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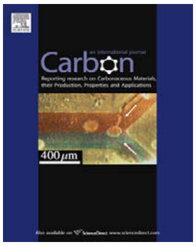

Continuum theory of carbon phases

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ABSTRACT

We constructed a continuum theory of carbon phases based on the Landau theory of phase transitions. Our theory ties up many seemingly unrelated data on the carbon system. Transformations between graphite, diamond, and liquid-carbon are described by the Landau–Gibbs free-energy which depends on two order parameters: crystallization and structural. The barrier-height and gradient-energy coefficients were calculated from the nucleation data obtained in the studies of diamond/graphite and diamond/liquid-carbon systems. The boundary of the absolute stability of the graphitic phase was interpreted as the spinodal point of the free-energy, which allowed us to calculate the pressure dependence of the barrier-height coefficient. The continuum model yielded a value of 1.66 J/m^2 for the graphite/liquid-carbon interface energy, which continues the trend of the elements of Group IV. We also analyzed stability of nanostructured amorphous carbon and interpreted it as the transition state of the free-energy function. This conjecture helped us to explain results of the experiments on the focused ion-beam irradiation of CVD-diamond nanofilms. The present theory may be used for the large-scale modeling of graphite and diamond crystallization; it can also be extended to include other structural modifications of carbon or an entirely different element such as silicon.

1. Introduction

1.1. *Carbon phases*

Carbon is one of the most abundant elements in the universe and the most versatile material known to a man. This element is the basis of life on Earth and constitutes interiors of the celestial objects: outer planets, Uranus and Neptune, and white dwarf stars. Carbon is often considered to be silicon of the future because of the unique properties resulting from the variety of possible structural forms. A wide range of electronic properties of carbon from insulating/semiconducting diamond to metal-like graphite, nanotubes, and graphene sheets yields many technological applications in different areas of human activity. Such versatility of this element in nature results from the unique property of a carbon atom to form bonds of many different configurations, called hybridizations: liner sp^1, planar sp^2, tetrahedral sp^3, etc. All of this causes great scientific interest in thermodynamic properties of carbon.

Equilibrium carbon phases have been studied for many years. Despite the tremendous technical difficulties of experimental studies (temperatures of up to 10,000 K and pressures of 100–1000 GPa) the phase diagram of carbon has been created [1–3]. Thermodynamic databases helped develop fairly good bulk-thermodynamic free-energy functions that reproduce the low-temperature portion of the carbon phase diagram [4]. Because of the experimental difficulties, the theoretical (density functional) and numerical (MC and MD) methods of study of carbon phases gained popularity in the scientific community [5–15]. The phase diagram of carbon most commonly considers three clearly distinguished phases:

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graphite, diamond, and liquid carbon, although there is a number of high energy phases, e.g. bc8 and simple cubic, which were found to be metastable at low pressure and temperature [5] and stable at high pressure conditions [6]. Analysis of the behavior of graphite under conditions of isotropic pressure brought a surprising result that at least its rhombohedral modification can transform into diamond without thermal activation at 80 GPa [7]. Although these studies are still work in progress and the experimental phase diagram in its finality is still to be drawn, many features have been clarified recently: for instance, a triple point of coexistence of the three phases has been found to be around the temperature of 4250 K and pressure of 15 GPa, see [8] and Fig. 1.

Experimental results on liquid carbon are scarce because of the extreme conditions and/or short times of observations of the liquid state. However, a maximum in the melting temperature of graphite as a function of pressure has been observed in a number of studies [1–3]. Explanations of the maximum led to the introduction of two types of liquids: low-pressure graphite-like predominantly-sp^2 and high-pressure diamond-like predominantly-sp^3 [15]. Ree et al. [9–11] conducted MD simulations and presented the isotherms of liquid carbon exhibiting a clear Van der Waals type dependence between the mostly sp^2 and sp^3 liquids. As a result, a liquid–liquid phase transition (LLPT) has been predicted. Moreover, a second triple point of coexistence of the two liquids and graphite and a critical point of the coexistence of the two liquids at the temperature around 9000 K and pressure of 11 GPa have been conjectured [9–11], although these did not follow from the experimentally observed properties of the liquid [1–3]. Numerical modeling of carbon structures relies heavily on the choice of the interaction potential, which is being constantly revised approaching the “real” interaction of carbon atoms. Recently Wang et al. [12] and Ghiringhelli et al. [8] presented calculations using an improved interaction potential and found no evidence of LLPT or the critical point for liquid carbon. However, there are no doubts that as pressure increases atomic coordination of carbon undergoes an adjustment from three- to four- and higher-fold numbers [6].

Carbon may also exist in another solid-state form, amorphous [16,17]. Classification of carbonacious materials as ‘amorphous’ is not straightforward as many different systems fall into this category. One of the important parameters of such materials is the sp^3/sp^2 ratio. Amorphous carbon with high ratio, usually at or above 70%, is called tetrahedral (ta-C); it is also often called diamond-like carbon due to similarity of electrical and mechanical properties of ta-C to those of diamond. There is another category of amorphous carbon that attracts attention of the researchers-*nanostructured amorphous carbon* (na-C). Na-C can be manufactured using several different techniques: chemical vapor deposition (CVD) of carbon atoms, focused ion beam bombardment (FIB) of carbon

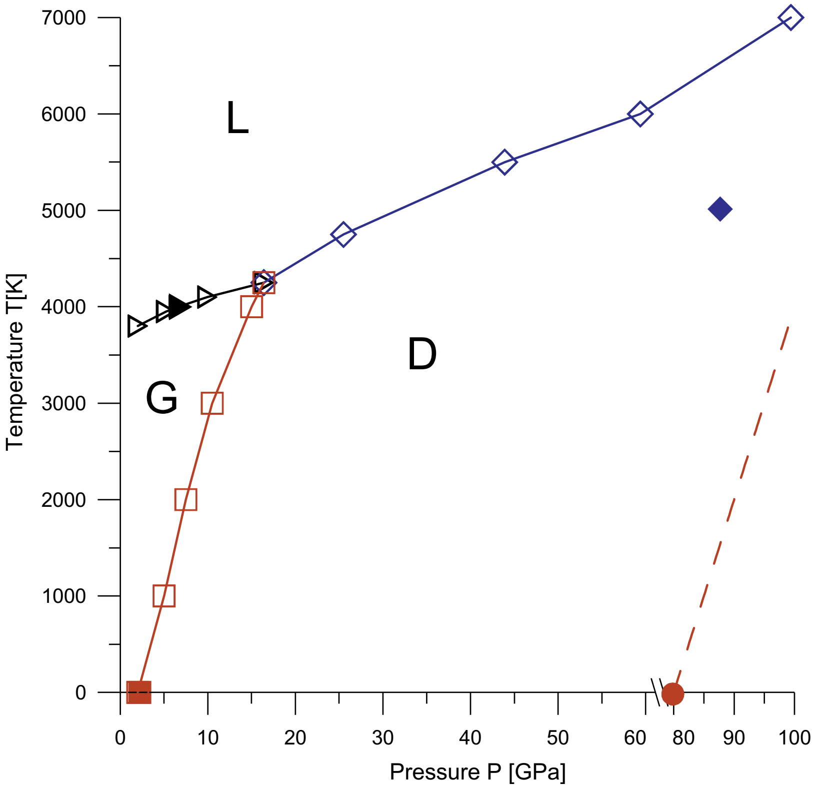

Fig. 1 – Low temperature–pressure region of the carbon phase diagram. G-graphite, D-diamond, L-liquid carbon regions. Solid lines-phase boundaries based on the data of [8]; dashed line-graphite/diamond spinodal line based on the data of [7]. Red square-($T = 0$ K, $P = 1.36$ GPa); red circle-($T = 0$ K, $P = 80$ GPa); black triangle-($T = 4000$ K, $P = 6.7$ GPa); blue diamond-($T = 5000$ K, $P = 85$ GPa). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)