohesive energy of silicon (0.19 eV/atom) of Fahy, Wang, and Louie is outside the error bars, though better than the error in the local-density approximation cohesive energy (0.6 eV/atom) that they present for comparison.

APPENDIX

This appendix is devoted to the exposition of some basic notions and principles regarding cohesive energies. Although the constituent parts of the material given here are standard, to our knowledge a practical presentation is lacking in the literature. We restrict our considerations to pure crystals.

The cohesive energy of a crystal in a specified thermodynamic condition (referred to as the *standard state*; see below) is[4–6] the difference between the energy of the dispersed gas of its constituent atoms (or molecules) at absolute zero of temperature and the energy of the crystal, again, at absolute zero of temperature. At this temperature enthalpy is equal to the internal energy. This fact establishes the link between the cohesive energy and *enthalpy of formation* (also known as the *heat of sublimation* or *latent heat*), corresponding to the change of zero-temperature enthalpies in the process of forming a crystal out of isolated atoms.

When a pure substance is placed in a vacuum chamber, one can, by changing the temperature, change the state of the system along the sublimation curve in the pressure-temperature (P-T) plane. On this curve the solid coexists in equilibrium with its vapor. The sublimation curve is described mathematically by the Clapeyron equation.[11,12] The enthalpy of formation at temperature T, upon assumption that the vapor can be considered as an ideal gas, can be shown to be equal to $-R \, d \ln P / d(1/T)$, where R is the molar (universal) gas constant. The value 4.55 eV/atom obtained by Batdorf and Smits[9] indeed corresponds to the estimation of the heat of sublimation for silicon in the temperature range 1200 °C–1350 °C.

Since heat of sublimation depends on temperature, knowledge of this quantity at low temperatures requires knowledge of vapor pressures at equally low temperatures. However, at these temperatures, due to the fact that vapor pressures of solids are extremely low, use of the simplified Clapeyron equation is impractical. A way out of this experimental dilemma is offered by the (approximate) Kirchhoff equation,[11] which in combination with Clapeyron's equation gives rise to an expression, say, $f(T)$, which is linear in $1/T$ and whose slope is equal to the heat of sublimation at 0 K times some numerical constant. Hence heat of sublimation at 0 K can be obtained by evaluating $f(T)$ at at least two different temperatures. These temperatures can in principle be chosen arbitrarily; however, since one wishes to measure vapor pressures at rather high temperatures, T's are normally taken to be large. It should be mentioned that due to the fact that one of the contributing terms to $f(T)$ is obtained through integration of a function involving c_p, i.e., the constant-pressure heat capacity of the solid, over the interval $[0, T]$, the latter choice of the T's necessitates knowledge of c_p over a rather large range of temperatures.

At high temperatures vapor pressures are obtained by using, e.g., *Langmuir's evaporation* method or a variation of that, referred to as *Knudsen's effusion* method.[11] In these methods one effectively measures the rate of evaporation of the solid and subsequently obtains the pres-

sure through an approximate expression which establishes a linear relationship between the two quantities. The measurements by Davis, Anthrop, and Searcy[3] referred to in our discussions above are based on the Knudsen effusion method. These authors use high-temperature heat capacity data of Olette (their Ref. 11). Note that at low temperatures c_p of a solid is almost equal to its c_v, and the latter quantity at low temperatures can be accurately described by the Debye T^3 relation.

Thinking of formation of a solid from its constituent atoms as a chemical reaction we realize that in this context "heat of sublimation" is the same thing as "heat of reaction."[13] Using the van't Hoff equation (or the van't Hoff *isobar*), this quantity, at any temperature T, can be shown to be proportional to the derivative with respect to $1/T$ of the logarithm of the equilibrium constant $\mathscr{H}$ at T. In this respect the van't Hoff equation is identical to the simplified Clapeyron equation, $\mathscr{H}$ playing the role of pressure. Determination of the heat of reaction based on the measurements of the equilibrium constant is normally referred to as the "second-law" method.[14] To avoid direct measurements of the low-temperature equilibrium constants, which is as impractical[13] as measurements of the low-temperature equilibrium pressures of the solid gases, one employs here the so-called Nernst equation[13] which in this case is identical to the combined Kirchhoff-Clapeyron equation, giving $f(T)$. Note that the value for $\Delta H^0_{298 \text{ K}} = 4.86 \pm 0.13$ eV/atom given by Zmbov, Ames, and Margrave[10] for silicon has been obtained by the second-law method.

The so-called "third-law" method of determination of $\Delta H^0_{298 \text{ K}}$,[14] on the basis of which Zmbov, Ames, and Margrave obtain $\Delta H^0_{289 \text{ K}} = 4.76 \pm 0.13$ eV/atom (approximately equal to their "best" value), might be considered not only as a method of evaluation of $\Delta H^0_{289 \text{ K}}$ but also as a means of testing the consistency of the thermodynamic data. To clarify this point we need to introduce a number of quantities used in the description of the third-law method. Let $\mathscr{G}(T)$ denote the "Gibbs energy function" defined as $[G^0(T) - H^0_{298.15 \text{ K}}]/T$, in which $G^0(T)$ stands for the standard-state Gibbs free energy. In a chemical reaction, $H^0_{298.15 \text{ K}}$ can be shown to change according to the relation[14] $\Delta H^0_{298.15 \text{ K}} = \Delta G^0(T) - T\Delta \mathscr{G}(T)$, in which the "standard Gibbs-free-energy change" $\Delta G^0(T)$, following the van't Hoff equation, is equal to $-RT \ln \mathscr{H}$. As we observe, in the ideal case, the combination $\Delta G^0(T) - T\Delta \mathscr{G}(T)$ ought to be equal to a constant value $(\Delta H^0_{298.15 \text{ K}})$ for *all* temperatures. This is a rather severe test of the mutual consistency of the experimental data. We observe also that in our case the value of the standard-state enthalpy of formation at $T = 298.15$ K is rather a by-product of such a consistency test. As a matter of fact reasonable agreement between the values for $\Delta H^0_{298.15 \text{ K}}$ obtained by both the second-law and the third-law method should also be considered as a necessary condition for the reliability of the thermodynamic data.

We now explain briefly how cohesive energies can be obtained from thermodynamic tables. As mentioned earlier, enthalpy of formation is a function of temperature. Some sources of thermodynamic data present the *stan-*

dard enthalpy of formation (see below) at only one temperature. This temperature which is called *reference* temperature is commonly chosen to be 298.15 K. In the thermodynamic tables properties of the *standard* states are commonly indicated by the superscript 0. Standard state for crystalline solids (abbreviated by cr) in a well-defined crystallographic modification or liquids (l), is chosen to be that of the pure substance under a pressure of either 101 325 Pa ($= 1$ atm) or 100 000 Pa ($= 1$ bar; more recent tables use 1 bar as standard pressure). For gases (g), the standard state is that of ideal gas at 101 325 or 100 000 Pa.

Knowledge of the standard-state enthalpy of formation at the reference temperature 298.15 K is not sufficient to calculate the cohesive energy. The majority (but not all) of the tables also present $H^0_{298.15\,K} - H^0_{0\,K}$, corresponding to the crystal state, liquid state, or ideal-gas (vapor) state (see, e.g., Ref. 15; the JANAF tables[7] go much further and give $H^0_T - H^0_{298.15\,K}$ for a variety of temperatures). Here H^0_T stands for the (standard-state) enthalpy at temperature T. This is enough to calculate (standard-state) cohesive energies. Let $\Delta_f H^0_T \equiv (H^0_T)_g - (H^0_T)_{cr}$, then for the standard-state cohesive energy $\Delta_f H^0_{0\,K}$ (subscript f stands for *formation* so that $\Delta_f H^0_T$ effectively means standard-state enthalpy of formation of the gas from the crystal, both in their standard states at T) we have[4,16]

$$\Delta_f H^0_{0\,K} = \Delta_f H^0_{298.15\,K}$$
$$+ (H^0_{0\,K} - H^0_{298.15\,K})_g$$
$$- (H^0_{0\,K} - H^0_{298.15\,K})_{cr}. \qquad (A1)$$

As an example let us evaluate the right-hand side of Eq.

(A1) for silicon. To this end we use the data given in the JANAF tables.[7] We note, however, that JANAF is one of the few thermodynamic tables which gives $\Delta_f H^0_{T=0\,K}$ as well, so that in practice we do not really need to do such a calculation if we access to these tables. Here we find $\Delta_f H^0_{298.15\,K} = 450.000$ kJ/mol, $(H^0_{T=0\,K} - H^0_{298.15\,K})_g = -7.550$ kJ/mol, and $(H^0_{T=0\,K} - H^0_{298.15\,K})_{cr} = -3.218$ kJ/mol. Equation (A1) yields $\Delta_f H^0_{T=0\,K} = 445.668$ kJ/mol or simply 4.619 eV/atom.

Finally, we make some comments regarding the values of the phonon zero-point energies (ZPE) which should be subtracted from the computational total energies (which assume stationary ions). Normally, the phonon ZPE at low temperatures is obtained using the simple Debye model which gives[17] a ZPE (per atom) of $9k_B\Theta_D/8$, where Θ_D is the Debye temperature. It has become common practice to consider the Debye temperature as a function of temperature,[18] defined so that the experimental heat capacity at all temperatures is reproduced by the Debye formula. Unlike the heat capacity which for low temperatures is almost entirely determined by the long-wavelength acoustic phonons (excluding cases in which the optical modes are softened), the ZPE involves contributions from all phonon modes. At very high temperatures, the heat capacity involves the zeroth moment of the phonon density of states, so that use of $\Theta_D(T)$, $T \to \infty$, in the above expression guarantees that the zeroth moment of the phonon density of states is exactly described by the Debye model. Though the ZPE involves the *first* moment of the phonon density of states we estimate that the errors in the ZPE obtained by using the Debye model are of the order of 0.01 eV/atom and therefore do not affect our conclusions.

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