Iodine is a covalent crystal

© I.A. Stepanov

Institute of Physical Chemistry, University of Freiburg,
79104 Freiburg, Germany

E-mail: istepanov@email.com

(Received 5 October 2004
Revised 9 December 2004)

Earlier it has been supposed that the lattice energy of iodine is about 70 kJ/mol, therefore, it was considered to be a molecular crystal. In the present paper, it is shown that the lattice energy of iodine is at least 10 times bigger, thus iodine is a covalent crystal. In the previous works the role of fluctuations was not taken into account.

1. Introduction

Earlier it was supposed that in molecular crystals, otherwise called van der Waals crystals, the molecules cohere for the most part by their mutual van der Waals attraction and this attraction is very weak. This was supported by the fact that the measured sublimation energies are approximately equal to the lattice energies calculated using the van der Waals potential [1,2]. Tne sublimation energy of I_2 is equal to 63.7−74.2 kJ/mol [2–4], the calculated one is 71.4−74.2 kJ/mol [3,4]. Iodine was considered to be a molecular crystal.

However, calculation of the lattice energies has one disadvantage: fluctuations are not taken into account. One calculates the energy required to transfer the molecule from its equilibrium position to infinity, practically to $r_{\max}$. Due to fluctuations, the molecule will rupture the intermolecular bond earlier than at $r_{\max}$. How much earlier?

2. Theory

In physics of strength of solids it is proven long ago that more than 90% of the energy required to break the interatomic bond is provided by fluctuation and the role of the external stretching force is less than 10%. It has been proven in the works of S.N. Zhurkov and his workers [5–8] and references therein. If to decrease the depth of the potential well slightly, the probability of the rupture fluctuation increases dozen times because this probability depends exponentially on the depth U and temperature: $\exp(-U/kT)$. Max Born calculated the energy of chemical bond in crystal (without taking fluctuations into account) and multiplied by the number of molecules. The strength of a solid obtained like this is called the theoretical strength of a solid. The actual strength of solids is much less (by 1 to 2 orders of magnitude) than that theoretical one predicted by crystal lattice theory [5,6]. The physics of strength approach is justified in this paper because the mechanical failure energy U_0 is found to coincide with the sublimation energy Q, i.e., the interatomic binding energy [5,6], (see Table).

In [6] it was obtained that the breaking strength of a body under load is

$$\sigma_* = E\varepsilon_* - \alpha ET/3 \cdot \ln \tau/\tau_0, \qquad (1)$$

where E is Young's modulus, α is the thermal expansion coefficient of the surface of the solid (it is several times greater than the bulk value [6]), T is temperature, ε_* is the relative elongation at which the interatomic bond becomes unstable and breaks, τ is the lifetime (i.e., the time during which the load is withstood), τ_0 is the period of thermal oscillations of atoms. Experimental and theoretical estimates of the breaking strain of the interatomic bond give $\varepsilon_* \approx 0.2$ [6].

From Eq. (1) it is clear that the actual breaking strength consists of an athermal component $\sigma_0 = E\varepsilon_*$ and a component $\sigma_{T,\tau} = \alpha ET/3 \cdot \ln \tau/\tau_0$ which depends on temperature and time. The athermal component is seen to be equal to the theoretical strength. The other component is responsible for the temperature and time dependence of the strength. One can interpret $\sigma_{T,\tau}$ as the local pressure due to anharmonically vibrating atoms. This fluctuating thermal pressure stretches the interatomic bonds and contributes to their deformation and rupture caused by the external load. An estimate of the thermal fluctuation stress $\sigma_{T,\tau}$ shows that it is large [5,6]. For instance, the theoretical strength of aluminum is 10^7 kPa, the thermal fluctuation stress $\sigma_{T,\tau} = 9.9 \cdot 10^6$ kPa, the actual strength $\sigma_* = 10^5$ kPa. Therefore, according to physics of strength, interatomic bond failure occurs when the bond is stretched by an external force and thermal fluctuation causes it to rupture.

To sublimate a crystal, one has to introduce a quantity of heat into it. The intermolecular distances increase but the

The mechanical failure energy U_0 and the sublimation energy Q for some substances [5,6]

Substance	U_0, kJ/mol	Q, kJ/mol
Zn	125	130
Al	217	230
Ag	259	284
Cu	326	334
Mo	752	669
Fe (steel-3)	418	405

intermolecular bonds failure is caused by fluctuations. This quantity of heat is about 63.7−74.2 kJ/mol but the theoretical energy of intermolecular bonds is more than 10 times higher, i. e. greater than 640−740 kJ/mol. The cohesive energy of molecular crystals is of the order 0.1 eV/molecule, and that of covalent solids is of the order 10 eV/atom [1]. The quantity 64−74 kJ/mol is about 0.7−0.8 eV/molecule, so the energy of intermolecular bonds of iodine is greater than 7−8 eV/molecule. In [6] an interesting result has been obtained

$$Q = U_0 = \varepsilon_* C/\alpha, \qquad (2)$$

where C is the atomic specific heat.

In iodine the first and the second next neighbour distances are 3.50 and 3.93 Å [9]. They are noticeably less than the double van der Waals radius 4.3 Å [9] (the distance between the atoms in the molecule is 2.72 Å) and the second next neighbour distance in the van der Waals crystal which is about 4.6 Å. It is because there is covalent intermolecular interaction [4,10–14]. This interaction is strong, about 40% of the energy of dissociation of the molecules [4]. So, one can make a conclusion: the good agreement between the experimental and calculated sublimation energies of iodine is just an accident or a correlation.

Really, the previous point of view was suspicious: the covalent forces play a big role in interaction between molecules but the cohesive energy of the crystal is so weak as the van der Waals one. Iodine crystals, although molecular, show interesting semiconducting properties and it was found that the phenomenological behaviour of iodine is not fundamentally different from other covalent or ionic crystals [15]. One can strongly suggest that iodine is a covalent crystal.

References

[1] J.M. Ziman. Principles of Solid State Theory. Cambridge University Press, Cambridge (1971). P. 110–111.
[2] K. Yamasaki. J. Phys. Soc. Jap. **17**, 1262 (1962).
[3] F. Vovelle, G.C. Dumas. Molec. Phys. **34**, 1661 (1977).
[4] H.G. Drickamer, R.W. Lynch, R.L. Clendenen, E.A. Perez-Albuerne. Sol. State Phys. **19**, 135 (1966).
[5] R.V. Regel, A.I. Slutsker, E.E. Tomashevskii. Kinetic Nature of the Strength of Solids. Nauka, Moskow (1974).
[6] S.N. Zhurkov. Fiz. Tverd. Tela **22**, 3344 (1980).
[7] I.A. Stepanov. Fiziko-Khim. Mekh. Mater. **31**, 36 (1995).
[8] I.A. Stepanov, J. Macromol. Sci. Phys. B **36**, 117 (1997).
[9] F. van Bolhuis, P.B. Koster, T. Migchelsen. Acta Cryst. **23**, 90 (1967).
[10] B.V. Shanabrook, J.S. Lannin. Solid Stat. Commun. **38**, 49 (1981).
[11] B.V. Shanabrook, J.S. Lannin, J.S. Hisatsune. Phys. Rev. Lett. **46**, 130 (1981).
[12] N. Orita, K. Niizeki, K. Shindo, H. Tanaka. J. Phys. Soc. Jap. **61**, 4502 (1992).
[13] T. Itoh, K. Kambe. J. Phys. Soc. Jap. **12**, 763 (1957).
[14] H.A. Bent. Chem. Rev. **68**, 587 (1968).
[15] A.A. Braner, R. Chen. J. Phys. Chem. Solids **24**, 135 (1963).