THEORETICAL STUDY OF CARBON PHASES

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Introduction

Four allotropic modifications of carbon (diamond, graphite, carbyne, fullerite) are known at present.

Variety in properties of carbon materials is caused by the electron structure of a carbon atom. Redistribution of electron density, electron clouds of different modifications forming around the atoms, hybridization of orbits (sp^3-, sp^2-, sp-hybridization in diamond, graphite, carbyne respectively) are responsible for existence of different crystalline allotropic phases. The diamond structure is three-dimensional, spatial, the graphite one is quasi-two-dimensional, schistose, planar, the carbyne one is quasi-unidimensional, threadlike, linear.

The mechanism of reconstruction in the crystal lattices is determined by forming different carbon modifications and consists in changing configurations of external valence electron clouds. This mechanism is controlled by the charge state of carbon atoms and their different valence [1]. Carbon atoms can be tetra-, tri- and bivalent. The type of the bond between carbon atoms can be different (single-, two- and tri-paired).

Fig.1 illustrates the experimental phase diagram for carbon with the temperature and pressure ranges in which the phases of diamond D, graphite G, melt M and the probable metal phase MP are realized [2-3]. The diagram does not show other known crystalline carbon forms.

The study of known allotropic carbon modifications, calculation of free energy and thermodynamic potentials of phases, their comparison for different carbon structures, evaluation of energy parameters to determine conditions for possible phase transitions, plotting the phase diagram for carbon are of scientific interest.

Theory

The calculations have been carried out using molecular-kinetic theory [4, 5] ignoring the correlation in substitution of lattice sites by atoms of different sorts (in fullerite - by different C_{60}, C_{70} molecules) and with the assumption on geometrical perfection of phase crystal lattices and single-domain crystal structure. Interatomic (intermolecular) interaction is considered in two coordination spheres.

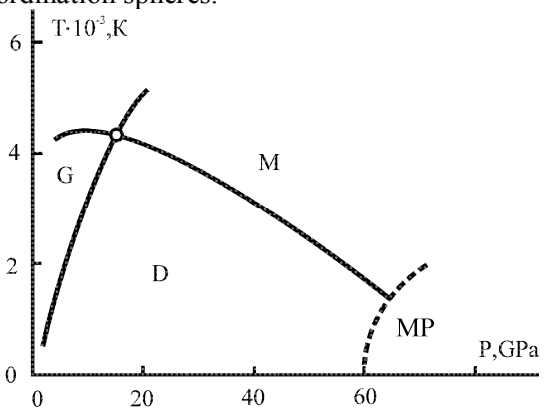

Fig.1. Experimental state diagram for carbon phases. D - diamond, G - graphite, M - melt, MP - probable metal phase. The triple site is marked with the circle.

Comparing equations for free energies of carbon phases, we write the overall formula for free energy of D, G, C, F for one lattice site. This formula has the following form:

$$f_i = e_i - \omega_i \eta_i^2 + \frac{1}{2} kT\Delta_i, \qquad (1)$$

where e_i is energetic parameter, ω_i is ordering energy, η_i is order parameter for each carbon phase, k is Boltzmann's constant, T is absolute temperature, index *i* denotes one of the D, G, C or F phases and

$$\Delta_i = (c_1 + \frac{1}{2}\eta_i)ln(c_1 + \frac{1}{2}\eta_i) + (c_1 - \frac{1}{2}\eta_i)ln(c_1 - \frac{1}{2}\eta_i) + (c_2 + \frac{1}{2}\eta_i)ln(c_2 + \frac{1}{2}\eta_i) + (c_2 - \frac{1}{2}\eta_i)ln(c_2 - \frac{1}{2}\eta_i). \qquad (2)$$

The e_i and ω_i values in (1) for D, G, C, F phases equal to, respectively:

$$e_D = -2[c_1(\upsilon'_{11} + 3\upsilon''_{11}) + c_2(\upsilon'_{22} + 3\upsilon''_{22}) + c_1c_2(\omega'_D + 3\omega''_D)],$$

$$\omega_D = \frac{1}{2}(\omega'_D + 3\omega''_D) \qquad \text{for D phase,} \quad (3)$$

$$e_G = -\frac{3}{2}[c_1(\upsilon'_{11} + 2\upsilon''_{11}) + c_2(\upsilon'_{22} + 2\upsilon''_{22}) + c_1c_2(\omega'_G + 2\omega''_G)],$$

$$\omega_G = \frac{3}{8}(-\omega'_G + 2\omega''_G) \quad \text{for G phase,} \quad (4)$$

$$e_C = -\frac{2}{9}[c_1(11\upsilon'_{11} + \frac{5}{2}\upsilon''_{11}) + c_2(11\upsilon'_{22} + \frac{5}{2}\upsilon''_{22}) + c_1c_2(11\omega'_C + \frac{5}{2}3\omega''_C)],$$

$$\omega_C = \frac{5}{36}\omega''_C \qquad \text{for C phase,} \quad (5)$$

$$e_F = -3[c_1(2\upsilon'_{11} + \upsilon''_{11}) + c_2(2\upsilon'_{22} + \upsilon''_{22}) + c_1c_2(2\omega'_F + \omega''_F)],$$

$$\omega_F = \frac{1}{4}(2\omega'_F - 3\omega''_F) \quad \text{for F phase,} \quad (6)$$

where $\upsilon'_{ij}, \upsilon''_{ij}\,(i,j=1,2)$ are energies of interaction between C_1 and C_2 atoms at the distances r_1, r_2, c_1, c_2 are their atomic concentrations. The derived formulae define the dependence of free energy of carbon phases on their crystal composi tion, temperature, order parameter and energetic constants.

The thermodynamical potential for one lattice site can be written as follows:

$$\varphi_i = (e_{0i} - \omega_{0i}\eta_i^2)[1 + \frac{P}{P'} + n(\frac{P}{P'})^2] + \frac{1}{2}kT\Delta_i +$$
$$+ \omega_{0i}(1 - æP)P, \quad (7)$$

where ω_{0i} is the atomic volume of the crystal at P=0, $æ = -\frac{1}{V}\frac{\partial V}{\partial P} \approx 10^{-2}$ GPa^{-1} is the compressibility of the crystal. Formula (7) determines the dependence of thermodynamical potential on the temperature, pressure, order parameter and energetic constants.

The curve plots of temperature dependence of thermodynamic potentials for carbon phases have been constructed by formula (7) for chosen energetic constants (according to the relashinships between atomic volumes and average values of atomic radii) and different pressures P/P′. For all phases i = 1, 2, 3, 4 the thermodynamical potential is decreased with increasing temperature. On the other hand, the growth of pressure increases the thermodynamical potential.

The phase diagram given in Fig.2 has been plotted by the intersection points of $\varphi_i(T)$ curves for different pressures. Fig.2 shows that beginning from the values $P/P' = 0{,}15$ temperatures of phase transitions rise with increasing pressure what corresponds to experimental data for the diamond-graphite transition. At low pressures, the tem-perature of phase transition can slightly drop with increasing pressure as it was found out for the equilibrium curve between phases 2 and 3.

Conclusions

The theory for phase transitions in allotropic carbon modifications has been developed. The possible ordering of atoms and fullerenes in phases has been considered. The statistical calculation of free energies and thermodynamic potentials for carbon D, G, C, F phases has been made, their dependences on the phase composition, temperature, pressure, order parameter and energetic constants have been established.

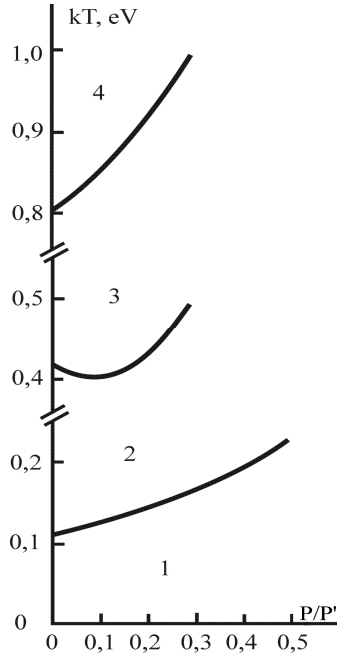

Fig. 2. The phase diagram calculated for carbon.

The curves for temperature dependence of thermodynamic potentials at different values of external pressure have been plotted using the chosen energetic parameters. The possible values of temperature and pressure for phase transitions have been determined by the intersection sites of these curves.

The phase diagram has been constructed with estimation of the temperature and pressure ranges, in which different carbon phases can be realized. As found out, the pressure range of the diamond phase existence narrows with temperature increase. For other phases this range is expanded.

The experimental verification of obtained regularities of carbyne and fullerite phases realization is of interest to physicist-theorists.

References

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