



X-RAY DIFFRACTION STUDY OF SPHALERITE-CINNABAR PHASE TRANSITION IN $\text{Hg}_{0.985}\text{Co}_{0.015}\text{S}$

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Abstract

Investigation of $\beta\text{-Hg}_{0.985}\text{Co}_{0.015}\text{S}$ (sphalerite type) to $\alpha\text{-Hg}_{0.985}\text{Co}_{0.015}\text{S}$ (cinnabar type) phase transition was performed at high pressure-high temperature conditions at a synchrotron radiation X-ray source. The high pressures and temperatures were obtained with the help of a multianvil X-ray diffraction press, MAX80. The studied p - T range was 0-43 kbar and 27-650 °C. On uploading, the phase transition from $\beta\text{-Hg}_{0.985}\text{Co}_{0.015}\text{S}$ to the α form occurs at about 14 kbar. A significant simultaneous contribution of both phases is observed between 10 and 18 kbar. On uploading at 650 °C, the transition to the α form occurs at 17 kbar. The α - β phase boundary is found to be shifted in the p - T phase diagram versus lower temperatures and higher pressures as related to binary HgS compound.

1. Introduction

Semimagnetic II-VI semiconductors involving substitution of some amount of 3d transition metals (TM) at cationic sites of tetrahedral structures (zincblende, wurtzite) exhibit interesting physical properties. Such TM-containing mixed crystals are a subject of investigations of magnetic interactions between the paramagnetic ions and their influence on the physical properties of the host material. The fact that the energy gap and other material parameters strongly depend on external magnetic field may lead to various applications of these crystals.

Among possible (II,TM)VI (TM = Mn, Fe, Co) solid solutions, those based on mercury were not much studied up to now. All II-VI binary compounds crystallise in a tetrahedral structure (sphalerite or wurtzite). HgS is the only exception from this rule: the form stable at ambient temperature, $\alpha\text{-HgS}$, is a precursor of a non-tetrahedral (hexagonal) cinnabar structure. However, it has been shown that the sphalerite type structure ($\beta\text{-HgS}$, which is the high-temperature form) may be stabilised by partial substitution of Hg atoms by, *e.g.*, a 3d metal: Mn [1], Fe [2-3] or Co [2-3]. A number of papers on physical properties of Mn and Fe substituted $\beta\text{-HgS}$ have appeared. The properties of $\beta\text{-Hg}_{1-x}\text{Co}_x\text{S}$, have not been studied yet except the classical [3] and quantum [4] transport. It seems that cobalt-containing mercury chalcogenides (HgS, HgSe, HgTe) can be particularly interesting because of the possible acceptor-like character of Co substitution. In particular, due to the high concentration of native defects, HgSe is always highly

degenerated n-type material (*i.e.* it exhibits a high free-electron concentration). However, doping of HgSe with Co results in a significant decrease of the free-electron concentration (being accompanied by an increase of electron mobility); Co in HgSe acts as an acceptor [5]. Electron transport data taken for $\beta\text{-Hg}_{1-x}\text{Co}_x\text{S}$ [3, 4] suggest a similar behaviour of Co also in β mercury sulphide.

2. Experimental

Single $\text{Hg}_{0.985}\text{Co}_{0.015}\text{S}$ crystal was grown by the Bridgman method. The Co to Hg ratio was determined by the ICP chemical analysis using an emission spectrometer BAIRD ICP2070 with plasma excitation. The reference samples for the chemical analysis were prepared from certified base standards, 1000 $\mu\text{g/ml}$, supplied by TEKNOLAB and measured before and after each measurement of the $\text{Hg}_{1-x}\text{Co}_x\text{S}$ sample. A Bragg-Brentano diffractometer employing Ni-filtered $\text{CuK}\alpha$ radiation was applied for the characterisation of crystals at ambient conditions. X-ray energy-dispersive powder diffraction experiments at high pressures and temperatures were performed using an X-ray diffraction press (MAX80) at the F2.1 beamline (HASYLAB at DESY, Hamburg). The p - T range was 0-43 kbar and 27-650 °C. The diffraction angle Θ was fixed at about 3°. The X-ray detection system was based on a solid state Ge detector of resolution 155 eV at energy 5.9 keV.

Each specimen studied at HP-HT conditions had a form of a cube with an edge of 8 mm and it was built from several hundred microns thick horizontal wafers of diameter 0.5 - 1.5 mm containing phases of $\text{Hg}_{0.985}\text{Co}_{0.015}\text{S}$ and NaCl pressure marker separated by a hexagonal boron nitride (BN) layer. The wafers were prepared by fine grinding and pressing small pellets. The $\text{Hg}_{0.985}\text{Co}_{0.015}\text{S}$ powder was diluted with BN in order to reduce absorption. The wafers were mounted in a BN cylinder inside a vertical cylindrical graphite heater located in the middle of a cube made of boron-epoxy composite. The temperature was measured with accuracy ± 10 °C with the help of a NiCrSi/NiSi thermocouple mounted within the cube.

3. Results and discussion

Laboratory angle-dispersive diffractometric measurements show that there is no trace of either $\alpha\text{-Hg}_{1-x}\text{Co}_x\text{S}$ nor other secondary phases in $\beta\text{-Hg}_{0.985}\text{Co}_{0.015}\text{S}$ crystal. The

lattice parameter for β - $\text{Hg}_{0.985}\text{Co}_{0.015}\text{S}$ is 5.838(1) Å. Its value is smaller than that reported for β -HgS (5.8517 Å [6]) what illustrates the fact that the Co substitution causes a contraction of the crystal lattice of β -HgS.

The solubility of Co in α and β phases of HgS at high temperatures and pressures is not known. The solubility of Mn in α -HgS has been reported to be $x_{\text{max}}=0.1$ [1]. As the investigated Co-containing sample is of a much lower Co content, we assume that in the studied temperature range the solubility limit is not exceeded neither for α nor for β phase. The applied energy-dispersive X-ray diffraction could not be applied for experimental verifying of this assumption, because the method sensitivity for minority phases is poor.

On uploading, between 10 and 18 kbar there is a significant simultaneous contribution of both $\text{Hg}_{0.985}\text{Co}_{0.015}\text{S}$ phases. The $\beta \rightarrow \alpha$ phase-transition point was estimated as the mean value of this interval, i.e. 14 kbar. At this pressure, signals of both phases are strong. Examples of powder diffraction patterns changing with the applied pressure are given in Fig. 1. On uploading at 650 °C, the transition of β - $\text{Hg}_{0.985}\text{Co}_{0.015}\text{S}$ to the α -form occurring at 17 kbar is very sharp. Downloading at this temperature caused returning to the β phase between 18 and 14 kbar. Due to the applied large pressure-step size, the transition pressure was not determined more accurately. In the final run performed at ambient temperature after the above described high-tempera-

ture runs, the peak broadening occurring on uploading was much less severe; other phase-transition properties remained the same.

The phase transition points found for $\text{Hg}_{0.985}\text{Co}_{0.015}\text{S}$ are located at higher pressures than the phase boundary for the binary HgS determined by DTA [7], what agrees with the expectation of stabilisation of the β -phase by substitution of Hg by Co atoms. The $\alpha \rightarrow \beta$ phase boundary is found to be shifted in the p - T phase diagram versus lower temperatures and higher pressures as related to binary HgS compound. A hysteresis is observed during the phase transition at a fixed temperature. The pressure-temperature behaviour of $\text{Hg}_{0.985}\text{Co}_{0.015}\text{S}$ is similar to that of $\text{Hg}_{1-x}\text{Mn}_x\text{S}$ and $\text{Hg}_{1-x}\text{Fe}_x\text{S}$ briefly described in [8] and [9], respectively.

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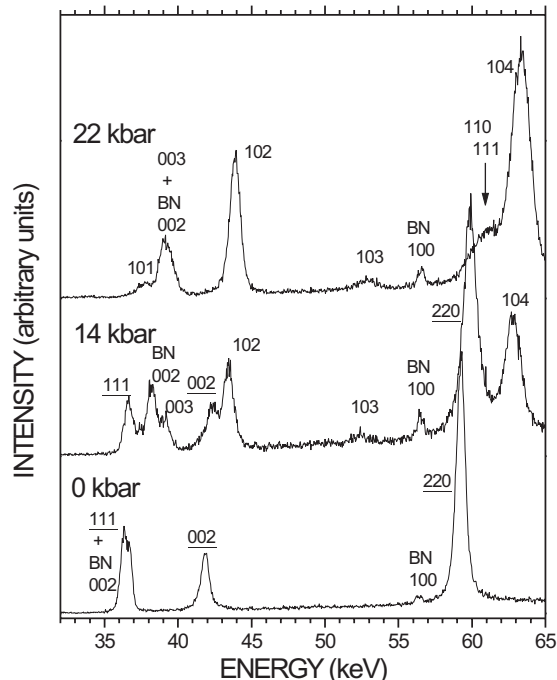


Fig. 1. Powder patterns for $\text{Hg}_{0.985}\text{Co}_{0.015}\text{S}$ measured using the diffraction angle $\theta = 2.9050^\circ$: β phase at 0 kbar, β phase coexisting with phase at 14 kbar and phase at 22 kbar. The Miller indices of phase are underlined. The 002 and 100 peaks of hexagonal boron nitride (BN) mixed with the sample are indicated.