Nonequilibrium phase transitions and amorphization in Si, Si/GaAs, Ge, and Ge/GaSb at the decompression of high-pressure phases

V. V. Brazhkin, A. G. Lyapin, S. V. Popova, and R. N. Voloshin
Institute of High Pressure Physics, Russian Academy of Sciences, 142092 Troitsk, Moscow Region, Russia
(Received 19 July 1993; revised manuscript received 18 July 1994)

The evolution of nonequilibrium phase transitions during the decompression of high-pressure modifications of Si, Si/GaAs, Ge, and Ge/GaSb at different temperatures was studied. At temperatures below 120 K, the amorphization of Si and Ge high-pressure phases occurs upon the release of pressure. The positions of the transitions to metastable crystalline Si and Ge phases and of the amorphization of silicon and germanium on the P-T plane were found. The increase of the concentration of the A^3B^5 components in Si-based and Ge-based solid solutions (GaAs in Si and GaSb in Ge) leads to the same change of the type of transitions as the decrease of the temperature does. This makes the preparation of bulk amorphous tetrahedral Si-based and Ge-based semiconductors possible, using the decompression of high-pressure phases, even at room temperature. The kinetics of the nonequilibrium transitions to crystalline phases and of the amorphization is briefly discussed.

I. INTRODUCTION

In order to produce amorphous substances of different natures in recent years, in addition to the regular methods (quenching from melt, sputtering, evaporation) a number of solid-state amorphization techniques (ball milling, irradiation, fast diffusion, amorphization of high-pressure phases, etc.[1–3]) were used. Until now samples of the amorphous tetrahedral semiconductors Si, Ge, etc. as well as of solid solutions silicon-A^3B^5 and germanium-A^3B^5 have only been prepared in a form of thin layers ($\sim 10^{-3}$ mm) (Refs. 4 and 5) by sputtering or evaporation. This is because of the problems encountered when the preparation of tetrahedral glasses was attempted by quenching from the melt.[6]

On the other hand, it is not clear which of the characteristics of amorphous Si and Ge films are connected to the technology of preparation and influence of the substrate, and which are the characteristics of the disordered tetrahedral network of Si or Ge atoms. The method of solid-state amorphization of high-pressure phases by compression and decompression[3] seems to be very interesting and promising. A disordered state of the tetrahedral semiconductors GaSb, GaAs, GaP, Si, and Ge could be produced recently by decompression of high-pressure phases.[7–10]

The mechanism of a solid-state amorphization under high pressure is not clear yet.[3] One of the most frequently used models, the "cold melting" one, is based on the extrapolation of melting lines into the region of stability of a solid phase.[11–14] This model, however, cannot provide the correct sign of the heat effect on the amorphization and structure of the short-range order of the resulting phase.[15] The concept of a mechanical instability of the lattice at definite P, T parameters seems to be more fruitful. The lattice instability can be caused by softening of phonon modes in a metastable crystal.[16]

In accordance with results of Refs. 10 and 17, one can prepare Si and Ge in disordered form by decompression only at sufficiently low temperatures ($\simeq 100$ K). In order to extend the possibility to prepare the pure amorphous tetrahedral phase in a wide P-T range it would be interesting to study phase transitions during decompression of the solid solutions based on the high-pressure phases of Si and Ge.

In this work the pressures at which the high-pressure phases of Si and Ge as well as solid solutions $Ge_{1-x}(GaSb)_x$ and $Si_{1-x}(GaAs)_x$ transform to metastable crystalline and amorphous phases were studied as a function of temperature. As a result, the corresponding kinetic lines of these transitions were determined.

II. EXPERIMENTAL DETAILS

We use the toroidal high-pressure chamber[18] to produce pressures of 1–13 GPa. Si or Ge single-crystal cylinders (2 mm in diameter, 1 mm height) and polycrystal cylinders of solid solutions $Ge_{1-x}(GaSb)_x$ or $Si_{1-x}(GaAs)_x$ (3 mm in diameter, 2 mm height) were placed into a container made of NaCl, pyrophylite, or graphite with a pressure-transmitting medium of pipestone. The nonhydrostaticity near the sample was estimated to be less than 0.2 GPa. The samples were heated by passing an AC current through a nickel or graphite heater or through the sample itself. In low-temperature experiments the chamber was placed in a vessel filled with liquid nitrogen. The temperature 80–1500 K was measured by a chromel-alumel thermocouple placed near the heater or the sample. Melting and metal-semiconductor transitions were detected by a change in the resistivity. Phase analysis of the resulting materials was done by x-ray technique, and calorimetric studies were carried out using Derivatograph C (Hungary). The calibration procedure of the Derivatograph is described in detail in Ref. 15. To produce the metallic high-pressure phases Si II, Ge II (β-Sn structure), and the solid solu-

0163-1829/95/51(12)/7549(6)/$06.00 ©1995 The American Physical Society

tions of these phases $Ge_{1-x}(GaSb)_x$, $Si_{1-x}(GaAs)_x$, the samples were pressurized to 8–13 GPa and were held at 300-1000 °C. The decompression was done isothermally, at a pressure change rate of ~ 1 GPa/min.

III. RESULTS AND DISCUSSION

Upon decreasing the temperature of the decompression a change of the types of the transitions was observed: Si II → Si I, Si II → Si III, and Si II → amorphous Si (*a*-Si); Ge II → Ge I, Ge II → Ge III, Ge II → (Ge IV + Ge V), and Ge II → amorphous Ge (*a*-Ge) (see Figs. 1 and 2). Here Si III and Ge III are well-known metastable modifications of Si and Ge: bcc ($a = 6.64$ Å, $Ia3$, $Z = 16$) and tetragonal ($a = 5.80$ Å, $c = 6.63$ Å, $P4_3212$, $Z = 12$), respectively. The Ge IV phase has a bcc structure similar to that of Si III ($a = 6.97$ Å). As reported in Ref. 19, the same phase was obtained during decompression of Ge II at the temperature of dry ice. Ge V has the structure of Lonsdeylite type ($a = 3.94$ Å, $c = 6.55$ Å, $P6_3mmc$, $Z = 8$); it forms when heating the sample to room temperature. Complete Ge IV → Ge V transition is observed at $T \approx 370$ K and heating rate 20 K/min. The Si III phase transforms upon heating to $T \approx 480$–520 K ($P = 0.1$ MPa) to the Si IV phase which has a Lonsdeylite type structure ($a = 3.80$ Å, $c = 6.28$ Å).

All phase transitions have a finite pressure width of 0.5–1 GPa. The figures and tables present the values corresponding to half of the change in resistivity registered during transitions.

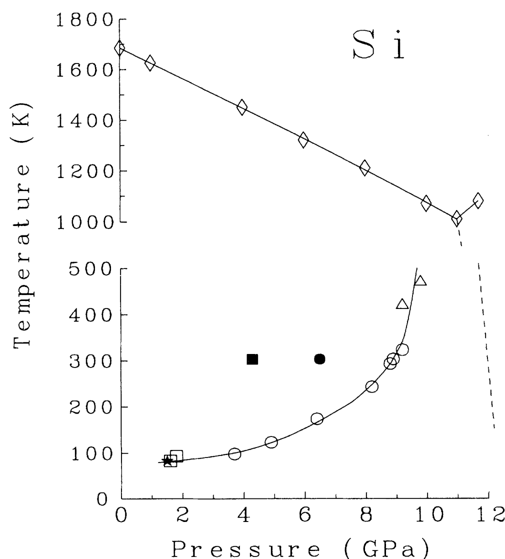

FIG. 1. *P-T*–phase diagram of Si with equilibrium and nonequilibrium transitions. Equilibrium transitions are melting (diamond) and Si I → Si II (dashed line). Nonequilibrium ones are Si II → Si I (triangle), Si II → Si III (opened circles), Si II → *a*-Si (starlet from Ref. 17, opened squares—present data), Si/GaAs II → Si/GaAs III (closed circle), and Si/GaAs II → *a*-Si/GaAs (closed square).

Upon decreasing the temperature, around the temperatures where the types of the transitions changed, mixtures of the corresponding phases were formed after decompression in a wide temperature interval of $\Delta T \sim 50$ K (see Figs. 1 and 2). Transitions to a mixture of crystalline and amorphous phases of pure Si and Ge are reached only at low temperatures ($T < 150$ K for Ge and $T < 120$ K for Si). At higher temperatures the substances transform to metastable crystalline phases as shown in Figs. 1 and 2. To retard these transitions and to promote the amorphization at higher temperatures, the solid solutions of A^3B^5 compounds in Si and Ge were used. The increase of the concentration of A^3B^5 (GaSb for Ge II and GaAs for Si II) leads to the same change of the type of the transitions at decompression as the decrease of the temperature does. (See Tables I, II, and Figs. 3 and 4.)

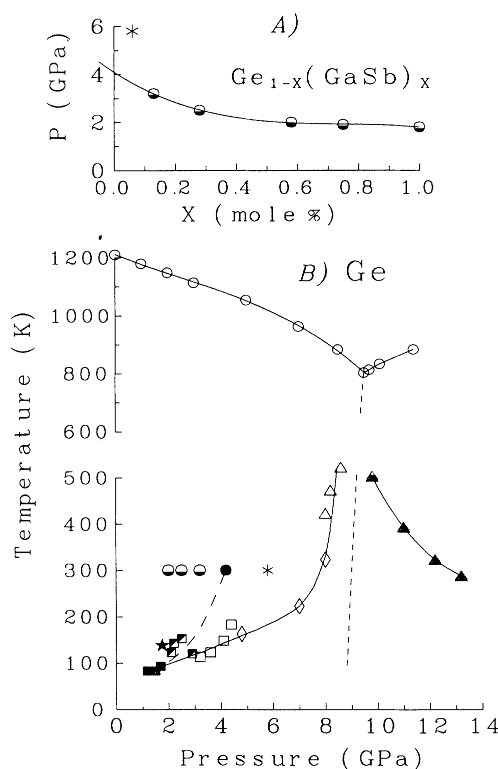

FIG. 2. (a) Concentration dependence of the amorphization pressure of solid solutions $Ge_{1-x}(GaSb)_x$ (semiopened circles) at room temperature and its extrapolation to pure Ge. The asterisk indicates the transition Ge/GaSb II → Ge/GaSb IV. (b) P, T – phase diagram of Ge with equilibrium melting point (opened circles) and Ge I ↔ Ge II equilibrium transition (short-dashed line). Nonequilibrium transitions are presented: Ge I → Ge II (closed triangles), Ge II → Ge I (opened triangles), Ge II → Ge III (diamonds), Ge II → Ge IV (opened square), Ge II → mixture of Ge IV, and *a*-Ge (semiopened squares), Ge II → *a*-Ge (starlet from Ref. 17, closed squares—present data), Ge/GaSb II → *a*-Ge/GaSb (semiopened circles), Ge/GaSb II → Ge/GaSb IV (asterisk), the extrapolation for Ge II → *a*-Ge transition from (a) (closed circle), and the approximation of the amorphization line of Ge (long-dashed line).

TABLE I. Concentration dependence of the transition pressure and type of the phases obtained at decompression of $Si_{1-x}(GaAs)_x$ high pressure alloys ($T = 300$ K).

X_{GaAs} (%)	P_{tr} (GPa)	Phase produced
0	8.9	Si III ($a = 6.64$ Å)
0.05	6.5	Si/GaAs III ($a = 6.67$ Å)
0.11	4.3	a-Si/GaAs
>0.11	4.3	a-Si/GaAs + GaAs/Si ($a = 5.65$ Å)
±0.01	±0.5	

Analyzing the data obtained on the $Ge_{1-x}(GaSb)_x$ system we can assume that it is possible to prepare a continuous set of solid solutions between the high-pressure phases Ge II and GaSb II with β-Sn structure. In the case of silicon it was possible to dissolve up to 11 mol% of GaAs in Si II. The lattice parameter of the metastable solid solutions obtained [Si/GaAs III, Ge/GaSb III, Ge/GaSb IV, and Ge/GaSb V, where, for example, designation Si/GaAs III corresponds to a solid solution $Si_{1-x}(GaAs)_x$ with Si III-like structure] increases approximately linearly with increasing the concentration of A^3B^5, following Vegard's rule.

As the temperature is increased the Ge/GaSb IV phase transforms to the Ge/GaSb V phase, with a hexagonal Lonsdale structure, at sufficiently moderate temperatures (≈ 330–370 K). Thus at room temperature a mixture of Ge/GaSb IV and Ge/GaSb V phases is formed over a few hours (Fig. 4). The Ge V phase has only been prepared before in the form of a thin layer ($\sim 10^{-3}$ mm) by indenting the Ge I phase.[20] Upon heating, the phases Si IV, Ge V, Si/GaAs IV, and Ge/GaSb V transform into the equilibrium phases Si I and Ge I or to the solid solutions Si/GaAs I and Ge/GaSb I, respectively (see Table III). This is accompanied by a weak (< 0.5 kJ/mol) heat absorption. The question of the relative stability of the Si IV versus Si I and Ge V versus Ge I phases requires further studies due to the high degree of disorder in these modifications (see Fig. 4).

At high temperatures amorphous Si-based and Ge-based solid solutions transform to the corresponding crystalline solid solutions (see Table III). Subsequent heating of the crystalline solutions leads to the formation of eutectic mixtures. Crystalline solid solutions of Ge I and GaSb I, which can be formed in a wide concentration range, may be conditionally classified into two groups according to Ref. 5: the diamondlike Ge/GaSb I and sphaleritelike GaSb/Ge I (see Table III).

It appeared surprising that a relatively low concentration of the A^3B^5 component in the Si-based and Ge-based solid solutions (~ 10 mol%) leads to the changes of the transition kinetics which are equivalent to those caused by a twofold-to-threefold decrease of the temperature. For relative concentration $x > 0.12$, bulk amorphous tetrahedral samples can be prepared by decompression even at room temperature. The substituted atoms are likely to be distributed homogeneously in the amorphous matrix. This is supported by the appearance of the metastable crystalline supersaturated Si/GaAs I and Ge/GaSb I solid solutions after annealing of the amorphous phases. The transitions Si II → Si III, Ge II → Ge III, and Ge II → Ge IV have a martensiticlike nature but at sufficiently high temperatures (150–300 K) involve diffusion processes.[21] In the case of solid solutions the diffusion processes are retarded.

The concentration dependence of the pressure of transition to an amorphous phase, $P_{am}(x)$, can be measured in the wide concentration range for the solid solutions a-$Ge_{1-x}(GaSb)_x$ (see Fig. 2). Extrapolating $P_{am}(x)$ to $x = 0$ one can estimate the pressure corresponding to the transition Ge II → a-Ge at room temperature if the transitions Ge II → Ge I, Ge II → Ge III, and Ge II → Ge IV were "frozen" (see Fig. 2). The concentration dependence $P_{am}(x)$ is weak for $x > 0.5$. This behavior is obviously connected to the weak concentration dependence of the width of the semiconducting gap[22] and to the weak variation of the P-T–phase diagram in this concentration range.

Unfortunately, it is difficult to perform this extrapolation for a-$Si_{1-x}(GaAs)_x$ and therefore we have assumed that $P_{am}\{Si\} \sim P_{am}\{a\text{-}Si_{1-x}(GaAs)_x\}$. As a result, the

TABLE II. Concentration dependence of the transition pressure and type of the phases obtained at decompression of $Ge_{1-x}(GaSb)_x$ high pressure alloys ($T = 300$ K).

X_{GaAs} (%)	P_{tr} (GPa)	Phase produced
0	8.0	Ge III ($a = 5.80$ Å, $c = 6.63$ Å)
0.02		Ge/GaSb III ($a = 5.82$ Å, $c = 6.65$ Å)
0.04	7.1	Ge/GaSb III ($a = 5.83$ Å, $c = 6.67$ Å)
0.06		Ge/GaSb IV ($a = 7.02$ Å) + Ge/GaSb V ($a = 3.97$ Å, $c = 6.60$ Å)
0.08		Ge/GaSb IV ($a = 7.05$ Å) + Ge/GaSb V ($a = 3.98$ Å, $c = 6.63$ Å)
0.1		Ge/GaSb IV ($a = 7.07$ Å) + Ge/GaSb V ($a = 4.00$ Å, $c = 6.65$ Å)
0.12–0.6	3.2–2.0	a-Ge/GaSb
0.6–1.0	2.0–1.8	a-GaSb/Ge
±0.01	±0.3	

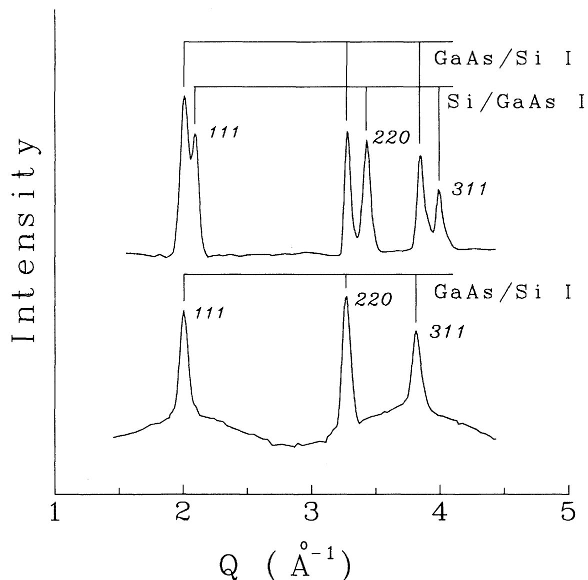

FIG. 3. X-ray diffraction patterns for $Si_{1-x}(GaAs)_x$ alloy. Bottom curve indicates a mixture of amorphous Si/GaAs and crystalline GaAs/Si I (sphaleritelike structure) phases. The top curve corresponds to the same sample after annealing at 800 °C.

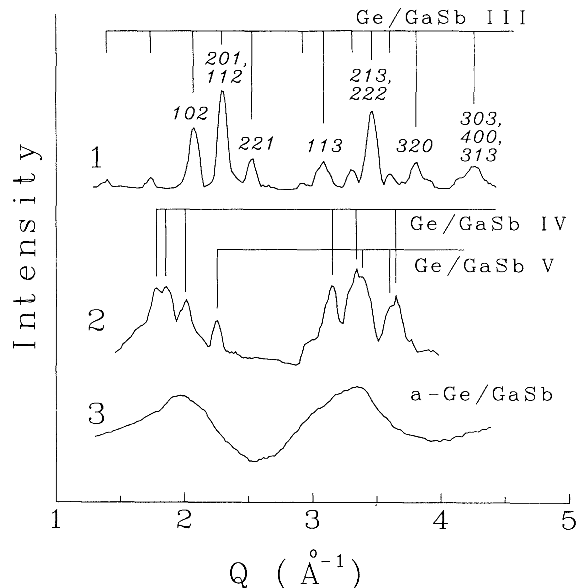

FIG. 4. X-ray diffraction patterns for different metastable Ge/GaSb alloys: Ge/GaSb III with mole concentration $x_{GaSb} = 0.02$ (curve 1; unmarked crystallographic indexes are 101, 111, 103+220, 301, 223), the mixture of Ge/GaSb IV (the peaks 121, 123, and 400 are indicated), and Ge/GaSb V (the peaks 100, 002, 101, 110, 103, and 112 are indicated) with $x_{GaSb} = 0.1$ (curve 2) and a-$Ge_{0.86}(GaSb)_{0.14}$ alloy (curve 3).

kinetic lines of amorphization may be extrapolated up to the temperature $\simeq 300$ K [see Figs. 1 and 2(b)]. Thus we have established the position of the lines corresponding to the transitions to metastable crystalline phases and to the amorphization of Si II and Ge II phases on the P-T plane at a fixed rate of pressure change.

In the framework of the classical theory of nucleation and crystal growth, the value of the pressure hysteresis for the transitions to the crystalline phases $\mid P_{tr} - P_{eq} \mid$, where P_{eq} is the equilibrium pressure, should be approximately proportional to $T^{-1/2}$.[23] The data corresponding to the Si I $\rightarrow$ Si III transition are in good agreement with this relation in the wide temperature interval. In the case of Ge, the situation is more complicated.

In order to explain the amorphization line, high-pressure solid-state amorphization can be considered in the framework of the model of the mechanical instability of the lattice. In this model, the amorphization pressure at $T = 0$ should correspond to the mechanical instability of the lattice of the Si II and Ge II phases. The instability is caused by the vanishing of an elastic modulus and the corresponding phonon softening.

Extrapolation to low temperatures gives $P_{am}\{Ge\}_{T\rightarrow 0} = P^*\{Ge\} = (-2) \pm 2$ GPa for Ge. For Si, the correct extrapolation is more difficult, and the linear one gives $P^*\{Si\} \sim 0$ GPa. Extrapolation of the pressure dependence of the bulk moduli $K(P)$ (Refs. 24 and 25) and frequencies of optical modes in the center of Brillouin zone[26] gives large negative values of the pres-

TABLE III. Transformations of the metastable Si/GaAs and Ge/GaSb phases (type, temperature of transition, heat release, and activation energy of process) at heating ($P = 0.1$ MPa).

Initial phase	Phase obtained	T_{tr} (K)	Q (kJ/mole)	E_{act} (kJ/mole)
Si/GaAs III	Si/GaAs IV	500–550	6	150
a-Si/GaAs ($x_{GaAs} \leq 0.11$)	Si/GaAs I	900–950	12	320
Si/GaAs IV	Si/GaAs I	950–1050		
Si/GaAs I	Si I + GaAs I	1000–1100	3	300
Ge/GaSb III	Ge/GaSb I	550–600	8	160
Ge/GaSb IV	Ge/GaSb V	330–370	2–4	90
a-Ge/GaSb ($0.12 < x_{GaSb} \leq 0.6$)	Ge/GaSb I	650–750	10–12	300–400
a-Ge/GaSb ($0.6 < x_{GaSb} \leq 1$)	GaSb/Ge I	500–650	12–18	160–350
Ge/GaSb V	Ge/GaSb I	750–800		
Ge/GaSb I or GaSb/Ge I	Ge I + GaSb I	800–900	2–6	
		±30	±1.5	±30

sure of lattice instability (from −9 GPa to −11 GPa for both Si and Ge).

It is well known[27] that the diamondlike structure of Si I and Ge I phases may be obtained from the β-Sn type lattice of Si II and Ge II phases by the shear $(-\epsilon_1/2, -\epsilon_1/2, \epsilon_1)$ with the subsequent bulk strain $(\epsilon_2, \epsilon_2, \epsilon_2)$. The transitions Si II $\rightarrow$ Si I and Ge II $\rightarrow$ Ge I have a martensitic nature. Due to the large volume changes ($\Delta V/V \sim 0.2$), they occur with large hysteresis at low temperature, whereas they involve diffusion processes at high temperature. The conditions of the β-Sn type lattice stability are $c_{11} - c_{12} > 0$, $(c_{11} + c_{12})c_{33} - 2c_{13}^2 > 0$, $c_{44} > 0$, and $c_{66} > 0$. The instability of the Si II and Ge II phases corresponding to the transformation to tetrahedrally-bonded structure (II $\rightarrow$ I transition) is governed by the decrease of the $(c_{11} + c_{12})c_{33} - 2c_{13}^2$ elastic modulus. One can suppose that the amorphization of Si II and Ge II is associated with softening of the acoustic phonon modes, which in the long-wave limit corresponds to this modulus. Unfortunately, data on the pressure dependence of the elastic constants and phonon spectra of Si II and Ge II high pressure phases are not available in the literature.

A line of amorphization at finite temperatures and experimental times corresponds to finite values of the elastic constants because of the possibility of activation processes. Therefore, the experimental amorphization line should be shifted from the P-T region of the lattice instability to lower temperatures. The shift should increase with temperature. On the other hand, the melting line does not correspond to zero values of elastic constants either and it is shifted from the region of lattice instability to lower temperatures. That is why the experimental curve of the amorphization at high temperatures may be located in the vicinity of the extrapolation of the melting curve. The vicinity of these curves at finite temperatures was one of the main arguments in favor of the "cold melting" approach. The experimental data obtained in the present work for Si and Ge indicate that amorphization lines do not coincide with the extrapolations of melting curves, although they may lie close to them (see Figs. 1 and 2).

An intensive nucleation without growth of the crystal grains results in the formation of a highly stressed conglomeration of nuclei, which can simultaneously or subsequently relax to an amorphous network. The heat release during amorphization may be related to this relaxation. The tetrahedral short-range order of the resulting state is defined by the most stable (in this P-T region) sp^3configuration of valence electrons.

The transformation should begin in the defective regions (grain boundaries, twins, etc.) to minimize the elastic stresses arising from the large volume change. Consequently, at the initial stages of the transformation, the amorphous phase may have rather complicated morphology.

IV. CONCLUSION

We conclude that the set of regimes of nonequilibrium phase transitions during decompression of Si and Ge high-pressure phases at different temperatures terminates at low temperatures in amorphization processes. The increasing concentration of A^3B^5 compounds in Si-based and Ge-based solid solutions changes the kinetics of these transitions just like the decrease of the temperature does.

The P-T positions of the lines of different phase transformations as well as the lines of amorphization of Si II and Ge II phases were found in a wide temperature range. Subsequent studies of the amorphization of Si and Ge at helium temperatures and the measurement of the pressure dependence of elastic constants and phonon spectra of Si II and Ge II phases are needed.

ACKNOWLEDGMENTS

This work was supported in part by a Soros Foundation Grant awarded by the American Physical Society. The authors are grateful to Professor E.G. Ponyatovskii and Dr. S.V. Demishev for useful discussions and to V.G. Velikanov for technical assistance.

[1] W.L. Johnes, Prog. Mater. Sci. **30**, 811 (1986).
[2] A.W. Weaber and H. Bakker, Physica B **153**, 93 (1988).
[3] E.G. Ponyatovsky and O.I. Barcalov, Mater. Sci. Rep. **8**, 1471 (1992).
[4] See *Amorphous Semiconductors*, edited by M.H. Brodsky (Springer-Verlag, Berlin, 1979).
[5] K.C. Cadien, B.C. Muddle, and J.E. Greene, J. Appl. Phys. **55**, 4177 (1984).
[6] N.F. Mott and E.A. Davis, *Electron Processes in Noncrystalline Materials* (Clarendon, Oxford, 1979).
[7] S.V. Demishev, Yu.V. Kosichkin, A.G. Lyapin, N.E. Sluchanko, M.M. Alexandrova, V.I. Larchev, S.V. Popova, and G.G. Scrotskaya, J. Non-Cryst. Solids **97&98**, 1459 (1987).
[8] A. Polian, J.P. Itie, C. Jouberthil-Carlon, E. Dortyge, A. Fontaine, and H. Tolentino, High Pressure Res. **4**, 309 (1990).
[9] S.T. Weir, Y.K. Volira, I.A. Vanberborgh, and A.L. Ruoff, Phys. Rev. B **39**, 1280 (1989).
[10] V.V. Brazhkin, A.G. Lyapin, S.V. Popova, and R.N. Voloshin, Pis'ma Zh. Eksp. Teor. Fiz. **56**, 156 (1991) [JETP Lett. **56**, 152 (1992)].
[11] O. Mishima, L.D. Calvert, and E. Whalley, Nature **314**, 76 (1985).
[12] P. Richet, Nature **331**, 56 (1988).
[13] R.J. Hemley, A.P. Jephcoat, H.K. Mao, L.C. Ming, and M.H. Manghnani, Nature **334**, 52 (1988).
[14] D.D. Klug, Y.P. Handa, J.S. Tse, and E. Whalley, J. Chem. Phys. **90** (4), 2390 (1989).
[15] V.V. Brazhkin, S.V. Popova, and R.N. Voloshin, J. Non-

cryst. Solids **136**, 241 (1991).

[16]N. Binggeli and J.R. Chelikowsky, Phys. Rev. Lett. **69**, 2220 (1992).

[17]M. Imai, T. Minomura, K. Yaoita, and K. Tsuji, *Proceedings of the IV International Conference on High Pressure in Semiconductor Physics, Chalkidiki, Porto Carras, Greece, 1990* (Aristotle University of Thessaloniki, Thessaloniki, 1990), p. 188.

[18]L.G. Khvostantsev, L.F. Vereschagin, and A.P. Novikov, High Temp. High Pressures **9**, 637 (1977).

[19]C.H. Bates, F. Dachille, and R. Roy, Science **147**, 860 (1965).

[20]V.G. Eremenko, Sov. Phys. Solid State **17**, 1647 (1975).

[21]V.D. Blank, Z.V. Malushitskaya, and B.A. Kulnitskii, in *Abstracts of XXX Annual Meeting of Europe High Pressure Research Group* (Institute of Physics, Azerbaijan Academy of Sciences, Baku, 1992), p. 63; Fiz. Tech. Visokih Davlenii **3**, 28 (1993).

[22]L.C. Davis and H. Holloway, Solid State Commun. **64**, 121 (1987).

[23]J.W. Christian, *The Theory of Transformations in Metals and Alloys*, 2nd ed. (Pergamon, Oxford, 1975), Pt. 1.

[24]H. Olijnyk, S.K. Sikka, and W.B. Holzapfel, Phys. Lett. **103A**, 137 (1984).

[25]Y.K. Vohra, K.E. Brister, S. Desgreniers, A.L. Ruoff, K.J. Chang, and M.L. Cohen, Phys Rev. Lett. **56**, 1944 (1986).

[26]H. Olijnyk, High Pressure Res. **10**, 461 (1992).

[27]M.J.P. Musgrave and J.A. Pople, Proc. R. Soc. London **268**, 474 (1962).