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RELATIONS BETWEEN THE COHESIVE ENERGY, MOLAR VOLUME, BULK MODULUS, AND SOUND VELOCITY IN ALKALI HALIDES

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Attention is drawn to the existence of hitherto unnoticed simple linear correlation between the cohesive energy density (internal pressure, E_c/V, where E_c is the molar bonding energy, and V - molar volume) and the bulk modulus B. By analyzing the experimental data available in the literature, it has been found that for alkali halides:

$$B = k\frac{E_c}{V}$$

were k is a proportionality factor, the same for all the alkali halides.

The existence of this correlation leads to others, hitherto unrevealed relations between the cohesive energy, E_c, and different physical properties of condensed phases. For example, as the sound velocity u in liquids is related to the bulk modulus B and the mass density, ρ, by

$$u^2 = \frac{B}{\rho}$$

the two relations above lead to:

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

where μ is the molar mass, and c – proportionality factor. Experimental data available in the literature confirm the validity of this relation.

Other consequencies of the revealed relations are also discussed.

Key words: cohesive energy density, bulk modulus, sound velocity, alkali halides.

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 develope, 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 molar energy of cohesion E_c, to the molar volume V, may be expressed in units J/m^3, 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

$$B_T = -V_T \Big/ \left(\frac{dV}{dp} \right)_T ,$$

were V_T is the volume at temperature T. Its value may be expressed in units of pressure (N/m^2 = Pa) or in J/m^3. 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 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. In order to check this supposition in Table 1 we collected the available literature data on the cohesive energy (per mole) E_c [3-6] of 20 alkali halides. On this basis the cohesive energy density E_c/V has been calculated and plotted against the values of bulk modulus of corresponding salts (fig. 1). As it is seen, the experimental data points on figure 1 are only slightly scattered along the straight line described by equation

$$B = k \frac{E_c}{V} , \tag{1}$$

were k is a constant proportionality factor (k = 0,855±0,025).

Table 1

Experimental data on the molar mass, molar volume, cohesive energy, bulk modulus and sound velocity (liquid state, melting point) of alkali halides.

Halide	Molar mass μ $\left[\frac{\text{g}}{\text{mole}}\right]$	Molar volume V $\left[\frac{\text{cm}^3}{\text{mole}}\right]$	Cohesive energy E_c $\left[\frac{\text{kJ}}{\text{mole}}\right]$	$\frac{E_c}{V}$ [GPa]	Bulk modulus B [GPa]	$\frac{E_c}{\mu}$ $10^{-6}\left[\frac{\text{m}^2}{\text{s}^2}\right]$	Sound Velocity u $\left[\frac{\text{m}}{\text{s}}\right]$
LiCl	42,39	20,48	831,2	40,59	32,88	19,61	2050
NaCl	58,44	26,93	762,9	28,33	23,23	13,05	1756
KCl	74,56	37,66	692,5	18,39	17,40	9,29	1590
RbCl	120,92	43,81	665,6	15,19	15,60	5,50	1280
LiF	25,94	11,28	1012,3	89,76	69,80	39,02	2573
NaF	46,99	18,36	914,1	49,80	46,10	19,45	2082
KF	58,10	23,43	793,7	33,88	30,50	13,66	1835
RbF	104,47	26,99	758,0	28,08	26,20	7,26	1380
CsF	151,90	42,31	740,7	17,51	23,50	4,88	1200
LiBr	86,85	25,10	793,7	31,62	25,67	9,14	1477
NaBr	102,90	32,06	725,3	22,63	19,20	7,05	1340
KBr	119,01	43,28	662,7	15,31	14,80	5,57	1273
RbBr	165,38	49,37	637,6	12,92	13,00	3,86	1112
LiI	133,84	32,97	742,6	22,53	18,83	5,55	1232
NaI	149,89	40,84	681,9	16,70	15,10	4,55	1140
KI	166,01	53,21	626,1	11,77	11,70	3,77	1110
RbI	212,37	59,82	605,9	10,13	11,20	2,85	1007
CsCl	168,36	42,41	669,0	15,78	16,87	3,97	1160
CsBr	212,81	47,93	645,0	13,46	18,00	3,03	1118
CsI	259,81	57,61	612,0	10,62	12,40	2,36	923

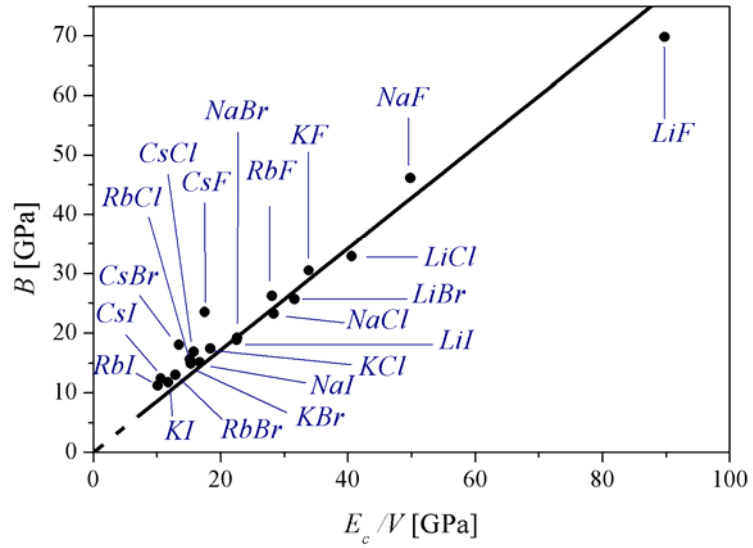

Fig. 1. Linear correlation between the experimental data on the bulk modulus B and cohesive energy density E_c/V

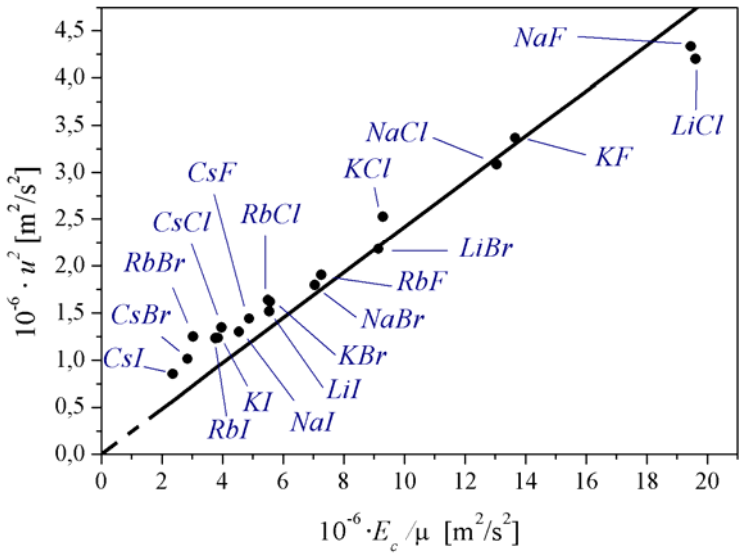

Fig. 2. Linear correlation between the experimental data on the squared sound velocity u^2 of liquid alkali halides at the melting point and their mass density of the cohesive energy at absolute zero, E_c/μ

The standard deviation of the experimental data points from values determined by eq. (1) is 3,54 GPa, and the correlation factor R depicting the quality of revealed relationship is very high – $R = 0{,}9855$. So, the experimental data available in the literature confirm the hypothesis on the existence of the proportionality between the bulk modulus and the cohesive energy density, and the agreement is surprisingly good.

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

For example, as the sound velocity u in the liquid phase is related to the bulk modulus B and mass density ρ by equation

$$u = \sqrt{\frac{B}{\rho}} \tag{2}$$

then, from relation (1) it simply follows that

$$u^2 = c\frac{E_c}{\mu}, \tag{3}$$

were μ is the molar mass, and c – proportionality factor, the same for all the alkali halides. The term E_c/μ on the right side of equation (3) has dimensions m^2/s^2 and has the meaning of the mass density of cohesive energy.

In order to check the validity of equation (3), in Table 1 the experimental data on the sound velocity u of liquid alkali halides at their melting points [5, 7] are collected together with the values of their molar masses. On this basis the plot of the mass energy density E_c/μ versus the squared value u^2 of the sound velocity has been prepared (fig. 2).

The experimental data points on figure 2 are scattered along the straight line predicted by equation (3), with the proportionality factor $c = 0{,}242 \pm 0{,}008$. The correlation factor amounting $R = 0{,}9953$ is very high. So, it may be concluded that the experimental data strongly corroborate the existence of the predicted linear correlation between the squared sound velocity in liquid alkali halides and the mass density of their cohesive energy.

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. metals and condensed rare gases).

As the values of the bulk modulus are related with other elastic moduli (shear modulus, Young modulus) [8], 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/μ. The search for such correlations will be continued.

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СПІВВІДНОШЕННЯ МІЖ ЕНЕРГІЄЮ ЗВ'ЯЗКУ, МОЛЯРНИМ ОБ'ЄМОМ, МОДУЛЕМ ОБ'ЄМНОЇ ДЕФОРМАЦІЇ І ШВИДКОСТІ ЗВУКУ В ЛУЖНИХ ГАЛОГЕНІДАХ

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Розглянуто лінійну кореляцію між енергією зв'язку та модулем об'ємної деформації. Наявність цієї кореляції спричинює невідомі досі лінійні співвідношення між енергією зв'язку та різними фізичними властивостями конденсованих фаз.

Ключові слова: енергія зв'язку, модуль об'ємної гнучкості, звукова швидкість, лужні галогеніди.

СООТНОШЕНИЕ МЕЖДУ ЭНЕРГИЕЙ СВЯЗИ, МОЛЯРНЫМ ОБЪЕМОМ, МОДУЛЕМ ОБЪЕМНОЙ ДЕФОРМАЦИИ И СКОРОСТЬЮ ЗВУКА В ЩЕЛОЧНЫХ ГАЛОГЕНИДАХ

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Рассмотрена линейная корреляция между энергией связи и модулем объемной деформации. Наличие этой корреляции вызывает неизвестные до сих пор линейные соотношения между энергией связи и разными физическими свойствами конденсируемых фаз.

Ключевые слова: энергия связи, модуль объемной гибкости, звуковая скорость, щелочные галогениды.

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