

STRUCTURAL MECHANISMS OF Si(Ge) I → III PHASE TRANSFORMATIONS

V. D. Blank, Z. V. Malyushitska, B. A. Kulnitskiy

The Institute for High Pressure Physics of Russian Academy of Sciences, 142092, Troitsk, Moscow region, Russia

The phase transitions in Si and Ge under conditions of shear deformation at pressure have been investigated. The possibility of direct transitions Si (Ge) I → III at pressures $P_{Si} = 2.7 \pm 0.2$ GPa, $P_{Ge} = 3.3 \pm 0.2$ GPa has been shown. On the basis of the experimental data the T-P- γ (shear) phase diagrams of Si and Ge have been conducted structured. It is shown that Si III and Ge III are distorted variants of lonsdeilite-type structure. The dimensional and orientational relationships (OR) between Si (Ge) I and Si (Ge) III-structures have been determined. OR for Si and Ge were found to be the same:

$$(111)_I \parallel (100)_{III},$$

$$[\bar{1}10]_I \parallel [010]_{III}.$$

The determined crystallogometric relations were confirmed by means of the investigations by electron microscopy methods.

Introduction. Silicon and germanium are covalent crystals, which display a semiconductor (I) to metal (II) transition at high pressure. With increasing pressure up to ~ 12 GPa at room temperature Si and Ge transform from normal diamond-cubic structure (I) to the tetragonal β -Sn structure (II). The I → II transition pressure appears to be strongly affected by the presence of shear stresses. On release of pressure metallic phases II transform into metastable semiconducting phases III. J. S. Kasper and S. M. Richards have determined the crystal structures of Si III and Ge III phases [1], but they came to the conclusion that there does not appear to be any simple mechanism of transforming the diamond structure into the new structures, for example, by simple shearing. Si III has a body-centered cubic structure, $a = 6.636 \text{ \AA}$, sp. gr. $Ia\bar{3}$, $Z = 16$. The structure of Ge III is tetragonal, $a = 5.93 \text{ \AA}$, $c = 6.98 \text{ \AA}$, sp. gr. $P4_32_12$, $Z = 12$. Si (Ge) III-phases have distorted tetrahedral bonds and a higher density ($\sim 10\%$) than normal diamond structures I. It is further unclear whether Si (Ge) III are formed from Si (Ge) I or from Si (Ge) II. The transitions between I, II, III phases were found to be very sensitive to shear. The purpose of the present report is to investigate the possibility of the direct Si (Ge) I → III-phase transformations under conditions of shear deformation at high pressure up to 12 GPa.

In order to study the influence of shear deformation on the transitions in Si and Ge the experiments were carried out using electrical resistance and optical properties. In an attempt to shed light on the formation mechanisms for Si (Ge) III we have studied the crystallogometric relations between diamond structures I and metastable phases III. The electron microscopy investigation of the Si (Ge) III → I-phase transformations provided a convincing verification of proposed I-III orientational relationships (OR).

The effect of shear deformation on the phase transitions under high pressure. Diamond anvil cells and Bridgman-type anvil cells were designed for investigations of solids under conditions of uniaxial stress and shear deformation in a plane perpendicular to the stress axis [2-4]. Pressure (up to ~ 50 GPa) is generated by the movement of the piston. A sample under study is placed between two diamond

anvils. The angle of shear can be adjusted by hand or by the electrical motor with any speed. The angle of shear is unlimited.

The calibration of optical untransparent anvils was carried out using two methods: a variation of electrical resistance with pressure in Bi, Pb, Se, Zn S et al. pressure fixed points and the ruby luminescence. In the last case the lower cemented tungsten carbide anvil was replaced with a natural diamond single crystal and as a pressure gauge the ruby $\text{Al}_2\text{O}_3 + 0.5\% \text{Cr}^{3+}$ was added to the Si (Ge) powder in a 1: 30–50 ratio. The pressure distribution in a sample was measured at a constant load that provided a secure determination of the pressure value. The optical and electrical resistivity calibrated curves $P = f(F)$, where F is a load, are consistent well.

For electrical resistance measurements the Si (Ge) samples by size $5 \cdot 10^{-4}$ m were placed in the centre of a tablet which was made of a sturdy pressured paper. A thin copper foil was located on the anvil to improve the contact.

The semiconductor-to-metal transitions in Si and Ge were examined by optical method in the chamber with the diamond anvils ~ 0.6 mm in diameter. The pressure was determined using the variation of R_1 -line wave length of the ruby luminescence: $d\lambda/dP = 0.0365$ nm/kbar [5]. The ruby luminescence was excited by the He-Cd laser ($\lambda = 441.6$ nm). The experiments were performed on base of automatic spectral complex KSWU-23. The Si (Ge) I-II transitions were recorded visually and by means of the telecast apparatus. As the reflection coefficient of a conductor is less than that of a metal the formation of high-pressure metallic phase was observed as a white spot on the background of dark semiconducting phase. Compressing a tablet of a substance under study we observed the appearance of high-pressure phase in the centre of the anvils. With increasing load a size of metal area extended. Experimentally the pressure distribution along the anvil diameter was recorded and a pressure value on the boundary of the semiconductor-to-metal transition was determined before and after shear deformation under constant load. The $\text{Al}_2\text{O}_3 : \text{Cr}^{3+}$ powder with particles sizes 2–3 mkm was deposited on the diamond anvil with a tablet of a substance under study, then it was exposed to light and a ruby luminescence spectrum was picked.

X-ray diffraction studies of samples deformed under pressure were performed on a HZG-4B diffractometer with monochromatized Cu K_α radiation. Thermal analyses were conducted by means of differential scanning microcalorimeter DSM-2M. The electrical resistance measurements were carried out under conditions of constant shear deformation (at the rate $u = 0.14 \frac{\text{degree}}{\text{sec}}$).

Every electrical resistance curve $\frac{\Delta R}{R_0} = f(p)$ for Ge and Si (Fig. 1) contains the two discontinuities:

$$\text{for Ge: } p_1 = 3.4 \pm 0.3 \text{ GPa, } p_2 = 4.2 \pm 0.3 \text{ GPa;}$$

$$\text{for Si: } p_1 = 2.8 \pm 0.2 \text{ GPa, } p_2 = 5.4 \pm 0.4 \text{ GPa.}$$

It was assumed that the first discontinuity was concerned with the phase transition $\text{I} \rightarrow \text{III}$ and the second one — with the phase transition $\text{III} \rightarrow \text{II}$. These results are in agreement with the data of optical measurements. Fig. 2 demonstrates the typical curves of pressure distribution in Ge tablet at uniaxial compression before (a) and after (b) shear deformation. The disposal of semiconductor-metal boundary before and after shear deformation is shown by arrows. The similar

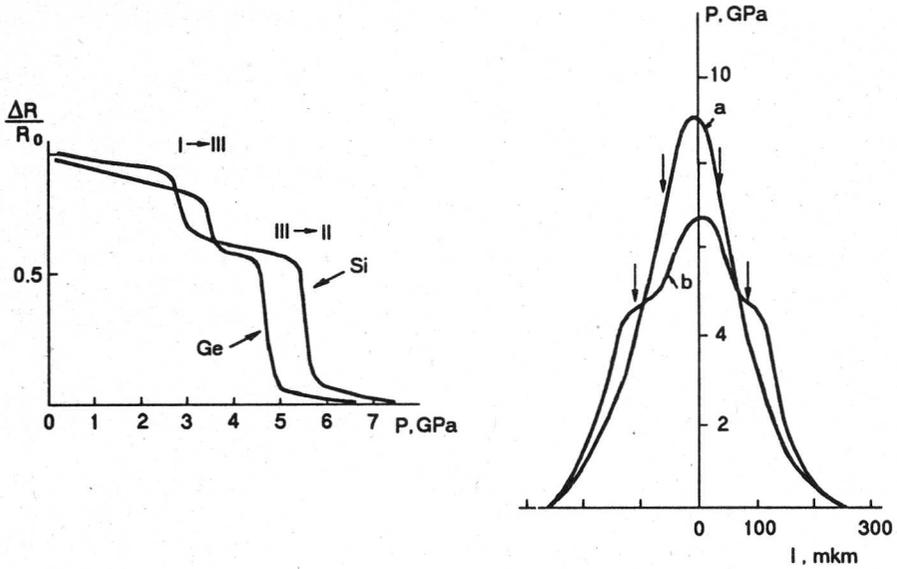


Fig. 1. Electrical resistance variation, $\Delta R/R_0$, for silicon and germanium at constant shear as a function of applied pressure, p

Fig. 2. Pressure distribution determined by optical method in Ge sample

behaviour have pressure distribution curves for silicon. The pressures of semiconductor-metal phase transition at uniaxial stress conditions were found to be the following:

$$\text{for Ge } p = 7.1 \pm 0.4 \text{ GPa,}$$

$$\text{for Si } p = 8.2 \pm 0.3 \text{ GPa.}$$

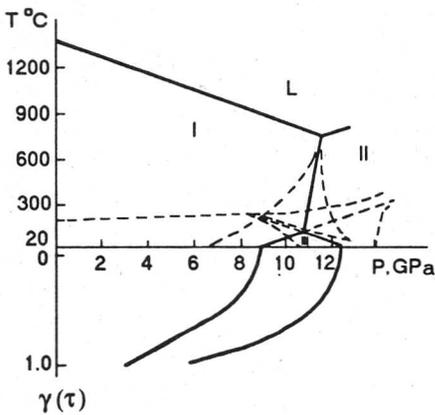
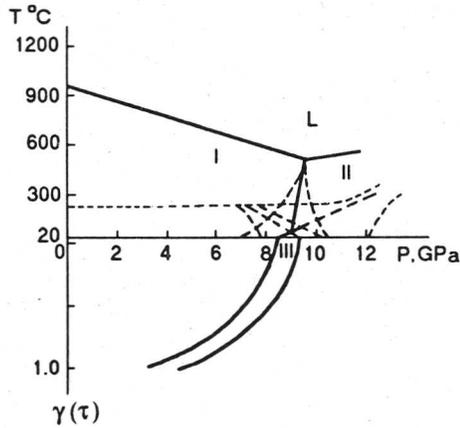
The pressures of this phase transition at shear deformation conditions were found to be the following:

$$\text{for Ge } p = 4.9 \pm 0.4 \text{ GPa,}$$

$$\text{for Si } p = 5.4 \pm 0.4 \text{ GPa.}$$

Table. Pressure for transitions in Si and Ge determined with optical and electrical methods under conditions of shear deformations

Substance	transition I → III	Pressure, GPa				
		shear $\varphi = 10^\circ$	transitions to metallic state		reverse transitions II → I + III	
			uniaxial compression		uniaxial compression	
			optical	electrical	without shear	shear $\varphi = 10^\circ$
Si	2.7 ± 0.2	5.2 ± 0.4	8.2 ± 0.3	10.5 ± 1.0	4.7 ± 0.3	2.7 ± 0.2
Ge	3.3 ± 0.3	4.5 ± 0.4	7.1 ± 0.3	8.5 ± 0.5	4.3 ± 0.3	2.3 ± 0.2


 Fig. 3. p - T - γ phase diagram of silicon

 Fig. 4. p - T - γ phase diagram of germanium

The experimental data are represented in Table.

Analysis of experimental data allows to conclude that at shear deformation conditions in Ge and Si the $I \rightarrow III \rightarrow II$ phase transitions take place, that is the mechanism of the phase transitions at shear deformation conditions is other than the mechanism of the phase transition at hydrostatic conditions ($I \rightarrow II$). The pressure of semiconductor-metal transition is rather less than the pressure of reverse metal-semiconductor transition.

On the basis of the experimental data and publications the T - p - γ (shear) phase diagrams of Si and Ge have been constructed. Fig. 3 demonstrates the Si-phase diagram which is similar to Ge-phase diagram (Fig. 4). The area under horizontal line corresponds to the existence region of Si (Ge) III phase in shear conditions. The hysteresis curves of the $I \rightleftharpoons II$, $I \rightleftharpoons III$ and $II \rightleftharpoons III$ transformations are shown by dotted lines.

Crystallographic analysis of structures. Analysing a tetrahedra arrangement in the Si III-Ge III-diamond-and lonsdeilite structures the two different compression-shear deformations have been suggested by means of those the Si (Ge) $I \rightarrow III$ phase transitions may be carried out. We came to a conclusion that the Si (Ge) III structures may be represented as the two variants of the distorted lonsdeilite type structure with different degree of disordering. In support of this, necessary minimal displacements (within interatomic distances) have been found. The dimensional and orientational relationship between Si (Ge) I and Si (Ge) III structures have been determined.

Si $I \rightarrow III$ transition. The projection of the Si III structure on (100) is shown at Fig. 5. The plane atomic layers at $X = 0.4; 0.6; 0.9$ and 1.1 have been identified with dense-packed layers ...ABBA... of the lonsdeilite structure. We have obtained a lonsdeilite structure from Si III structure using regular tetrahedra which have the edges $a_0\sqrt{2}/2 = 3.84 \text{ \AA}$ where a_0 is unit cell parameter of the Si I. The atomic displacements have been estimated to be within the values $0-1.6 \text{ \AA}$. The mechanism of transforming lonsdeilite to the Si III-structure incorporates the 13.6 % compression of all dense-packed layers along $[\bar{1}10]$ of the original diamond structure. This compression is accompanied by a rupture of every layer on the

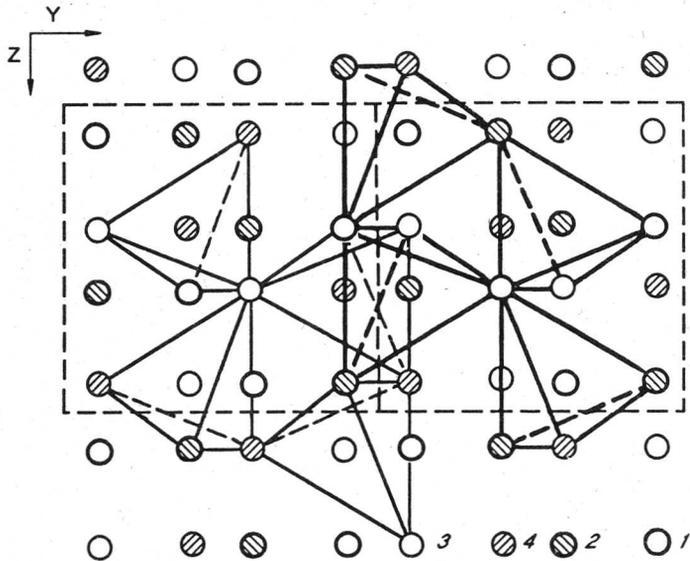


Fig. 5. Projection of the Si III-structure on (100). The elevation along X is denoted by number 1, 2, 3, 4, which correspond $X = 0.4; 0.6; 0.9; 1.1$ in fractions of the cell length, respectively

isolated plane zigzag chains and its alternative shearing along $[11\bar{2}]$ that results in the 5.8 % expansion along $[111]$ of the diamond structure. The relations of the Si I and Si III-structure correspondence have been found as follows:

$$a_1 = 2/3a_0\sqrt{3} = 6.27 \text{ \AA}; \quad b_1 = a_0\sqrt{2} = 7.68 \text{ \AA}; \quad c_1 = 1/2a_0\sqrt{6} = 6.65 \text{ \AA}$$

where $a_0 = 5.43 \text{ \AA}$ is unit cell parameter of Si I; a_1, b_1, c_1 are the parameters of the Si I-structure cell with $Z = 16$ that is equivalent to unit cell of Si III. The 8.7 % volume change under the Si I \rightarrow III transition is consistent with experimental data [1]. The presumed atomic displacements have made it possible to determine the tetrahedra arrangement in the Si III structure (see Fig. 5). OR for I \rightarrow III phase transformations in silicon and germanium (Fig. 6) are the same: $(111)_I \parallel (100)_{III}$ and $[\bar{1}10]_I \parallel [010]_{III}$.

Ge I \rightarrow III transition. On examination of the Ge III-structure projection on (100) shown in Fig. 7 we can see that the Ge III structure contains the vertical alternative-directed chains of strongly distorted tetrahedra. These tetrahedra chains arranging between the parallel sections of base zigzag lines forms the rows. In Fig. 7 zigzag lines have been marked using the angles α which were equal 120° . Assuming that the Ge III structure may be effected by transforming of the straight lonsdeilite rows into zigzag tetrahedra rows we carried out a corresponding geometric construction which we have named "a goffer". The Ge III-structure projections on (100) and (010) have been obtained thus. As a general deformation the lonsdeilite-to-Si III transformation incorporates the 9.2 % compression along $[111]$ of diamond structure, while along $[\bar{1}10]$ and $[11\bar{2}]$ of the relative perpendicular directions the dimensions original structure conserve constant within accuracy to $\pm 1\%$.

The relations of Ge I and Ge III-structure correspondence have been found as follows:

$$a_1 = 2/3a_0\sqrt{3} = 6.53 \text{ \AA}; \quad b_1 = 3/4a_0\sqrt{2} = 6.00 \text{ \AA}; \quad c_1 = 1/2a_0\sqrt{6} = 6.92 \text{ \AA}$$

where $a_0 = 5.66 \text{ \AA}$ is unit cell parameter of Ge I; a_1, b_1, c_1 are the parameters of Ge I-structure cell with $Z = 12$ that is equivalent to unit cell of Ge III. The 9.6 % volume change under the Ge I \rightarrow III transition is consistent with experimental data [1]. OR between Ge I and Ge III-structures is shown in Fig. 6. We came to the conclusion that a formation of Ge III is caused by little atomic displacements (from 0.64 to 2.29 \AA), however, they are distinguished by the value and the sign in all directions.

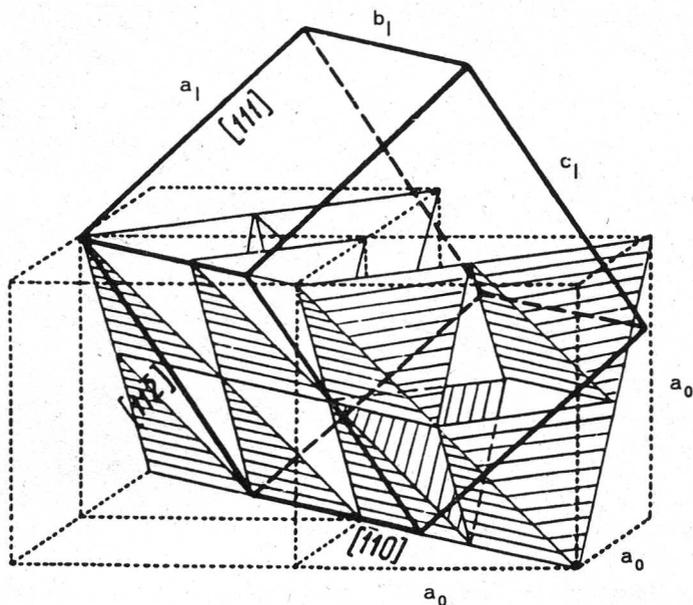


Fig. 6. Tetrahedra arrangement in the unit cell of Ge I and the location of the Ge III-structure unit cell

It is probably this transition should be accompanied by a rupture of the most bondings. In consequence the Ge I \rightarrow III transformation may be represented as disordering of diamond-type structure into amorphous-like state that is confirmed by a physical properties similarity of Ge III and amorphous Ge [6]. The further details about the structural mechanisms of Si (Ge) I \rightarrow III phase transitions are in Ref. [7,8].

Electron microscopy investigation. High pressure and shear deformation treated silicon and germanium have been investigated by means of transmission electron microscopy. The samples consisted mainly of retained Si I (Ge I) phase, while in some regions Si III (Ge III) fragments were observed.

Fig. 8 *a, b* demonstrates the two-phase region of silicon object. The fragment of high pressure phase Si III having irregular shape, disposes inside the initial grain of Si I phase. Dark field image (Fig. 8, *b*) represents the phase III as the part of region with irregular shape.

The superimposed selected-area field diffraction pattern and its diagram is shown in Fig. 8 *c, d*. We can distinguish here two different spot patterns, one of them due to the Si I-phase and the other due to the Si III-phase. Indexation of the patterns gives the following zone axes: $[14\bar{1}]_{\text{Si I}}$ and $[211]_{\text{Si III}}$. Further we choose on the pattern coincident spots (belonging to the same radius-vectors). These spots are

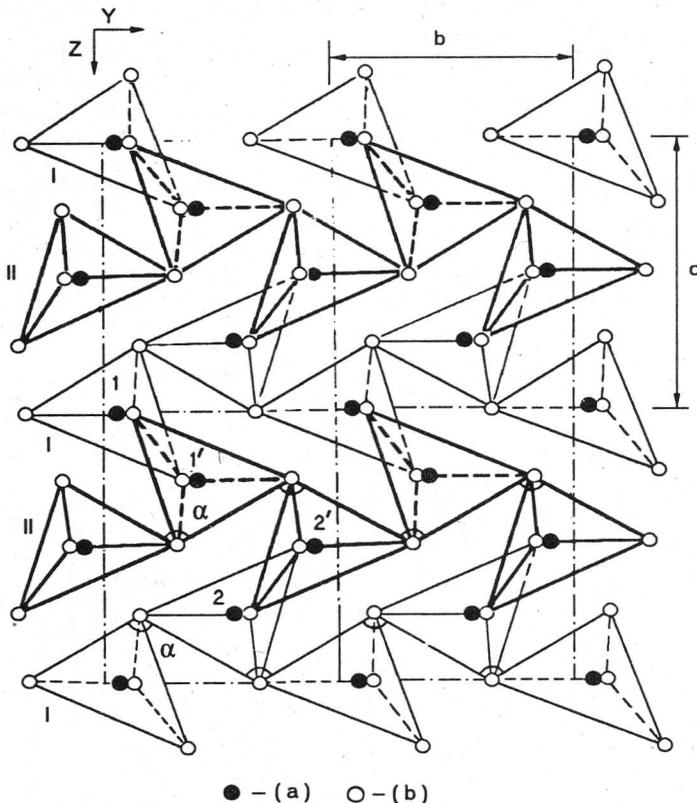


Fig. 7. Projection of the Ge III-structure on (100). (a) and (b) correspond atoms on centres and on vertices of distorted tetrahedra; 1.1' and 2.2' are down- and upward-directed tetrahedra; I and II is lower and upper tetrahedra layer, respectively

$(3\bar{1}\bar{1})_{\text{Si I}}$ and $(1\bar{2}0)_{\text{Si III}}$. The angle between these two radius-vectors is less than three degrees.

The OR between Si I and Si III can be described by matrices which determine the orientational and dimensional correspondence between the atomic lattices. As soon as the both lattices have cubic symmetry the matrices for the planes and for the dimensions are the same:

$$\begin{pmatrix} h \\ k \\ l \end{pmatrix}_{\text{Si III}} = \begin{pmatrix} 0.48 & 0.48 & -0.48 \\ -0.43 & 0.43 & 0 \\ 0.33 & 0.33 & 0.66 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}_{\text{Si I}} \quad (1)$$

The multiplication of the matrix and $[14\bar{1}]_{\text{Si I}}$ direction indices leads to [2.88; 1.29; 1]. The angle between this direction and [211] in the diamond-structure is 6.8°. Putting the indices $(3\bar{1}\bar{1})_{\text{Si I}}$ into (1) gives the coordinates, which differs from $(1\bar{2}0)_{\text{Si III}}$ for less than 3°.

The little discrepancy has been found between experimental data and theory. This discrepancy was found to be within the limits of experimental error.

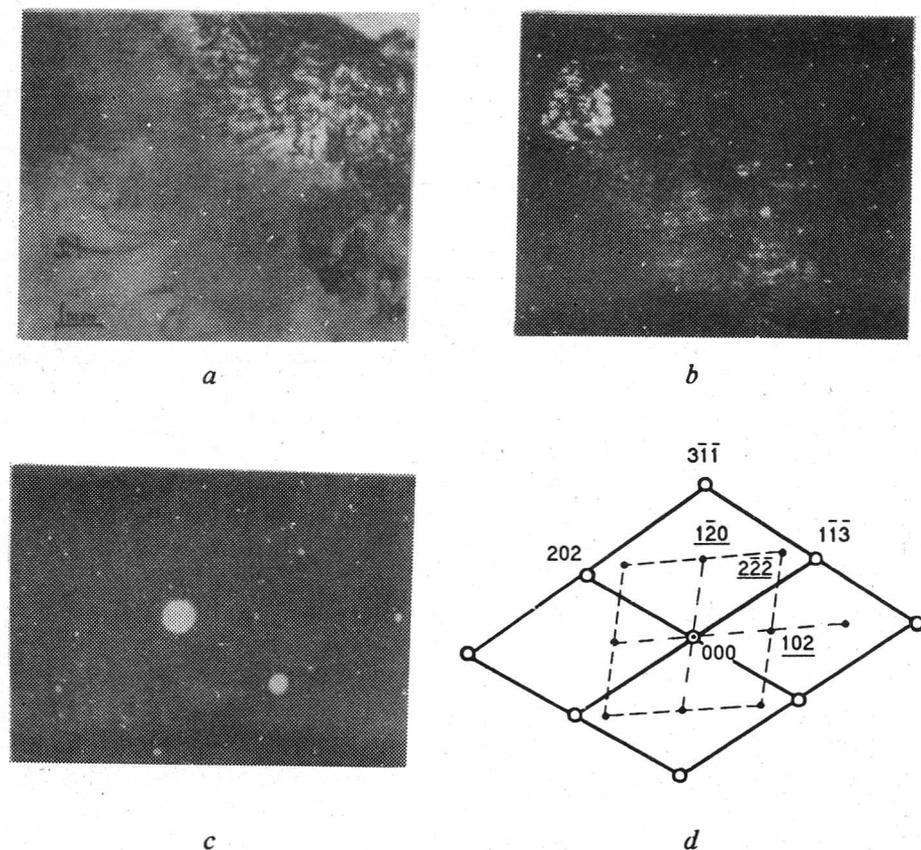


Fig. 8. Region of pressure- and shear deformation-treated Si foil with Si I- and III-phase: *a* — Bright-field micrograph; *b* — Dark-field image in $(120)_{\text{Si III}}$; *c* — Superimposed selected-area field diffraction pattern; *d* — Diagram of the pattern

The similar analysis has been carried out for five superimposed electron diffraction patterns of silicon. All the results were found to be the same. Analogous results have been observed for germanium.

Conclusions.

1. The experimental evidence of possibility of direct Si (Ge) I \rightarrow III phase transformations have been received.
2. The dimensional and orientational relationships between Si (Ge) I and Si (Ge) III crystal structures have been determined by the crystallographic analysis.
3. The determined crystallographic relations were confirmed by means of the Electron Microscopy investigations.

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