PACS numbers: 01.65. + g, 61.50.Ks, 64.70.kd DOI: 10.1070/PU2008v051n10ABEH006616

## Structural phase transitions in highly compressed substances and the synthesis of high-pressure phases

### S V Popova, V V Brazhkin, T I Dyuzheva

This report is devoted to studies of structural phase transformations under pressure that have been performed at the Institute for High Pressure Physics, Russian Academy of Sciences (IHPP). Conditionally, this activity can be subdivided into the study of transformations under pressure in crystals *in situ* (mainly, by X-ray diffraction) and the synthesis of new phases that are metastable at normal pressure. The study of solid-state amorphization and transformations in disordered media (liquids, glasses) under pressure deserves independent examination. Each of these areas has been considered in more than a hundred articles; here, we briefly mention what are, in our opinion, only several of the most important results of such studies.

Pioneering work on the study of the high pressure influence on the crystal structure of substances by X-ray diffraction was performed at the IHPP in 1950-1960 in the group headed by S S Kabalkina with the use of a pistoncylinder apparatus with beryllium windows. The maximum pressures in this cell were 2 GPa, which is insufficient for studying phase transitions in the majority of simple inorganic substances. However, for organic molecular compounds, this pressure range is sufficiently high. At the IHPP, the compressibility and polymorphism of paraffins, urea, and isomorphic hydrocarbons of the group of linear polyphenyls were studied [1]. A noticeable breakthrough in the field of X-ray diffraction studies at high pressures was the creation (in the 1960s) of X-ray diffraction high-pressure devices of the 'chechevitsa' (lentil) type with hard-alloy anvils and the use of amorphous boron as the pressure-transmitting medium transparent to X-rays. These devices made it possible to conduct studies at pressures of 16-18 GPa. In this pressure range, structural phase transitions in many elemental substances and simple compounds have been discovered. Special attention should be given to the discovery and study of structural transformations in Ga, Si, Ge, Sb, Bi, A<sup>III</sup>B<sup>VI</sup> compounds (CdS, CdSe, CdTe),  $MF_2$  (M = Mn, Co, Ni, Zn), and  $Mg_2X$  (X = Si, Ge, Sn) [1]. The next step in the development of X-ray diffraction studies under pressure was the creation of a high-pressure cell with diamond anvils with the range of working pressures to 50 GPa. Such cells were used to study the polymorphism of transition metal hydrides (TiH<sub>2</sub>, ScH<sub>2</sub>, ZrH<sub>2</sub>) [2-4], phase transitions in A<sup>III</sup>B<sup>VI</sup> compounds (TIS, TISe, InS, InTe) [5, 6], and transformations in metal trifluorides (LaF<sub>3</sub>, CeF<sub>3</sub>) [7]. As a separate reference, the detection and study of the 'collapse' of compressibility in compounds such as UO<sub>3</sub>, ReO<sub>3</sub> [8, 9] deserve mention.

Another approach to the study of phase transitions and polymorphism under pressure *ex situ* consists in the method of quenching high-pressure phases, including new compounds that are metastable under normal conditions. One of the first metastable phases obtained at the IHPP was stishovite—an ultradense phase of silica with a rutile-type structure [10]. The possibility of the existence of structures with a sixfold coordination of silicon atoms relative to oxygen atoms has enormous importance for understanding the internal structure of the Earth and planets. In subsequent years, a large series of works on the study of polymorphism of  $AX_2$  compounds such as fluorides, sulfides, selenides, and tellurides of simple and transition metals was performed at the IHPP [11]. The data obtained confirm conclusions (based on crystallochemical considerations) that during compression there must appear structures in which progressively more dense packings of atoms and molecules are realized with an appropriate increase in the coordination number. It is hardly expedient to analyze the pressure influence on the synthesis of new compounds in binary systems on the basis of the comparison of the coordination numbers of initial components and their compounds. In this case, it is better to use a 'volumetric' factor, since the application of pressure favors alloying reactions proceeding with a decrease in the specific volume. Note that the effects of the so-called 'chemical compression' in the compounds can be very significant. Thus, the extrapolated volume per atom of Si and Ge in binary compounds corresponds to the ultradense modifications of Si and Ge that are stable only at megabar pressures. As interesting examples of new compounds synthesized under pressure, we can mention tungsten germanides and rhenium carbides. In the W-Ge system, no intermediate phases exist at atmospheric pressure, while under a pressure of 8 GPa four metastable phases have been synthesized from a mixture of elements, namely, two phases of W5Ge3 composition and two phases of WGe<sub>2</sub> composition [12]. In the Re-C system at normal pressure, no intermediate phases are present either, while at 4 GPa an ReC phase with a hexagonal structure of the  $\gamma'$ -MoC type is formed from a mixture of elements upon heating, and at pressures of more than 10 GPa, a superhard ReC phase with a cubic structure of the NaCl type is crystallized [13, 14]. Some interesting results were obtained when studying polymorphism of hydroxyl-containing compounds using the example of systems such as  $M_2O_3 - H_2O$  (M = Fe, Al, Sc, La) [15]. Depending on the P, T conditions of synthesis, the compounds MO(OH) and  $M(OH)_3$  with different structures were obtained [15]. These results are extremely important for the solution to the problem of the existence of bound water in the Earth's mantle. For  $MF_3$  compounds (M = Sc, La, Y), the following sequence of structural transformations has been established: ReO<sub>3</sub> type  $\rightarrow$  YF<sub>3</sub> type  $\rightarrow$  LaF<sub>3</sub> type [15]. In this case, the first type of transformation in the trifluorides (ReO<sub>3</sub> type  $\rightarrow$  YF<sub>3</sub> type) is accompanied by a record change in the specific volume ( $\sim 53\%$ ).

Some groups of substances synthesized at high pressures should be considered separately. This refers, for example, to new superconductors synthesized under pressure. Thus, in the 1970s at the IHPP the compound Nb<sub>3</sub>Ge was for the first time synthesized under pressure in the bulk with a record temperature (for that time) of the superconducting transition  $T_{\rm c} = 22.3$  K [16]. Using high pressures, it was possible to synthesize a series of new superconductive sesquicarbides of rare-earth elements [17]. Many high-pressure modifications have not only sufficiently high  $T_c$ , but also high values of critical magnetic fields and currents [17, 18]. It is sufficient to mention the synthesis of a metastable superconductive  $(T_c = 10 \text{ K})$  high-pressure phase of TaN with a cubic structure of the NaCl type [18]. Note that the bulk singlephase samples of the high-temperature superconductor HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> with a record high critical temperature  $(T_{\rm c} = 132 \text{ K at normal pressure})$  also was synthesized under

1065

pressure by researchers at Moscow State University and the Institute for High Pressure Physics, Russian Academy of Sciences [19]. A veritable development in the physics of superconductors and the physics of condensed matter as a whole was the high-pressure synthesis of superconductive diamond doped by boron [20]. The exceptional mechanical and thermal properties of diamond, together with sufficiently high values of  $T_c \sim 7$  K and upper critical fields of  $\sim 5$  T, make superconductive diamond one of the most promising materials for future electronics.

The study of carbon materials bears special mention. At the IHPP, during the entire 50-year period of its existence comprehensive studies of the graphite-diamond transition have been carried out. In recent years at the IHPP pressureinduced phase transitions have been actively investigated for new metastable carbon modifications-C<sub>60</sub> fullerites and carbines [21]. During the transformation into the stable phases of carbon (graphite and diamond), these carbon states undergo a number of transformations into carbon forms that are intermediate in energy. Thus, C<sub>60</sub> fullerite undergoes one-, two-, and three-dimensional polymerization of  $C_{60}$  molecules at high pressures and temperatures; with a further increase in pressure and (or) temperature, the fullerites are transformed into bulk amorphous states [22]. A number of carbon modifications obtained from fullerites possess unique mechanical properties [23]. A P, T treatment of carbines leads to the synthesis of metastable amorphous phases of carbon with interesting electron-transport properties [24].

In the case of polycrystalline samples of the new materials obtained using high pressures, it is frequently impossible to solve the crystal structure and perform a detailed study of physical properties. In this connection, an especially urgent problem is growing large single crystals of high-pressure phases that are metastable under normal conditions. In recent years, interesting results have been obtained at the IHPP in this field. In particular, large single crystals (several mm in size) of high-pressure phases of silica (coesite and stishovite), TiO<sub>2</sub>, FeO(OH), etc. have been grown [25, 26]. In growing single crystals, the need to correctly determine crystal structure manifested itself vividly when studying highpressure phases of  $Mg_2X(X = Sn, Ge, Si)$ . It turned out that these modifications crystallize into structures with incommensurate crystal lattices, which, certainly, could not be established from the powder-diffraction data [27].

The term 'structural transformations' is traditionally related to crystalline substances. However, at a high pressure, as was shown in a whole series of experimental works performed at the IHPP, changes in the short-range-order structure in melts and glasses can occur not only gradually, in a wide P, T range, but also sufficiently sharply. In this case, a change in the short-range-order structure is accompanied by 'jumps' in the volume and physical properties, similar to the case of first-order transitions in crystals. Such transitions were found both in elemental melts (sulfur, selenium, iodine [28]) and in the melts of binary compounds (for example,  $As_4S_4$  [29]).

The high pressure influence on the structure of a material has one additional aspect: compression can lead to a disordering of the crystal structure. This phenomenon, known as solid-state amorphization, has been investigated in a series of works performed at the IHPP, which made it possible to establish the main laws governing this process. The investigation of the solid-state amorphization of stishovite upon heating made it possible to study the kinetics of this process; in particular, it was found that the activation energy of the amorphization process is low in comparison with the activation energy of diffusion [30]. These results, together with the discovered softening of the shear modulus upon solid-state amorphization of the ices of H<sub>2</sub>O and D<sub>2</sub>O [31], made it possible to construct a model of solid-state amorphization. Note that the solid-state amorphization of high-pressure phases is the only process which enables producing bulk samples of amorphous tetrahedral semiconductors on the basis of Si and Ge, and  $A^{III}B^V$  compounds [32].

The investigation of phase transformations in glasses  $(SiO_2, GeO_2, B_2O_3)$  [33] made it possible to establish that these transformations can occur in a wide range of pressures and temperatures and are characterized by an unusual logarithmic kinetics of transitions [34]. At present, at the institute work on the study of the structure of short-range order and the physical properties of melts under pressure actively continues [35]. The detection of specific transformations in glasses and melts once again demonstrated the generality of the phenomenon of structural phase transitions in condensed matter upon compression.

Acknowledgments. The authors are grateful to S M Stishov for the fruitful discussions. This work was supported in part by the Russian Foundation for Basic Research, project Nos 08-02-00014 and 07-02-01275, and by the Presidium of the Russian Academy of Sciences.

#### References

- Vereshchagin L F, Kabalkina S S *Rentgenostrukturnye Issledovaniya pri Vysokom Davlenii* (X-ray Diffraction Studies at High Pressures) (Moscow: Nauka, 1979) pp. 79, 81, 86, 94, 89, 150
- 2. Dyuzheva T I et al. Fiz. Tverd. Tela 33 2763 (1991)
- Bashkin I O, Dyuzheva T I, Lityagina L M, Malyshev V Yu Fiz. Tverd. Tela 35 3104 (1993) [Phys. Solid Slate 35 1528 (1993)]
- 4. Litaygina L M, Dyuzheva T I J. Alloys Comp. 179 69 (1992)
- Demishev G B, Kabalkina S S, Kolobyanina T N, Dyuzheva T I, Losev V G, in *High Pressure Sciences and Technology: Proc. XI* AIRAPT Intern. Conf. Vol. 1 (Ed. N V Novikov) (Kiev: Naukova Dumka, 1989) p. 137
- Kabalkina S S, Losev V G, Gasanly N M Solid State Commun. 44 1383 (1982)
- Dyuzheva T I et al. Neorg. Mater. 39 1384 (2003) [Inorg. Mater. 39 1198 (2003)]
- Dyuzheva T I, Bendeliani N A, Brazhkin V V, Kuznetshov L M J. Alloys Comp. 315 59 (2001)
- Dyuzheva T I et al. Dokl. Akad Nauk SSSR 298 100 (1988) [Sov. Phys. Dokl. 33 1 (1988)]
- 10. Stishov S M, Popova S V Geokhimiya (10) 832 (1961)
- 11. Itskevich E S, Popova S V Vestn. Akad. Nauk SSSR 9 59 (1980)
- 12. Popova S V Phys. Scripta T1 131 (1982)
- 13. Popova S V, Boiko L G High Temp. High Press. 3 237 (1971)
- 14. Popova S V, Fomicheva L N, Khvostantsev L G *Pis'ma Zh. Eksp. Teor. Fiz.* **16** 609 (1972) [*JETP Lett.* **16** 429 (1972)]
- 15. Bendeliani N A, Abstract of the Doctoral (Chem Sci.) Dissertation (Moscow: Moscow State Univ., Department of Chemistry, 1982)
- Vereshchagin L F et al. Pis'ma Zh. Eksp. Teor. Fiz. 26 536 (1977) [JETP Lett. 26 394 (1977)]
- Khlybov E P, Abstract of the Candidate's (Phys.-Math.) Dissertation (Moscow: Moscow State Univ., Department of Physics, 1985)
- Kazakov S M, Itskevich E S, Bogacheva L N Pis'ma Zh. Eksp. Teor. Fiz. 58 340 (1993) [JETP Lett. 58 343 (1993)]; Boiko L G, Popova S V Pis'ma Zh. Eksp. Teor. Fiz. 12 101 (1970) [JETP Lett. 12 70 (1970)]
- 19. Kuzemskaya I G et al. J. Superconduct. 11 117 (1998)
- 20. Ekimov E A et al. Nature 428 542 (2004)
- Brazhkin V V et al. Pis'ma Zh. Eksp. Teor. Fiz. 76 805 (2002) [JETP Lett. 76 681 (2002)]

- 22. Brazhkin V V et al. Phys. Rev. B 56 11465 (1997)
- 23. Brazhkin V V et al. J. Appl. Phys. 84 219 (1998)
- Demishev S V et al. Pis'ma Zh. Eksp. Teor. Fiz. 78 984 (2003) [JETP Lett. 78 511 (2003)]
- Dyuzheva T I, Litaygina L M, Bendeliani N A J. Alloys Comp. 377 17 (2004)
- Dyuzheva T I et al. *Kristallografiya* **51** 370 (2006) [*Crystallogr. Rep.* **51** 342 (2006)]
- 27. Bolotina N B et al. J. Alloys Comp. 278 29 (1998)
- 28. Brazhkin V V, Popova S V, Voloshin R N Physica B 265 64 (1999)
- 29. Brazhkin V V et al. Phys. Rev. Lett. 100 145701 (2008)
- Popova S V, Brazhkin V V, Voloshin R N, Grimsditch M Usp. Fiz. Nauk 172 486 (2002) [Phys. Usp. 45 445 (2002)]
- Stal'gorova O V, Gromnitskaya E L, Brazhkin V V Pis'ma Zh. Eksp. Teor. Fiz. 62 334 (1995) [JETP Lett. 64 356 (1995)]
- Brazhkin V V, Lyapin A G, Popova S V, Voloshin R N *Phys. Rev. B* 51 7549 (1995)
- 33. Brazhkin V V, Lyapin A G J. Phys: Condens. Matter 15 6059 (2003)
- Tsiok O B, Brazhkin V V, Lyapin A G, Khvostantsev L G Phys. Rev. Lett. 80 999 (1998)
- Brazhkin V V et al. (Eds) New Kinds of Phase Transitions: Transformations in Disordered Substances (NATO Science Ser. II, Vol. 81) (Dordrecht: Kluwer Acad. Publ., 2002)

PACS numbers: 61.50.Ks, **62.50.**–**p**, **74.70.**–**b** DOI: 10.1070/PU2008v051n10ABEH006617

## Studies of the thermodynamic, elastic, superconducting, and magnetic properties of substances at high pressures

L N Dzhavadov, E L Gromnitskaya, G N Stepanov, Yu A Timofeev

In this work, we briefly describe experimental methods developed at the Institute for High Pressure Physics, Russian Academy of Sciences (IHPP), and some experimental results obtained.

# 1. Method of pulse-adiabatic modulation of pressure

The first measurements of the temperature response of a system upon an adiabatic change in pressure were performed, apparently, by Joule [1]. However, systematic studies using this method were renewed only more than 100 years later [2-9], which can be explained by the complexity of such experiments when using inertial measuring devices. An isentropic compression can be realized using modernized high-pressure equipment intended for the creation of static pressures. However, the realization of this process for the interval of pressures above 100 MPa is difficult, since it is connected with the application/relief of a relatively large force in a period of time which is subject to a number of restrictions, such as the shockless character of compression on the one hand, and the absence of heat transfer on the other hand (hydrostaticity and the constancy of entropy, S = const). In addition, it is also necessary to take into account stress relaxation in the elements of the high-pressure equipment. One alternative is the modulation method — measurement of the derivative  $(\partial T/\partial P)_S$ . In this case, the necessary conditions can be ensured comparatively easily, although, to the detriment of informativeness, in the presence of a first-order transition, the small amplitude of pressure modulation can prove to be insufficient to change the concentration of phases

from 0 to 1. Among the diverse constructions of high-pressure apparatuses, it is apparently only the apparatus of the piston-cylinder type that makes it possible to control pressure, although even in this case there remain limitations caused by friction in the piston sealing. At the IHPP, a lowinertial version of controlling force was used. The front of the loading pulse at a low pressure does not exceed 10 ms. The static force is transferred to the piston through a spring, and the additional force for the modulation of pressure is applied directly to the piston [5]. The device makes it possible to record the temperature response of a sample upon a sharp change in pressure by about  $\pm 50$  MPa. The maximum pressure is 3 GPa; the permissible range of temperatures is 273-700 K. The pressure-transmitting medium is liquid. The criterion of adiabaticity is the presence of a cutoff in the  $\Delta T(t)$ curve.

When calculating thermodynamic functions from the results of adiabatic experiments, it is assumed that the system is in an equilibrium state and that the characteristic times of the relaxation processes, such as the diffusion mechanism of the formation of point defects (vacancies, interstitial atoms) is less than the time of measurement. Obviously, in this case the following condition must be satisfied:

$$\left(\frac{\partial T}{\partial P}\right)_{S,\,\Delta P>0} = \left(\frac{\partial T}{\partial P}\right)_{S,\,\Delta P<0}$$

Formally, the problem reduces to the solution of the differential equation

$$\left(\frac{\partial T}{\partial P}\right)_S = J_S(T, P)\,,$$

where  $J_S(T, P)$  is an analytical function which describes the results of measurements. The sought adiabatic curve  $T_S(T_0, P)$  for the initial (at P = 0) temperature  $T = T_0$  is found as a result of solving this equation, which can be performed numerically. Given a set of adiabatic curves and boundary conditions, for example, the temperature dependence of entropy at normal pressure S(T, 0), we can easily calculate the T-P dependence of such quantities as the entropy S, heat capacity  $C_P$ , and thermal expansion  $(\partial V/\partial T)_P$ . If in addition to these data we know the pressure dependence of volume at a certain temperature  $T_r$ , we can calculate the equation of state:

$$V(T, P) = V(T_{\rm r}, P) + \int_{T_{\rm r}}^{T} \frac{J_{S}(T, P) C_{P}(T, P)}{T} \, \mathrm{d}T$$

If  $C_V$  is a function of  $(T/\Theta)$  and if  $\Theta$  depends only on volume, the ratio  $(T/\Theta)$  and, consequently,  $C_V$  are also constant at the adiabatic curve. In this case, given  $J_S(T_S, P)$ , we can easily calculate the pressure dependence of the characteristic temperature  $\Theta$ .

Figure 1 displays the results of measurements for Li, Na, and K. As is seen, the values of the derivative  $(\partial T/\partial P)_S$  in the mixed state (i.e., in the mixture of solid and liquid phases) approach the appropriate derivative of the melting curve dT/dP. The relationship between the values of  $(\partial T/\partial P)_S$  and the slope of the melting curve dT/dP makes it possible to draw the conclusion that the adiabatic compression must lead to the crystallization of liquid sodium and to the melting of solid lithium.