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STUDY OF SOLID SOLUTIONS OF THE SYSTEMS

HgTe—HgS and HgSe—HgS

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Systems of solid solutions of binary compounds of the type A^II B^VI with isovalent cation substitution (^1-5) have been studied comparatively well, whereas solid solutions of such compounds with isovalent anion substitution remain almost uninvestigated. The systems HgS_xTe_{1-x} and HgS_xSe_{1-x}, which belong to the latter group and in which the existence of solid solutions was shown by E. I. Nikol' skaya and A. R. Regel' (^6-8), are of considerable interest because of the sharp difference in the electrophysical properties of the initial components; this makes it possible to hope to obtain a large set of semiconductor materials with smoothly adjustable parameters.

The synthesis of samples of various compositions ($0 \leq x \leq 0.4$) was carried out by us by the usual method—by melting the initial elements in evacuated quartz ampoules with the use of vibrational mixing and subsequent prolonged annealing at a temperature 200° below the melting point of each composition. Single crystals 10-14 mm in diameter and 20-40 mm long were grown by the Bridgman-Stockbarger methods and by horizontal zone melting, with subsequent prolonged annealing. Synthesis and crystal growth were carried out in one sealed ampoule without opening it.

Metallographic and x-ray diffraction investigations were performed on the samples, as well as quantitative chemical analysis of all the principal components in order to refine the compositions. The radioactive sulfur isotope S^35 was introduced into individual ingots to monitor the distribution of sulfur along the length and cross section of the ingot (by radioactivation, autoradiographic, and radiochemical methods). The composition of series samples was also determined by measuring the density and comparing it with the theoretically calculated value (^4). The totality of the results of these measurements shows that in the HgTe—HgS system there is practically no distribution of components along the length and cross section of the ingot, whereas in the HgSe—HgS system such a

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

distribution was observed.

Samples of the HgS_xTe_{1-x} system with $x > 0.2$ over the entire temperature interval studied (15–400° K) had an electronic type of conductivity. Samples of compositions $0 \leq x \leq 0.2$ in the investigated temperature interval had a negative sign of the Hall coefficient, although the temperature dependence indicated the presence of charge carriers of two types (electrons and holes) with a large mobility ratio; indeed, some of these samples, upon cooling to 10° K, showed a positive Hall coefficient.

Figure 1 presents the temperature dependences of the electrical conductivity and the Hall coefficient for samples of various composition. The curves for samples with $x = 0.05$; 0.10 and 0.20 have (at least in their high-temperature part) the form typical of semiconductors, whereas

as the curves for the sample with $x = 0.40$ reveal a metallic behavior of the electrical conductivity and a weak temperature dependence of the Hall coefficient (interpretation of the latter is still premature).

Fig. 1. Temperature dependence of the electrical conductivity (a) and the Hall coefficient (b) for samples of the system HgS_xTe_{1-x} with $x = 0.05$ (1); 0.10 (2); 0.20 (3) and 0.40 (4)

Investigation of the effect of annealing in various media on the electrical properties of samples of this system showed that, for samples with a low sulfur content, annealing in saturated mercury vapor improves the parameters;

Fig. 2. Temperature dependence of the electrical conductivity (a) and the Hall coefficient (b) for samples of the system HgS_xSe_{1-x} with $x = 0.05$ (1); 0.20 (2); 0.30 (3); 0.40 (4)

apparently, with such annealing the number of mercury vacancies (which determine the type of conductivity of the material) decreases. Annealing in mercury vapor has a very slight effect on the properties of samples of composition $x = 0.40$; annealing in saturated sulfur vapor has a considerably greater effect; the latter circumstance is apparently explained by the increasing complexity of the defect structure with increasing sulfur content (along with mercury defects, sulfur defects begin to play a role).

Samples of the system HgS_xSe_{1-x} in the temperature interval studied had electron-type conductivity. Figure 2 presents typical curves of the temperature dependences of the electrical conductivity and the Hall coefficient for samples

Fig. 3

Figure 3: Fig. 3

of various compositions. Up to the composition corresponding to $x \simeq 0.30$, the Hall coefficient (in the high-temperature part of the curves) changes little with temperature, and the temperature dependence of the electrical conductivity characterizes the materials as strongly degenerate semiconductors or semimetals. For the composition with $x = 0.40$, both parameters show semiconductor dependences; the band-gap width determined from the temperature behavior of the Hall coefficient is about 0.10 eV.

At a temperature of 77°K, the dependence of the Hall coefficient and thermo-emf on the magnetic-field strength was measured for samples of different composition, and the effective electron mass was determined (9); it increases with increasing sulfur content from $0.014\,m_0$ at $x = 0.05$ to $0.289\,m_0$ at $x = 0.30$.

For samples of this system with thicknesses of 15–30 μ, the spectral distribution of the absorption coefficient was measured at room temperature; in all cases the dependence of its square on photon energy had a significant linear portion, making it possible to determine the energy gap corresponding to direct optical transitions. For samples with $x = 0.05$, 0.10, and 0.30 it was about 0.145, 0.155, and 0.205 eV, respectively, whereas literature data give for this gap in mercury selenide a value of 0.10 eV (10). The long-wavelength regions of the curves of the spectral distribution of the absorption coefficient had portions where the latter depended linearly on the square of the wavelength (Fig. 3), making it possible to calculate the effective electron mass, increasing from $0.0070\,m_0$ at $x = 0.05$ to $0.0085\,m_0$ at $x = 0.10$ and $0.0210\,m_0$ at $x = 0.30$, which agrees well with the literature (“optical”) data for mercury selenide (11), whereas the results of determining the effective electron mass from electrical measurements agree satisfactorily with the corresponding literature data (12) for mercury selenide.

Fig. 3. Dependence of the absorption coefficient at 300°K on the square of the wavelength for samples of the system HgS_xSe_{1-x} with $x = 0.05$ (1), 0.10 (2), and 0.30 (3)

The effect of annealing in vacuum on the properties of samples of the system was investigated; such annealing somewhat decreases the carrier concentration and greatly increases their mobility, especially at low (15°K) temperature.

Photoconductive effects were measured on samples of both systems with thicknesses of 40–200 μ at temperatures of 15, 77, and 300°K. In all samples a photothermomagnetic effect was observed, and in some—a bolometric effect (13); the nature of these could be judged from their absolute magnitude, their dependence on sample thickness and temperature, and also from the phase-shift angle of the signal relative to the phase of the incident light flux. Thus, for the photothermomagnetic effect an inverse proportional dependence of the signal on sample thickness was observed, a sharp drop of the signal when the temperature was lowered to 15°K, and a phase-shift angle close to 45°, which was also observed in samples of bismuth-antimony alloys (14).

In individual samples of the system $\mathrm{HgS}_x\mathrm{Se}_{1-x}$ with $x \geq 0.20$, quantum effects were observed: photomagnetic effect and photoconductivity with a carrier lifetime of about 1 μsec, determined by the method of the ratio of the signals of these effects (15).

The foregoing makes it possible to conclude that, if in the system $\mathrm{HgS}_x\mathrm{Se}_{1-x}$ $(0 \leq x \leq 0.4)$ there are both semimetallic and semiconducting compositions (with the transition metal-semiconductor, accompanied by a sharp change in properties, occurring with increasing sulfur content in the solid solution), then in the system $\mathrm{HgS}_x\mathrm{Te}_{1-x}$ the opposite picture is observed—the weakening of semiconducting properties with increasing sulfur content in the samples (which may be explained either by the occurring

with the corresponding increase in structural defectiveness, or a change in band overlap).

At present, single crystals of these systems are being grown by the Czochralski method, and further investigations of optical transmission and reflection are being carried out in order to refine the band structure of the materials.

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Note: Figure translations are in progress. See original paper for figures.