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Polymorphism of silicon at high pressures

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Two methods (x-ray diffraction and the electrical resistivity measurements) were used in a study of the polymorphism of silicon at room temperature up to 160 kbar. The onset of the Si I→Si II semiconductor-metal transition was observed at $p \sim 80$ kbar. The two-phase region Si I+Si II extended above 160 kbar. The dependences of the change in the relative volumes with pressure were determined for the Si I and Si II phases. The volume change in the two-phase region (100–160 kbar) amounted to ~20%. The semiconductor phase Si III was found to be intermediate between the original diamond-type Si I and the metal Si II modifications.

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In spite of the fact that silicon has been the subject of fundamental investigations for many years and has been studied both under normal and hydrostatic pressure conditions,[1-4] some of the aspects of the polymorphism of this element are not yet clear. In particular, the ranges of stability of the various modifications have not yet been determined in the T–p diagram of silicon. We shall report a study of the polymorphism of silicon which was carried out at room temperature up to ~160 kbar. We used two methods: x-ray diffraction and measurements of the electrical resistivity in a high-pressure x-ray chamber[5].

The diffraction studies were carried out using the AgK_α radiation produced by a sharp-focus x-ray tube with a rotating anode (Rigaku-Denki RU-3H model) with a maximum output power of 6 kW (100 mA×60 kV). The small dimensions of a sample under high-pressure conditions (0.25 mm diameter and $h = 0.2$ mm height) determined the selection of the point projection of the focal spot (0.5×0.5 mm). The use of the RU-3H source required development of a special collating system and a press inside which a high-pressure chamber was placed.

The diffraction pattern was recorded of a photographic film placed in a cassette. The cassette window was covered by a palladium foil, which acted as the filter of the AgK_β radiation. The working conditions in the x-ray tube were 70 mA×55 kV. Under normal conditions the exposure time was 15 min but at high pressures it was 40–50 min.

We investigated p-type silicon with carrier density 10^{16} cm^{-3}. The silicon powder was first annealed at $T = 400$°C for 30–40 h in an evacuated ampoule. The pressure was estimated by mixing the silicon powder with NaCl or NaF powders. The pressure was deduced by x-ray diffraction from the compressibility of NaCl[6] or NaF.[7,8] The unit cell parameter of NaCl was calculated from the two reflections (200) and (220) but in the absence of superposition of the NaCl and Si I lines (diamond-type structure) use was made of the (222) and (420) reflections in the pressure range $p > 90$ kbar. The unit cell parameter of NaF was deduced from the (200), (220), (222) reflections. The pressure was estimated to within ~5%.

The electrical resistivity measurements were carried out by a two-contact method and the current was passed through hard-alloy anvils, insulated from the press by Textolite spacers. In some experiments the measurements of $R(p)$ were carried out by a method similar to that employed by Jeffery *et al.*[9] A channel in a pellet 0.35 mm in diameter was filled with NaCl and after a preliminary compaction, a recess 0.15 mm in diameter was drilled to accept the silicon sample. Some of the electrical resistivity measurements were carried out on Si samples without NaCl. In the process of measurements of $R(p)$ we always recorded the diffraction pattern of Si+NaCl or Si. This enabled us to relate the changes in the resistivity under pressure with changes in the crystal structure. In the experiments carried out on "pure" silicon the pressure was estimated from the compressibility of Si I using the data obtained for the NaCl or NaF mixtures.

Figures 1a and 1b show typical pressure dependences of the resistance of silicon. According to these dependences the fall of the resistance by approximately five orders of magnitude is followed by a kink at $p \sim 65$–70 kbar (Fig. 1a) or at $p \sim 75$–80 kbar (Fig. 1b) and a small change in the resistance, typical of the semiconductor—metal transitions. The x-ray diffraction patterns indicated the appearance of the strongest lines of the Si II phase (structure type β-Sn) at pressures of at least

75–80 kbar and right up to 160 kbar there was a range of coexistence of the Si I + Si II phases. Figure 1 demonstrates the influence of the pressure-transmitting medium on the transition. The fall of the resistance (Fig. 1) can clearly be explained by the fact that the appearance of a small amount of the metal phase Si II is sufficient to shunt the bulk of the semiconductor sample.

The dependences v/v_0 for silicon are plotted on the basis of the data obtained from 90 x-ray diffraction patterns. The parameters of the unit cell of Si II were determined from the (111), (220), (311), (400), (331), (422), and (511) reflections, the parameters of the Si II from the (200), (101) and (220), (211) doublets; in those cases when they were superimposed, use was made of the $c/a = 0.525 \pm 0.005$ ratio. The measured relative volumes of Si I and Si II were approximated by the method of least squares in accordance with the equation

$$v_1/v_{01} = a_0 + a_1(v_2/v_{02}) + a_2(v_2/v_{02})^2,$$

where v_{02} and v_2 are the volumes of the "standard" (NaCl or NaF) under normal conditions and under pressure. The coefficients of the above equations for Si I were as follows: $a_0 = 0.0767$, $a_1 = 1.6240$, $a_2 = -0.7015$, standard approximation error 0.0006; In the case of Si II: $a_0 = 0.3851$, $a_1 = 0.6630$, $a_2 = -0.3112$, standard approximation error 0.0001.

Figure 2 gives the results of the x-ray determinations of v/v_0 for Si I and Si II. The dependence of the relative change in volume on the pressure for the Si I phase (our results) is designated by 4 and lies between curve 1 (volume data of Bridgman[10]) and curve 2 (obtained in an x-ray cubic unit producing quasihydrostatic compression[11]). The volume data up to 40 kbar[13] and the x-ray diffraction data up to 80 kbar[14] are practically identical with curve 4. The change in volume as a result of the Si I → Si II transition is 20% at $p = 100$ kbar and 19.5% at $p = 150$ kbar. As in earlier investigations,[15–17] the difference between the dependences v/v_0 obtained for the Si I phase may be attributed to the influence of an inhomogeneous distribution of the stresses on the estimate of the pressure in a solid.

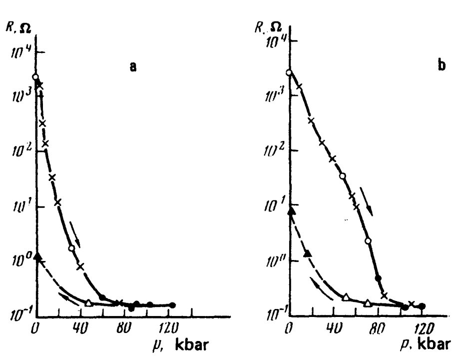

FIG. 1. Dependences of the electrical resistance of Si on pressure: a) $R(p)$ curve for Si placed directly in a boron pellet; b) $R(p)$ curve for Si surrounded by NaCl. Experimental points of $R(p)$: ×) without x-ray diffraction; ○), ●), △), ▲) with x-ray diffraction; ○) Si I; ○) Si I +Si II; △) Si I +Si II +Si III; ▲) Si I +Si III.

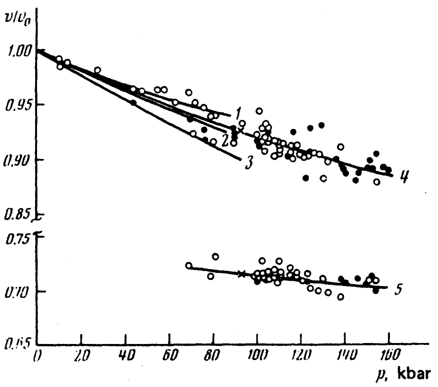

FIG. 2. Pressure dependences of v/v_0 for silicon: 1) v/v_0 for Si I (Bridgman's data[10]); 2), 3) v/v_0 for Si I (recent data[11,12]); 4) v/v_0 for Si I (our results); 5) v/v_0 for Si II (our results); ○) pressure estimated from the compressibility of NaCl[6]; ●) pressure estimated from the compressibility of NaF[7,8]; ×) results taken from Jamieson's paper[2] (the pressure was estimated on the basis of our data).

The influence of shear stresses on the phase boundaries of the T–p diagram of silicon has been pointed out on many occasions.[1–4] In particular, this may give rise to a discrepancy between the pressure at the onset of the transition to the metal state obtained in different high-pressure systems. This is further evidence that silicon cannot be used as a standard in pressure measurements.

Our x-ray diffraction study established that successive step like increase and reduction of the load produced the semiconductor phase Si III with the bcc lattice and $Z = 16$[4]. During unloading, this phase was observed at pressures below ~45 kbar. In the same way as in the investigations of Bundy[3] and of Wentorf and Kasper,[4] complete unloading resulted in retention of Si III in the metastable state mixed with the original Si I modification. The results of the x-ray diffraction investigations indicated that Si III, which is a high-pressure phase, is intermediate between Si I and Si II and that shear stressed facilitate the appearance and growth of this phase.

It follows that the general features of the phase diagram of silicon are similar to the phase diagram of germanium, given by Cannon,[18] except that the Si III and Ge III phases have different crystal structures.

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Magnetic properties and spin-reorientation phase transitions in intermetallic compounds $Nd_{1-x}U_xCo_5$

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The crystal structure of powders and the magnetic moments and magnetocrystalline anisotropy of single crystals, as functions of the uranium concentration and the temperature, have been investigated for the compounds $Nd_{1-x}U_xCo_5$. For comparison, the results of similar investigations are presented for $Y_{1-x}U_xCo_5$. In the compounds studied, the uranium is apparently nonmagnetic and gives up all electrons from its $5f$, $6d$, and $7s$ electronic shells to the $3d$ band of the cobalt, thereby decreasing the value of its mean magnetic moment. By variation of the uranium concentration, it is possible to vary substantially the temperature range of spin-reorientation magnetic phase transitions.

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1. INTRODUCTION

In recent years, a large number of uranium compounds have been synthesized, and their crystal structure and magnetic properties have been studied.[1] Some general rules have been established for the appearance of magnetism in them, as it depends on the U-U distance in the crystal lattice. In particular, it has been shown that in compounds of uranium with nonmagnetic elements, in which the U-U distance is larger than $\sim$3.5 Å, the uranium ions possess a magnetic moment that is due to the unfilled $5f$ electronic shell. In such compounds, high values of the magnetocrystalline anisotropy and of the magnetostriction may be observed in consequence of electrostatic interaction of the $5f$ shell with the crystalline field of the ligands,[2,3] as in the rare-earth metals and their alloys. At smaller U-U distances, the $5f$ electrons, together with the $6d$ and $7s$ electrons, apparently become collectivized, and the uranium ion (U^{6+}) is nonmagnetic. But so far there have been very few investigations devoted to clarification of the behavior of uranium in intermetallic compounds with rare-earth (R) and $3d$ transitional (T) metals, and of its effect on the values of the magnetic moment and magnetocrystalline anisotropy of these compounds. It is therefore of interest to study the magnetic properties of quasibinary compounds of the type $R_{1-x}U_xCo_5$. As is well known,[4] high-anisotropy alloys of the type RCo_5 are now widely used as magnetically hard materials. And those in which a spin-reorientation magnetic phase transition occurs on change of temperature 1) ($NdCo_5$, $PrCo_5$, $TbCo_5$, etc.) many find application as thermally sensitive elements (for example, in thermomagnetic generators [6] or thermometers [7]), or as media for thermomagnetic registration of information on magnetic domains.[8]

The present paper reports the results of an investigation of the crystal structure, magnetic moment, magnetocrystalline anisotropy, and spin-reorientation phase transitions in monocrystals of the quasibinary compounds $Nd_{1-x}U_xCo_5$. For comparison, magnetic properties are presented for monocrystals of $Y_{1-x}U_xCo_5$.

2. EXPERIMENTAL METHOD

The $R_{1-x}U_xCo_5$ ($0 \leq x < 1$) alloys were melted in an induction furnace in alundum crucibles, in a helium atmosphere. The phase composition of the alloys was monitored by metallographic, x-ray, and thermomagnetic methods. An x-ray determination of the lattice parameters of powder specimens of the alloys was made on a diffractometer URS-50IM, in K_α Fe radiation. For measurement of the magnetic properties, the following were used: a vibration magnetometer with static field up to 100 kOe ($77\ K \leq T \leq 1000\ K$), a pulse solenoid with field up to 100 kOe ($4.2 \leq T \leq 300$ K), and a torque magnetometer with field up to 28 kOe ($77\ K \leq T \leq 300\ K$).