MICROSCOPIC CALCULATION OF THE COMPRESSIBILITY OF HYDRIDES OF ALKALINE METALS

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Isotherms have been constructed and compressibilities and sound velocities have been calculated for the hydrides of alkaline metals on the basis of the functional theory of the local electron density, within the framework of the pseudopotential method. The expression obtained for the electron density distribution allows one to perform the analysis of the character of the binding forces and to determine the dependence of the degree of ionization on pressure in these compounds.

Recently, investigation of the properties of metal hydrides has received great attention. The band theoretical methods [1], as a rule, are too cumbersome to use for the description of thermodynamic properties of such systems. On the other hand, thermodynamic quantities are not very sensitive to the fine features of the electron spectrum [2]. The goal of this work is to calculate the thermodynamic functions of the hydrides of alkaline metals using the microscopic quantum-mechanical approach. There has been a calculation [3] of the binding energy and of the compressibility of these hydrides; however, the approach used in that paper was based on the postulated ionic character of the binding forces in the hydrides of alkaline metals. At the same time, the character of binding forces in these compounds is not obvious [4].

In order to construct a microscopic theory of binding forces and of thermodynamic functions of the hydrides of alkaline metals one can use the results of [5], where a calculation of the total binding energy for crystals with a nonmetallic character of binding forces has been performed. The method is based on a self-consistent solution of the equations of the electron density functional theory of Hohenberg and Kohn (see, for example, [1]). In this approximation, the Schrödinger equation has the form

$$\left[-\frac{1}{2}\Delta+W^{0}(\boldsymbol{r})+W^{scr}(\boldsymbol{r})\right]\psi_{\kappa}(\boldsymbol{r})=E_{\kappa}\psi_{\kappa}(\boldsymbol{r}), \tag{1}$$

where $W^0(r)$ is the unscreened pseudopotential, $W^{scr}(r)$ is the screening potential, which includes the Hartree potential and the exchange-correlation potential; $\psi_{\kappa}(r)$ is the pseudopotential function, E_{κ} is the κ-th energy level. The solution of Eq. (1) is sought in the form of a plane-wave expansion

$$\psi_{\kappa}(\boldsymbol{r})=|\kappa>+\sum_{\boldsymbol{g}}{}' a_{\kappa}(\boldsymbol{g})\,|\kappa+\boldsymbol{g}>. \tag{2}$$

Here, $|\kappa>=1/\Omega^{1/2}\exp(i\kappa\boldsymbol{r})$ is a plane wave. In [5], "effective matrix elements" were introduced, which can be expressed through coefficients $a_k(\boldsymbol{g})$ and are determined from the following system of equations:

$$\tilde{W}_{\kappa}(\boldsymbol{g})=W(\boldsymbol{g})+\sum_{\boldsymbol{g}'\neq\boldsymbol{g}}{}'\frac{\tilde{W}_{\kappa}(\boldsymbol{g}')\,W(\boldsymbol{g}-\boldsymbol{g}')}{E_{\kappa}-E^{0}_{\boldsymbol{g}+\kappa}}, \tag{3}$$

where $W(\boldsymbol{g})=<\kappa+\boldsymbol{g}|W(\boldsymbol{r})|\kappa>$ is the matrix element of the screened potential, $\tilde{W}_{\kappa}(\boldsymbol{g})=(E_{\kappa}-E^{0}_{\boldsymbol{g}-\kappa})\,a_{\kappa}(\boldsymbol{g})$ is the energy-dependent "effective matrix element." With the help of "effective matrix elements" the expressions for the wave function and the κ-th energy level can be written in the form

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$$\psi_{\kappa}(r) = |\kappa> + \sum_{g}{}' \frac{\tilde{W}_{\kappa}(g)\,|\kappa + g>}{E_{\kappa} - E^{0}_{g+\kappa}}, \tag{4}$$

$$E_{\kappa} = E^{0}_{\kappa} + \sum_{g}{}' \frac{\tilde{W}_{\kappa}(g)\; W^{*}(g)}{E_{\kappa} - E^{0}_{g+\kappa}}. \tag{5}$$

As is seen from Eqs. (3)-(5), the main difficulty in determining the wave function and the electron energy is due to the nonlocal character of "effective matrix elements." In order to avoid this difficulty one can average these equations over κ by introducing instead of $\tilde{W}_{\kappa}(g)$ the quantity $\tilde{W}(g)$, which is independent of κ and is determined from the following system of equations

$$\tilde{W}(g) = W(g) + \sum_{g' \neq g}{}' \tilde{W}(g')\, W(g - g')\, F(g'), \tag{6}$$

where $F(g) = < (E_{\kappa} - E^{0}_{g+\kappa})^{-1} >$ is the average value of the energy denominator in the band occupied by electrons. In this case, expressions for the band structure energy and the Fourier components of the density distribution of conduction electrons can be written in the form

$$E_{e} = \sum_{\kappa} (E_{\kappa} - E^{0}_{\kappa}) = \sum_{g}{}' \tilde{W}(g)\, W^{*}(g)\, F(g), \tag{7}$$

$$\rho(g) = \begin{cases} Z/\Omega_{0}, & g = 0 \\ (Z/\Omega_{0})\, C^{2}\Big[2\,\mathrm{Re}\,\tilde{W}(g)\, F(g) + \sum\limits_{g' \neq g}{}' \tilde{W}(g - g')\, W^{*}(g') \times \\ \qquad \times \Phi(g - g',\, g')\Big], & g \neq 0, \end{cases} \tag{8}$$

where Z is the valence; Ω_0 is the volume per ion; C is the normalization constant, which is determined from the condition that the number of particles in the system be conserved

$$C^{2} = \Big[1 + \sum_{g}{}' |\tilde{W}(g)|^{2}\, \Phi(g, g)\Big]^{-1}, \tag{9}$$

$\Phi(g, g') = < [(E_{\kappa} - E^{0}_{g+\kappa})(E_{\kappa} - E^{0}_{g'+\kappa})]^{-1} >$. Expressions for the functions $F(g)$ and $\Phi(g, g')$, as well as the procedure for a self-consistent nonlinear screening of the matrix elements of the pseudopotential, can be found in [5]. Within the framework of the method described above, the total binding energy of a crystal may be represented in the form

$$E = E_{es} + E_{c} + E_{el}, \tag{10}$$

where E_{es} is the energy of the ion electrostatic interaction, calculated using the Ewald–Fuks method; E_c is the band structure energy given by Eq. (7); E_{el} is the energy of the electron subsystem of the crystal

$$E_{el} = E_{0} \sum_{\kappa} < \kappa |\, W(r)\, | \kappa > + E^{0}_{xc} + \Delta E_{xs} - E_{ee}. \tag{11}$$

Here, $E_0 = (3\,10)\, Ze^{2}\kappa_{f}^{2}$ is the average kinetic energy of electrons; κ_f is the Fermi wave vector; e is the electron charge. The second term is the average value of the electron–phonon interaction

$$\sum_{\kappa} < \kappa |\, W(r)\, | \kappa > = Z \lim_{g \to 0} \Big[W^{0}(g) + \frac{4\pi e^{2}}{\Omega_{0} g^{2}} \Big], \tag{12}$$

where $W^{0}(g)$ is the unscreened matrix element of the pseudopotential. E^{0}_{xc} is the exchange-correlation energy of the homogeneous electron gas [6]

$$E^{0}_{xc} = Ze^{2}\,[-\,0.458\, r_{s} - 0.0575 + 0.0155 \ln(r_{s})]. \tag{13}$$

TABLE 1

	Li	Na	K	Rb	Cs
a	6,075	3.362	2,671	2,312	2.214
r_c	0,363	0,487	0,689	0,775	0,871
E_{exp}, J/mole	—0,714	—0,606	—0,510	—0,484	—0,451
E, J/mole	—0,670	—0,603	—0,512	—0,480	—0,453

TABLE 2

	LiH	NaH	KH	RbH	CsH
$\varkappa_{\text{exp}}$, N/m$^2\cdot10^{-10}$	3,472	—	—	—	—
$\varkappa^{[3]}$, N/m$^2\cdot10^{-10}$	3,436	2.288	1,479	1.294	1.156
$\varkappa$, N/m$^2\cdot10^{-10}$	4.348	3,040	1,618	1,311	1,030
v_s, m/sec$\cdot10^{-3}$	9,234	4,875	3,681	2,471	1,972

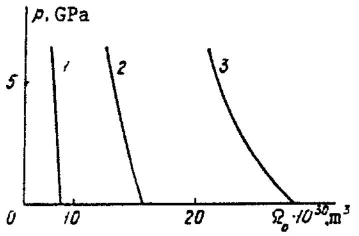

Fig. 1

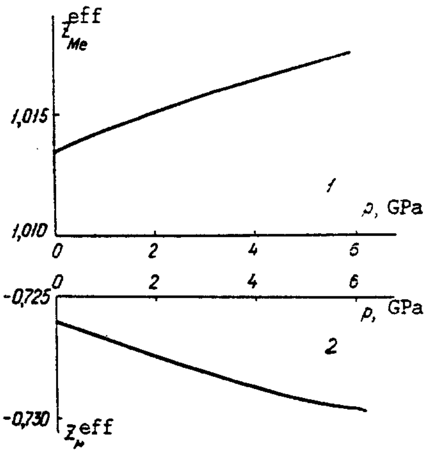

Fig. 2

Fig. 1. Isotherms for the hydrides of lithium (curve 1), sodium (curve 2), and potassium (curve 3) at T = 0 K.

Fig. 2. Pressure dependence of the effective charges of sodium and hydrogen ions in NaH compound: curve 1 is for sodium ion, curve 2 is for hydrogen ion.

where $r_s = (3\Omega_0/4\pi Z)^{1/3}$. ΔE_{xc} is the exchange-correlation energy of the inhomogeneous component of the electron distribution [5]; E_{ee} is the electron—electron interaction energy, which is taken into account twice in Eq. (7), and therefore must be subtracted from the total binding energy

$$E_{ee} = \frac{\Omega_0}{2} {\sum_g}' \frac{4\pi}{g^2} |\rho(g)|^2. \tag{14}$$

In calculating isotherms of the hydrides of alkaline metals the following equation of state for the crystal was solved

$$\left(\frac{\partial E}{\partial \Omega}\right)_S = -p, \tag{15}$$

from which the equilibrium value of the volume for a given pressure was found. The results of these calculations are presented in Fig. 1. Pseudopotentials from [7] were used as pseudopotentials for alkaline metals; furthermore, their parameters were matched beforehand to the equilibrium condition (15) with p = 0, and the energy was calculated using formula (10). Results of these calculations are presented in Table 1, where calculated and experimental values of the total binding energy of these metals are also given. It is seen from Table 1 that the calculated values and the results of experiment are in very good agreement, which is evidence supporting the use of the pseudopotential method for calculating thermodynamic characteristics of alkaline metals. It is seen from Fig. 1, where isotherms of the hydrides of alkaline metals are presented, that in the case of lithium hydride the isotherm is almost vertical, whereas for potassium hydride it has a much greater slope. The slope of the isotherm is determined by the adiabatic compressibility, which is given by the following equality [8]:

$$\varkappa_{ad} = -\Omega_0 \left(\frac{\partial p}{\partial \Omega}\right)_{ad}. \tag{16}$$

Knowing the compressibility, one can determine the velocity of sound in the substance (see for example [8])

$$v_{ss} = \left(\frac{\partial p}{\partial \sigma}\right)^{1/2}_{ad} = \left(\frac{\varkappa_{ad}}{\sigma}\right)^{1/2}, \tag{17}$$

where σ is the density of the substance. Results of the calculation of the compressibility and of the velocity of sound are presented in Table 2, where the results of [3] are also given. Unfortunately, experimental information on compressibility exists only for lithium hydride [3]; this value is also given in Table 2. It is seen from Table 2 that, as one would expect, the greatest compressibility is calculated for cesium hydride, and the smallest for lithium hydride; it is also seen that the calculated values of compressibility agree well with the data of [3] and with the experimental value for lithium hydride.

Results of the calculation of the effective charges of metal and hydrogen ions as functions of pressure for sodium hydride are presented in Fig. 2. These effective charges may be determined by integrating the expression for the electron density over the spheres having the Pauling radius and by adding the charge of the ionic core. One can see from Fig. 2 that in sodium hydride mainly ionic bonding is realized; however, the magnitudes of the anion and the cation charges are not equal. This is evidence that one cannot talk about pure ionic or metallic bonds in hydrides. The values of the effective charges, apparently, cannot be obtained in a unique way because there is no criterion for the choice of the ionic radii of the compound components. In particular, instead of the Pauling radii one could choose such radii for which the equality $|Z^{eff}_{Me}| = |Z^{eff}_{H}|$ is satisfied, as in the case in purely ionic comounds. This equality can be considered as an equation for determining the ion radii. However, solution of this equation for sodium hydride leads to an "overlap" between ions. This overlap decreases as pressure increases, which is evidence for increased strength of the ionic bond in NaH. One can come to the same conclusions by analyzing the pressure dependence of the effective charges, determined with the help of the Pauling radii (see Fig. 2). One can see that increased pressure leads to an increase of the effective positive charge of the cation in the hydride and to an increase of the absolute value of the effective negative charge of the anion.

Thus, the results obtained in this paper provide evidence for the fact that the described method gives the correct physical picture for the electron behavior in hydrides of alkaline metals and agrees with the existing ideas about the character of the binding forces in these compounds [4].

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ORIENTATIONAL BONDING OF PHASES ACCOMPANYING DIRECTED CRYSTALLIZATION OF THE EUTECTIC OF THE SYSTEM Si–TiSi$_2$

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The characteristic features of structure formation in cast and direct crystallized alloys of the system Si–TiSi$_2$ were studied. It is shown that the predominant orientation of the bonding of the phases in directionally crystallized eutectics (DE) of the system Si–TiSi$_2$, observed at the stage of steady-state growth, already appears on the surface of nucleation, which apparently indicates that the nucleation of the phases in the alloys of this system is of an epitaxial character.

There are a large number of works on the crystallography of conjugate phases in directionally crystallized eutectics (DE) [1, 2]. Their results, however, do not always agree, which is primarily a result of the local nature of the methods of study employed and the fact that only the stage of steady-state growth was analyzed. In [3] the stages of formation of orientational bonding of phases in several metallic DE with a low entropy of melting of the phases were studied by the method of texture diffractometry, which has the advantage that the information is integrated over a large cross-sectional area of the sample. The crystallography of nucleation of DE is in most cases random and the orientational bonding is established in the course of subsequent growth. Epitaxial bonding of phases on the nucleation surface was observed only in DE of the system Al–ξ(AlAg). Directionally crystallized eutectics with a high entropy of melting of the phases ($\Delta S_{melt} > 23$ J/(g·atom·K) [4]), having a tendency toward limitation during growth, have been virtually unstudied in this respect. In this work the formation of orientational bonding of phases in DE of the high-entropy system Si–TiSi$_2$ was studied. The entropies of melting of its phases equal $S^{Si}_{melt} = 27.59$ [5] and $S^{TiSi_2}_{melt} = 33.8$ J/(g·atom·K) [6] (estimated based on the latent heat of fusion), respectively.

MATERIAL AND EXPERIMENTAL PROCEDURE

The experiments were performed on alloys of the system Si–TiSi$_2$ with the eutectic (22% Ti by weight) and hypo- and hypereutectic (1-30% Ti by weight) compositions. The starting materials were titanium and silicon iodide of semiconductor purity. Directed crystallization was achieved following the procedure of [7] on a silicon seed with <111> orientation. A crystallization rate in the range $1.7\text{-}2 \cdot 10^{-2}$ mm/sec was chosen, while the temperature gradient G on the crystallization front (qualitatively estimated from the angle of growth of the ingot) was varied by varying the magnitude of the overheating of the melt. The microstructure was determined by the procedure of [8] and studied under an MIM-7 microscope. The texture was determined on a DRON-3 diffractometer with a GP-2 attachment in Cu_K radiation with back-and-forth motion of the sample in its own plane. The pole figures for the silicon phase were constructed for both the {220} and {111} reflecting surfaces, whose x-ray intensity is high. Because of the weakness of the reflection from the (040) plane, the normal to which, according to the data of [8] is the axis of growth of TiSi$_2$, the pole figures were

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