Relations between the cohesive energy, atomic volume, bulk modulus and sound velocity in metals

S Wacke¹, T Górecki², Cz Górecki¹, K Książek²

¹Department of Physics, Opole University of Technology, 75 Olimska str., 45-370 Opole, Poland
²Department of Physics, Opole University, 48 Oleska str., 45-052 Opole, Poland

e-mail: kasiak@uni.opole.pl

Abstract: By analysing the experimental data available in the literature, it has been found that the bulk modulus $B$ of metals is proportional to the cohesive energy density $E_c/V$. For metals which start to melt having the close packed structure A1 or A3 the proportionality factor in the aforementioned correlation is distinctly greater than that for metals melting from the A2 type structure. The existence of the correlation between the bulk modulus and the cohesive energy density leads to another, hitherto unrevealed correlation between the sound velocity, cohesive energy and the molar mass of metals: $u^2 \sim E_c/\mu$.

1. Introduction

The cohesive energy as well as the compressibility, or its reciprocal – bulk modulus, are important quantities determining the stability and other physical properties of condensed phases of substances. In the past several authors attempted to develop, both theoretically and semiempirically, formulas relating the cohesive energy and bulk modulus to various physical properties of solids, such as the melting temperature, atomic volume, lattice constants, vacancy formation energy, Debye temperature, valence of constituent atoms, etc. Attempts to find correlation between the cohesive energy and bulk modulus have been made, too [1-3]. All of the above mentioned relationships are, as a rule, restricted to some groups of substances of similar structure, bond type or other physicochemical property. A closer examination of these relationships suggests, that instead of searching for a direct relationships between the bulk modulus and the cohesive energy one should look for the relation between the bulk modulus and the volume density of the cohesive energy.

Cohesive energy density, defined as the ratio of the atomic energy of cohesion $E_a$, to the atomic volume $V$, may be expressed in units J/m³, or, equivalently, in the pressure units – Pa. It has the meaning of some internal pressure preventing the atomization of the condensed phase.

The bulk modulus $B$ (reciprocal of compressibility) of condensed phases defines their resistance against hydrostatic compression. At fixed temperature $T$, it is defined by the relation

$$B_T = -V_T \frac{dV}{dp}_T$$

where $V_T$ is the volume at temperature $T$. Its value may be expressed in units of pressure (N/m² = Pa) or in J/m³. So, the bulk modulus defines the volumetric energy density connected with the compression work.
The available literature data, give, as a rule, the values of $B$ determined at room temperature and under atmospheric pressure. In principle, when comparing the values of $B$ and $E_c$ for different substances, these values should be reduced to the temperature corresponding to the thermodynamically equivalent states, e.g. to the melting point, or to the absolute zero. Unfortunately, such reduction is often impossible because of the lack of appropriate data.

By changing the interionic or intermolecular distances, the compression work changes both the energy of their interaction (cohesion) as well as the volume of compressed material, consequently changing the cohesive energy density. So, intuitively, the bulk modulus should be related to the cohesive energy density. The purpose of the present study is to check this supposition.

2. Results and discussion

The available in the literature experimentally determined values of the bulk modulus $B$ [4,5,10], cohesive energy (per atom) $E_c$ [6] and of the atomic volume $V$ [6] of 31 metals are collected in Table 1. On this basis the cohesive energy density $E_c/V$ has been calculated and plotted against the values of bulk modulus of corresponding metals (Fig. 1).

At a first glance the distribution of experimental data points seems to confirm the prediction about the linear relationship between $E_c/V$ and $B$ – as a rule the metals with higher energy density are characterized by higher values of the bulk modulus. The scatter of the data points is, however, very large, and an attempt to fit them by a straight line gives a very unsatisfying result with a low value of the correlation factor $R = 0.85$.

A more detailed inspection of figure 1 revealed that there are two groups of data points scattered along two different straight lines. The first of them includes the first 15 metals (Cu – Os) listed in Table 1. The common feature of these metals is the close packed crystallographic structure (A1 or A3) in the whole temperature interval, ranging from absolute zero up to the melting point. The experimental data for these metals are well fitted with straight line described by relation

$$B = (4.068 \pm 0.193) E_c/V $$

(1)

The correlation factor for this empirical correlation is $R = 0.947$, and the relative standard deviation amounts 4.7%.

The second group of metals (last 16 in Table 1, Ca – Yb) consists of elements showing the temperature – induced polymorphism. Under normal pressure all of them display a body centered cubic structure (A2) just below the melting point. For these metals the relation between the bulk modulus $B$ and the cohesive energy density can be expressed by empirical relation

$$B = (2.010 \pm 0.116) E_c/V$$

(2)

with a correlation factor $R = 0.914$, and the relative standard deviation amounts 5.8%.

The revealed relationships between the cohesive energy density and bulk modulus open new possibilities for searching for other correlations between various properties of condensed phases, often very important both for pure science and applications.

For example, as the sound velocity $u$ is related to the bulk modulus $B$ and mass density $\rho$ by equation

$$u = f \sqrt{\frac{B}{\rho}}$$

(3)

where $f$ is a constant proportionality factor then, from relations (1) or (2) it simply follows that

$$u^2 = c \frac{E_c}{\mu}$$

(4)
were $\mu$ is the molar mass, and $c$ – proportionality factor, the same for a given group of metals. The term $E_c/\mu$ on the right side of equation (4) has dimensions m$^2$/s$^2$ and has the meaning of the mass density of cohesive energy.

Table 1 Experimental data on the molar mass $\mu$, atomic volume $V$, cohesive energy $E_c$ and sound velocity $u$ of metals

| Metals | $\mu$ [g/mole] | $V \cdot 10^3$ [nm$^3$] | $E_c$ [eV] | $E_c/V$ [GPa] | $B$ [GPa] | $E_c/\mu \cdot 10^6$ [m$^2$/s$^2$] | $u$ [m/s] |
|--------|----------------|------------------------|----------|--------------|--------|---------------------------------|--------|
| Cu     | 63.55          | 11.81                  | 3.49     | 47.28        | 142    | 5.30                            | 4880   |
| Ag     | 107.87         | 17.06                  | 2.96     | 27.76        | 102    | 2.64                            | 3830   |
| Au     | 196.97         | 16.96                  | 3.78     | 35.66        | 170.8  | 1.85                            | 3361   |
| Pb     | 207.2          | 30.33                  | 2.04     | 10.76        | 40.4   | 0.95                            | 2300   |
| Ni     | 58.69          | 10.94                  | 4.43     | 64.79        | 190    | 7.29                            | 5894   |
| Rh     | 102.91         | 13.77                  | 5.75     | 66.81        | 287    | 5.38                            | 6194   |
| Pd     | 106.42         | 14.72                  | 3.94     | 42.83        | 184.4  | 3.57                            | 4630   |
| Ir     | 192.22         | 14.14                  | 6.93     | 78.42        | 370    | 3.47                            | 5379   |
| Pt     | 195.08         | 15.10                  | 5.85     | 61.99        | 274.7  | 2.89                            | 4075   |
| Mg     | 24.31          | 23.23                  | 1.53     | 10.54        | 34.5   | 6.06                            | 5898   |
| Zn     | 65.38          | 15.24                  | 1.35     | 14.17        | 61.7   | 1.99                            | 4170   |
| Cd     | 112.41         | 21.58                  | 1.16     | 8.60         | 47.7   | 0.99                            | 2780   |
| Co     | 58.93          | 11.13                  | 4.39     | 63.11        | 167.1  | 7.18                            | 5827   |
| Ru     | 101.07         | 13.57                  | 6.62     | 78.05        | 327.1  | 6.31                            | 6534   |
| Os     | 190.23         | 13.99                  | 8.10     | 92.64        | 426    | 4.10                            | 5478   |
| Ca     | 40.08          | 43.48                  | 1.83     | 6.73         | 18.26  | 4.40                            | 4176   |
| Sr     | 87.62          | 56.32                  | 1.70     | 4.83         | 12.1   | 1.87                            | 2782   |
| Ce     | 140.12         | 34.37                  | 4.77     | 22.21        | 19.8   | 3.28                            | 2300   |
| Ti     | 47.87          | 17.65                  | 4.86     | 44.06        | 88.6   | 9.78                            | 6263   |
| Zr     | 91.224         | 23.27                  | 6.32     | 43.46        | 75.6   | 6.67                            | 4359   |
| Hf     | 178.49         | 22.16                  | 6.35     | 45.85        | 109    | 3.43                            | 3671   |
| Y      | 88.91          | 33.01                  | 4.39     | 21.28        | 49.2   | 4.76                            | 4217   |
| La     | 138.91         | 37.12                  | 4.49     | 19.35        | 26.8   | 3.11                            | 2772   |
| Pr     | 140.91         | 34.15                  | 3.9      | 18.27        | 25.5   | 2.67                            | 2660   |
| Nd     | 144.24         | 34.18                  | 3.35     | 15.68        | 29.2   | 2.24                            | 2718   |
| Sm     | 150.36         | 33.01                  | 2.11     | 10.23        | 29.98  | 1.35                            | 2702   |
| Tb     | 158.93         | 31.14                  | 4.1      | 21.07        | 40.7   | 2.48                            | 2920   |
| Dy     | 162.50         | 31.52                  | 3.1      | 15.74        | 43.3   | 1.84                            | 2958   |
| Ho     | 164.93         | 31.12                  | 3.0      | 15.42        | 40.8   | 1.75                            | 3039   |
| Er     | 167.26         | 30.64                  | 3.3      | 17.23        | 47.4   | 1.90                            | 3082   |
| Yb     | 173.05         | 30.02                  | 1.6      | 18.53        | 13.53  | 0.89                            | 1820   |
Figure 1. Linear correlation between the experimental data on the bulk modulus $B$ and cohesive energy density $E_c/V$. - structure A1 or A3, ▲ - structure A2, at the melting point.

Figure 2. Linear correlation between the experimental data on the squared sound velocity $u^2$ of metals and their mass density of the cohesive energy, $E_c/\mu$. - structure A1 or A3, ▲ - structure A2, at the melting point.

In order to check the validity of equation (4), in Table 1 the experimental data on the sound velocity $u$ [7,8,9] are collected together with the values of their molar masses. On this basis the plot of the mass energy density $E_c/\mu$ versus the squared value $u^2$ of the sound velocity has been prepared (Fig. 2). Similarly as in Fig. 1, the experimental data points in Fig. 2 are scattered along two different straight lines. The data for metals melting from the close packed structure A1 or A3, are well fitted by a straight line described by relation
The correlation factor for this empirical correlation is \( R = 0.905 \), and the relative standard deviation amounts 5.3\%.

For metals showing the temperature – induced polymorphism and melting from the body centered cubic structure (A2), the relation between the squared sound velocity \( u^2 \) and the mass density of cohesive energy \( E_c/\mu \) is well fitted by a straight line described by relation:

\[
u^2 = (5.796 \pm 0.309) E_c / \mu \tag{5}\]

The correlation factor for this empirical correlation is \( R = 0.938 \), and the relative standard deviation amounts 5.3\%.

The existence of the relationships presented in the present communication suggests that similar relationships should be valid for other classes of substances, with other nature of the interionic or intermolecular bonds (e.g. condensed rare gases and covalently bonded solids).

As the values of the bulk modulus are related with other elastic moduli (shear modulus, Young modulus) [4], the values of the two later moduli should be also simply related to the volumetric energy density \( E_c/V \), and the squared values of the longitudinal and transversal sound velocities in solids should correlate with the mass density of the cohesive energy, \( E_c/\mu \). The search for such correlations will be continued.

References

[1] Plendl J M Gielisse J M 1969 Compressibility and polymorphism of solids (Office of Aerospace Research, Bedford MA)

[2] Srivastava G P Weaire D 1987 The theory of the cohesive energies of solids Advances in Physics 36 463-517

[3] Plendl J M Mitra S S Gielisse P J 1965 Compressibility, cohesive energy, and hardness of non-metallic solids

[4] Górecki T 1980 The relations between the shear modulus, the bulk modulus and Young’s modulus for polycrystalline metallic elements Materials Science and Engineering 43 225-230

[5] Bernsztejn M L Zajmowskij W A 1973 Struktura i własności mechaniczne metali (Wydawnictwo Naukowo-Techniczne, Warszawa)

[6] Górecki T 1979 Vacancies and generalized melting curve of metals High Temperatures-High Pressures 11 683-692

[7] Shaikhiev G F Sulaimanova A S 1981 Rascet skorosti ultrazvuka v prostykh veshchestvakh po termiceskim konstantam Zhurnal Fizicheskoi Khimii 55 3024-26

[8] Shaikhiev G F Sulaimanova A S 1981 Temperaturnaia zavisimost skorosti ultrazvuka prostykh veshchestev v tverdom I zhidkom sostoianiyakh Zhurnal Fizicheskoi Kimii 55 2584-88

[9] Shaikhiev G A Sulaimanova A S 1981 Vzaimosviaz skachkov entropii i skorosti ultrazvuka v tocke plavlenia Zhurnal Fizicheskoi Khimii 55 2251-2256

[10] Kikoin I K 1976 Tablicy Fizicheskikh Velichin. Spravoenik (Atomizdat, Moscow)