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Compressibility and Polymorphism of Solids

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1. Atomistic formulation of compressibility Study of structural modifications of solids under high pressure, from an atomistic point of view, may start with an atomistic examination of compressibility.

The physical definition of cubic compressibility under zero pressure (initial compressibility) at a fixed temperature T , in general, is given by

$$(\alpha_0)_T = -\left(\frac{1}{V_0}\right)_T \left(\frac{dV}{dP}\right)_T, \quad (1)$$

where V_0 is the volume of a certain quantity of a substance under zero pressure, α_0 has the dimension of cm^2/dyn or cm^3/erg . Its reciprocal, the compression modulus thus defines a volumetric energy (erg/cm^3) which may be conceived as the resistance of a solid against pressure, or simply as its "compressive resistance".

When the relation between r_0^3 and α_0 is examined graphically, we observe (Fig. 1) that straight line relationships are obtained when we differentiate on the basis of valency. This result shows that the effective valency, rather than the structure type, gives rise to the various curves.

If, however, the compressibility data are plotted vs. r_0^3/Z , we obtain a uniform straight-line-relationship (Fig. 2), which may here be expressed by the bulk modulus as

$$K = \frac{1}{\alpha_0} = A \left(\frac{Z}{r_0^3} \right). \quad (2)$$

The factor, A , has the dimension of an energy (erg). It can be shown by means of equation (2), for the 60 solids considered here, that the factor A has a value of 5.4×10^{-12} erg, with an average error of $\pm 5\%$. This value is of particular interest, since it equals the stationary energy of an electron in the L-orbital, corresponding

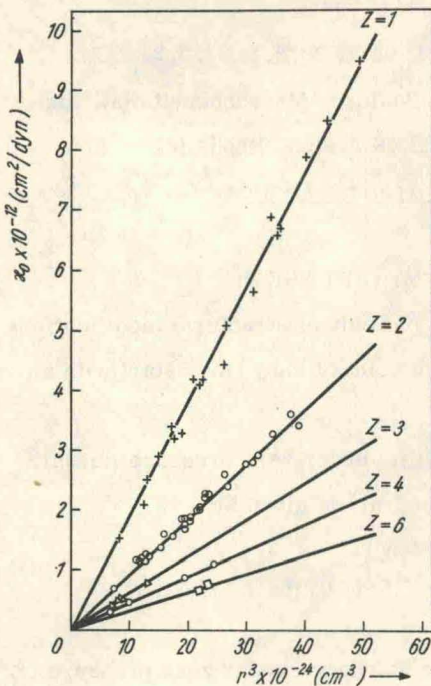


Fig. 1

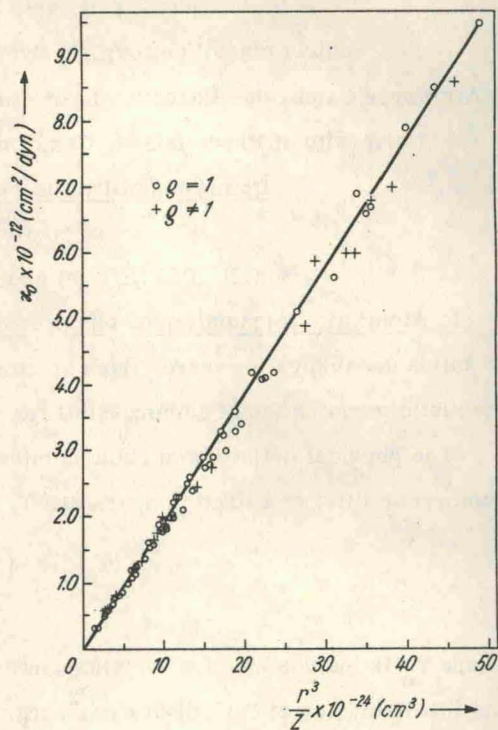


Fig. 2

Fig. 1. Compressibility vs. r_0^3 for compounds with valencies from one through six

Fig. 2. Compressibility vs. r_0^3/Z for compounds with $\rho = 1$ (o) and $\rho \neq 1$ (+). For further details see text

to the principal quantum number $n = 2$, according to Niels Bohr. Equating the constant in equation (2) with E_B ,

$$K = \frac{1}{\alpha_0} = - \frac{ZE_B}{r_0^3} \text{ (erg/cm}^3\text{)}, \quad (3)$$

where

$$-E_B = \frac{2\pi^2 e^4 m_0}{n^2 h^2} = 5.448 \times 10^{-12} \text{ erg}$$

Table 1

Data used for the substantiation of the introduction of the factor $\rho = CN/CN_0 \neq 1$

No.	Substance	Structure	$\alpha_0 (10^{-12} \text{ cm}^2/\text{dyn})$	
			Calculated	Experimental
1	KCl (5)	Rocksalt	5.69	5.63
1A	KCl (6)	Cesium-chloride	4.0 4.0	4.0 3.8
2	KBr (6)	Rocksalt	6.53	6.7
2A	KBr (6)	Cesium-chloride	4.7	4.8
3	RbCl (6)	Rocksalt	6.42	6.6
3A	RbCl (6)	Cesium-chloride	5.3	4.9
4	RbI (6)	Rocksalt	9.0	9.5
4A	RbI (6)	Cesium-chloride	7.3	7.1
5	Graphite (7)	Graphite	0.23	0.25
5A	Diamond	Diamond	0.17	0.17
6	Sn(grey) (8, 9)	Diamond	2.0	1.9
6A	Sn(white) (8, 9)	White tin	1.8	1.7
7	InSb (10)	Zincblende	2.00	2.0
7A	InSb (10)	White tin	1.70	1.70

(m_0 mass of electron, e charge of electron, h Planck's constant). Equation (3) represents an atomistic formulation of the bulk modulus of solids.

The atomistic expression of the bulk modulus given by equation (3) is interesting, not so much because of the vast majority of solids that obey it, but, more so, for the fact that a respectable minority of solids do not obey it without the introduction of an additional factor ρ . The meaning of factor ρ becomes apparent, when we study some solids of which complete data are available for polymorphic states with different atomic coordination before and after a pressure transition, see Table 1.

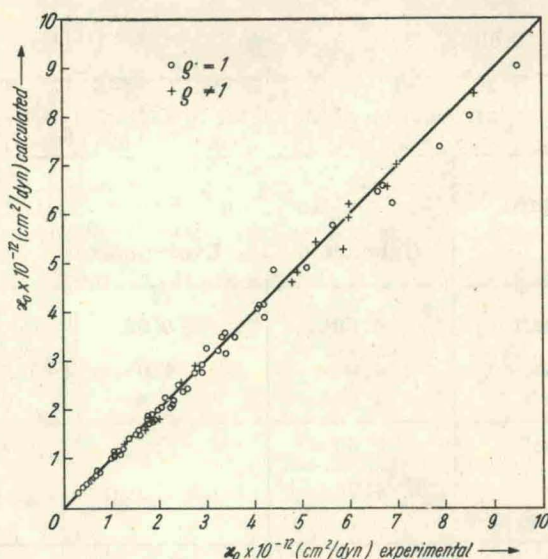


Fig. 3. Linear plot of values of compressibility calculated by the method proposed in this paper vs. experimental values

The data indicate that the ratio between the first order coordination numbers of two successive modifications is proportional to the ratio between the corresponding $r_o^3/Z\alpha_o$ values.

The largest series of those deviating solids, on which per-

tinent data are on hand, are the ones which normally crystallize in the cesium chloride structure. It is a well established fact that these solids have lower values of compressibility as compared to the related solids of the rocksalt structure, when both have approximately equal molecular weight (2). Moreover, many solids of the cesium chloride structure change to the rocksalt structure at higher temperatures, thus indicating that the disorder created with increasing temperature opens the structure and thus lowers the atomic coordination. Vice versa, related solids, which basically have the rocksalt structure, assume the cesium chloride structure at high pressures (3) or at low temperatures, thus indicating a tightening of the structure (Buerger's rule (4)). Equation (3) may now be extended to

$$K = \frac{1}{(\alpha_o)_T} = - \left(\frac{\rho Z E_B}{r_o^3} \right)_T \quad (\text{dyn/cm}^2 \text{ or erg/cm}^3), \quad (4)$$

Further justification for the use of the factor ρ may be obtained by comparing the calculated and experimental values of compressibility for solids for which $\rho \neq 1$. The agreement is found to be very good. The quantity $Z_a = \rho Z$, the "apparent valency", may or may not be an integer. It thus becomes natural to refer to a polymorphic structure of a chemical species as its "basic" structure, when equation (4) becomes satisfied for $\rho = 1$. Analogously, the structure becomes "elevated" for

values of $q > 1$, and "reduced" when $q < 1$. At 273 °K and one atmosphere, materials have their structures in one of three states. An increase of pressure induces transitions either from "reduced" states to "basic" states, or from "basic" states to "elevated" states, with temperature having the opposite effect. A substance occurring in the "reduced" state at ambient conditions is thus more likely to show transitions as a function of pressure than temperature. Structures in "elevated" or "basic" states at ambient conditions may become "reduced", except when a complete change of state (liquification or sublimation) provides a more proficient way of lowering the free energy of the system.

The final results for some 90 solids, representing all the states, are plotted as experimental vs. the proposed calculated values in Fig. 3. These solids represent binary, ternary, and quaternary compounds of about twenty-five differing structural types and valencies ranging from one through six.

A more complete account, including all physical data and references used, may be obtained in report form from the authors.

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