Neutron Diffraction Investigation of the Structural Transition in HgSe$_{1-x}$S$_x$ Ternary Mercury Chalcogenide Systems at High Pressures

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Abstract—The structure of HgSe$_{1-x}$S$_x$ ternary mercury chalcogenides at high pressures up to 35 kbar is investigated by neutron diffraction. It is found under pressure, that the HgSe$_{1-x}$S$_x$ compounds undergo a phase transition from the cubic sphalerite-type to the hexagonal cinnabar-type structure, which is accompanied by a jumpwise change in the unit cell volume and interatomic distances. The unit cell parameters and the positional parameters of Hg and Se (S) atoms in the high-pressure hexagonal phase are determined. A two-phase state is revealed in the phase transition region. © 2001 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

The investigation of mercury chalcogenides HgX (where X = S, Se, and Te) under pressure is of particular interest, because these compounds undergo structural [1–9] and electron phase transitions [10]. In recent years, the effect of pressure on the structure of compounds in binary mercury chalcogenide systems has been intensively studied by x-ray diffraction [5–9]. At pressure $P \approx 8–14$ kbar and room temperature, the HgSe and HgTe compounds undergo a structural phase transition from the cubic sphalerite phase (space group $F43m$) to the hexagonal cinnabar phase (space group $P3_{1}21$) [7], which is attended by a semimetal–semiconductor electron transition [10]. Bridgman [1] was the first to propose the structure of the high-pressure phase in HgSe and HgTe, which was subsequently confirmed in [2–5]. Another representative of this class of compounds, namely, HgS (cinnabar), has a similar hexagonal structure even under normal conditions [5]. High-pressure phases with a cinnabar-type structure are also observed in ZnTe and CdTe [6, 7]. As the pressure increases, chalcogenides of mercury, cadmium, and zinc undergo a phase transition from the hexagonal cinnabar-type to the cubic NaCl-type structure [6, 7]. The pressure of this transition increases with a decrease in the radius of the chalcogenide ion and is approximately equal to 80 kbar for HgTe and 160 kbar for HgSe and exceeds 200 kbar for HgS [5].

The cinnabar structure (Fig. 1) is intermediate between the cubic sphalerite structure with a coordination number of four and the NaCl structure with a coordination number of six and can be treated as a distorted NaCl lattice [7]. This structure is characterized by two positional parameters: Hg atoms occupy the 3a positions ($u$, 0, 1/3) and Se (S) atoms are located at the 3b positions ($v$, 0, 5/6) in the unit cell. The cinnabar structure in different compounds can differ substantially

Fig. 1. Projection of the hexagonal cinnabar structure onto the $xy$ plane. The $z$ coordinates of the chalcogen $X$ ($X = \text{Se}$ and S) and mercury atoms and the shortest distances $\text{Hg}1$–$X$, $\text{Hg}2$–$X$, and $\text{Hg}3$–$X$ are shown.
depending on the positional parameters \( u \) and \( v \). For example, the coordination number in the cinnabar structure is equal to \( 2 + 4 \) in HgS and \( 4 + 2 \) in HgTe and CdTe [6, 9].

The effect of pressure on the structure of compounds in the HgSe\(_{1-x}\)S\(_x\) and HgTe\(_{1-x}\)S\(_x\) ternary mercury chalcogenide systems has not been adequately investigated. It is known that under pressure, these compounds undergo electron phase transitions of the semimetal–semiconductor type which noticeably affect the thermoelectric and galvanomagnetic properties [11–14]. It should be noted that the resistivity jumps observed in HgTe and HgSe binary compounds correspond to the phase transition from the cubic sphalerite-type to the hexagonal cinnabar-type structure [1–7]. It was assumed that a transition of the sphalerite–cinnabar type also occurs in ternary compounds [11]. However, direct structural investigations of high-pressure phases in these compounds were not performed.

Since the amplitude of x-ray scattering by Hg atoms is considerably larger than that for chalcogenide atoms (\( X = \text{Se and S} \)), the accuracy in determining the location of \( X \) atoms in the structure by using x-ray diffraction analysis can be insufficiently high. It is more preferable to investigate the structure of mercury chalcogenides by neutron diffraction, because the amplitudes of neutron scattering by Hg and \( X \) atoms are comparable in magnitude.

In the present work, the structure of HgSe\(_{1-x}\)S\(_x\) ternary mercury chalcogenide compounds at pressures up to 35 kbar was studied by neutron powder diffraction.

2. EXPERIMENTAL TECHNIQUE

We studied the HgSe\(_{1-x}\)S\(_x\) compounds with sulfur content \( x = 0.302, 0.508, \) and 0.601, which were used in compression measurements of the electrical resistivity in our earlier works [11–14]. The synthesis of the samples was described in [11, 12]. The samples were characterized by x-ray and neutron diffraction analyses. The sample composition was determined by x-ray microanalysis on a Superprobe-JCXA-733 spectrometer [12].

The neutron diffraction investigations at pressures up to 10 kbar were performed on an IVV-2M stationary reactor (Institute of Metal Physics, Ural Division, Russian Academy of Sciences, Yekaterinburg) using a D7a diffractometer under normal conditions and a D3b diffractometer at high pressures. The wavelength \( \lambda \) of monochromatic neutrons was equal to 1.66 Å. The resolutions \( \Delta d/d \) of the diffractometers were 0.023 and 0.03, respectively. The time taken for one neutron diffraction pattern to be measured was approximately 12 h. Hydrostatic pressure was produced in a high-pressure piston–cylinder-type chamber fabricated from a TiZr alloy with an operating volume \( V \sim 1 \text{ cm}^3 \) [15]. Liquid Freon-11 with a boiling temperature of \( 25^\circ \text{C} \) served as the pressure-transferring medium. The usability of Freon-11 was limited by its crystallization at a pressure of 9.5 kbar.

The experiments at higher pressures (up to 35 kbar) were carried out in high-pressure chambers with sapphire anvils [16] with the use of a DN-12 spectrometer [17] and an IBR-2 pulsed high-flux reactor (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna). In this case, the volume \( V \) of the studied samples was \( \sim 2 \text{ mm}^3 \). The diffraction spectra were recorded at the scattering angle \( 2\theta = 90^\circ \). The diffractometer resolution \( \Delta d/d \) for this scattering angle at wavelength \( \lambda = 2 \text{ Å} \) was 0.02. The characteristic time of measuring one spectrum was 20 h. The pressure in the chamber was measured from the shift of the ruby luminescence line with an accuracy of 0.5 kbar. All the measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

Analysis of the x-ray and neutron diffraction patterns revealed that, under normal conditions, the HgSe\(_{1-x}\)S\(_x\) \((0.03 \leq x \leq 0.6)\) crystals have a cubic sphalerite structure and the unit cell parameter almost linearly decreases with an increase in the sulfur content \( x \) (Fig. 2).

Figure 3 displays fragments of the neutron diffraction patterns of the HgSe\(_{0.5}\)S\(_{0.5}\) compound at different pressures, which were recorded using the D3b diffractometer. The neutron diffraction patterns at normal pressure and \( P \approx 3 \text{ kbar} \) are virtually identical. At \( P = 6 \text{ kbar} \), the diffraction patterns exhibit new peaks whose intensities increase with a further increase in pressure, whereas the intensities of the reflections associated with the initial