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PROPERTIES OF Fe DOPED β -HgS UNDER HYDROSTATIC PRESSURE*

W. SZUSZKIEWICZ^a, C. SKIERBISZEWSKI^b, W. PASZKOWICZ^a, K. DYBKÓ^a,
J. DOMAGALA^a, E. DYNOWSKA^a, B. WITKOWSKA^a AND P. ZINN^c

^aInstitute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warsaw, Poland

^bHigh Pressure Research Center Unipress, Sokołowska 29, 01-142 Warsaw, Poland

^cGeoForschungsZentrum Potsdam, Telegrafenberg A17, 14473 Potsdam, Germany

High pressure- high temperature studies of the structural (zinc blende-cinnabar) phase transitions were performed in $Hg_{1-x}Fe_xS$ mixed crystals ($x < 0.1$) using synchrotron radiation and multianvil X-ray diffraction press. Pressure investigations of the Hall effect and conductivity of crystals containing up to a few percent of Fe were also performed at 295 K and 77 K. It was demonstrated that Fe in β -HgS creates deep, localized donor state resonant with the conduction band.

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Mercury sulphide is a II-VI semiconducting compound which crystallizes either in the cinnabar structure (α -HgS, wide gap semiconductor stable at ambient conditions) or in the sphalerite (zinc blende) type structure (metastable β -HgS, a zero-gap semiconductor). It is known that the phase transition $\alpha-\beta$ is observed at about 344°C at ambient pressure for pure mercury sulphide [1]. Twenty years ago it was demonstrated that the sphalerite type structure of HgS may be stabilized by a partial substitution of mercury by manganese [2]. Later, using the modified Bridgman method, big size, good quality monocrystals containing Mn, Fe, or Co were obtained [3]. In particular, β - $Hg_{1-x}Fe_xS$ monocrystals were grown for $0.02 < x < 0.11$ in the last few years. On the basis of classical and quantum transport measurements it has been suggested that iron in β -HgS could create a deep, localized donor state resonant with the conduction band [3, 4]. In particular, noticeable effect of low temperature mobility enhancement (well known from the previous investigations of similar II-VI semiconducting system: HgSe doped with Fe — see, e.g., [5]) was found in $Hg_{1-x}Fe_xS$ samples with the lowest possible Fe concentration (slightly below 2%) [3]. One of the necessary conditions to observe such effect is pinning at the Fermi energy to the resonant donor level

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and coexistence of empty and occupied donor states. However, there was no direct experimental evidence of the resonant character of Fe donor state in β -HgS.

Phase stability in III-V and II-VI semiconductors is one of important problems from the point of view of non-equilibrium growth techniques and possible applications of modern semiconductor materials. As it is well known, all mercury chalcogenides belong to the most ionic among binary II-VI semiconductors. However, only for HgS the ionicity exceeds the critical value of 0.785 proposed in Ref. [6] as the stability limit for tetrahedrally coordinated structures, but it is still close to this limit. Under these circumstances mercury sulphide can be considered as a very interesting material for the phase stability investigations and, in particular, for the studies of the influence of partial substitution of Hg or S by selected elements on the phase transition parameters.

The aim of this work was to investigate selected properties of $Hg_{1-x}Fe_xS$ crystals under hydrostatic pressure. First, the influence of Fe content on the host lattice properties is analysed (as it was mentioned before the presence of Fe stabilized the sphalerite phase). The second problem concerns the influence of Fe on the electronic properties (creation of deep state resonant with the conduction band). There exist a few papers related to the mercury sulphide phase transitions (see, e.g., [7-12]). Recently the phase transitions under hydrostatic pressure in $HgSe_{1-x}S_x$ crystals have also been investigated (see [13, 14] and references therein). It seems that the parameters describing the phase transitions were established for pure mercury sulphide. On the contrary, the information concerning the influence of doping on the changes of the phase transition parameters is very limited for other mercury chalcogenides and, in particular, is still lacking in the case of mercury sulphide containing transition metals.

High pressure-high temperature studies of the phase transition $\alpha-\beta$ for iron doped mercury sulphide were performed by X-ray energy-dispersive diffraction measurements using a synchrotron radiation F2.1 X-ray beamline in DESY (Hasylab). The $p-T$ range applied for the measurements above mentioned was 0-24 kbar and 27-700°C, respectively. The classical multianvil X-ray diffraction press, MAX80, was used for the measurements.

Figure 1 shows the typical spectra obtained for $Hg_{0.98}Fe_{0.02}S$ crystal at room temperature as a function of applied pressure. As one can see, with the increasing pressure value the intensity of peaks corresponding to the zinc blende phase decreases and new features due to the cinnabar phase appear. Similar patterns are obtained at higher temperatures. The same experiments were performed for a few samples with higher Fe content and, for the comparison, for $Hg_{0.98}Co_{0.02}S$ and $Hg_{0.98}Mn_{0.02}S$. The results show that at given temperature with increasing content of transition metal in the mixed crystal the phase transition starts at higher pressure. The parameters describing the phase transition obtained for $Hg_{0.98}Co_{0.02}S$ and $Hg_{0.98}Fe_{0.02}S$ are almost the same. The phase transition for $Hg_{0.98}Mn_{0.02}S$ sample starts at significantly (by a few kilobars) higher pressure. This unexpected property needs further investigations. Pressure dependence of the lattice parameter for β - $Hg_{0.9}Fe_{0.1}S$ is illustrated in Fig. 2.

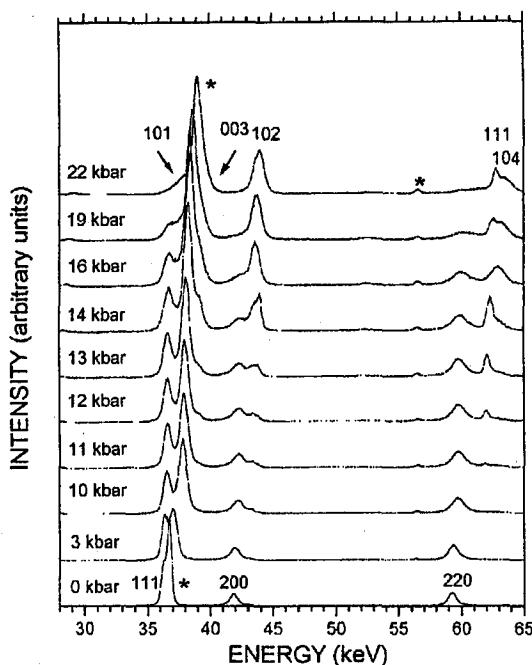


Fig. 1. Powder diffraction patterns of $\text{Hg}_{0.98}\text{Fe}_{0.02}\text{S}$ mixed crystal taken at room temperature using a synchrotron radiation and multianvil X-ray diffraction press. The applied diffraction angle was equal to $\theta = 2.905^\circ$. Peaks resulting from the diffraction on the zinc blende structure are indexed for the pattern taken at 0 kbar, those on the cinnabar structure are indexed for the pattern taken at 22 kbar, the starred peaks seen in the experimental spectra are due to the sample mounting (BN).

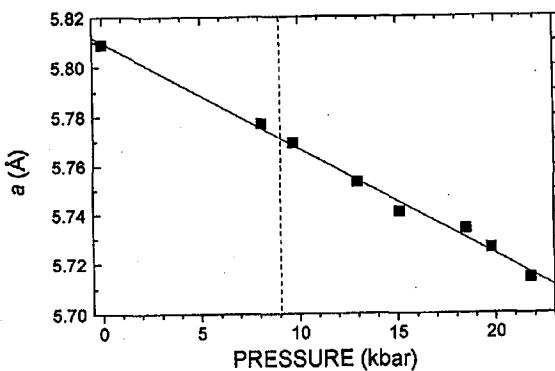


Fig. 2. Lattice parameter value versus pressure determined for $\beta\text{-Hg}_{0.9}\text{Fe}_{0.1}\text{S}$ at room temperature. Broken line denotes the lowest pressure value from which the contamination of α phase is also observed.

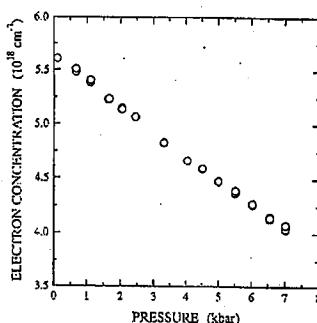


Fig. 3. Pressure dependence of the free electron concentration determined for $\text{Hg}_{0.98}\text{Fe}_{0.02}\text{S}$ sample at $T = 77$ K. Sharp increase in the resistivity (by several orders of magnitude) corresponding to the beginning of the phase transition starts at $p = 7.2$ kbar at this temperature.

Room temperature pressure investigations of the Hall effect and conductivity were performed for $\text{Hg}_{1-x}\text{Fe}_x\text{S}$ crystals with $x < 0.06$. The values of pressure at which the phase transition starts for each mixed crystal composition, determined by X-ray diffraction measurements and the transport measurements, within the experimental error are the same. The "hardening" of $\text{Hg}_{1-x}\text{Fe}_x\text{S}$ lattice with increasing Fe content in the mixed crystal was confirmed (roughly speaking doped crystal is more "stable" than the pure compound). The same behavior was previously found on the basis of transport measurements in the case of $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$ mixed crystals [15] so it seems to be typical of mercury chalcogenides.

For the sample with the lowest Fe content (slightly below 2%) the Hall effect and conductivity were measured also at 77 K as a function of the applied hydrostatic pressure. Free electron concentration determined from the experimental data is shown in Fig. 3. As one can see such concentration decreases almost linearly with increasing pressure. The pressure behavior of electron concentration indicates that (similarly to the case of HgSe), also in β -HgS iron does create a deep, localized, resonant with the conduction band state. In the case of investigated crystal (with the lowest iron concentration available by applied technology) the Fermi level is pinned to Fe level from the beginning, the Fermi energy slightly decreases with increasing pressure. The pressure coefficients describing the influence of pressure on β -HgS band structure are not known. However, one can take the values corresponding to HgSe as the first approximation. Under the above mentioned assumption, from the modeling of electron concentration as a function of pressure the value of the resonant Fe donor energy was determined. Iron level in β -HgS is located about 280 meV above the bottom of the conduction band. Its energy slowly decreases with increasing pressure. It should be stressed that it is the first direct evidence of the resonant character of Fe donor state in β -HgS. Value of iron level energy in β -HgS (highest than that corresponding to HgSe) confirms qualitatively the chemical trend expected from the analysis of HgS/HgSe band offset. For more precise determination of the resonant Fe level behavior, a better knowledge of the details of β -HgS band structure is required.

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