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Galvanomagnetic and Thermoelectric Properties of HgS_xTe_{1-x} Solid Solutions

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Homogeneous solid solutions have been obtained in the complete composition range for the HgS_xTe_{1-x} system, the variation in the lattice parameter obeying Vegard's law. The study of the electrical conductivity, Hall coefficient, electron mobility and Seebeck coefficients in the range 77 to 350° K indicated a transition from semiconductor behaviour (for samples with small x) to "metallic" behaviour (high x-values) due to the increase in the overlap between the valency and conduction bands.

1. Introduction

The recent emphasis on the study of mercury chalcogenides has led to an almost complete knowledge of the band structure of HgTe, however, less is known about HgSe and HgS.

HgTe is a semi-metal with a band structure similar to that proposed by Groves and Paul [1] for gray tin, having the Γ_6 and Γ_8 bands inverted [2] and an energy gap of 0.15 eV [3]. Unlike α-Sn, the zinc blende HgTe has a split heavy mass valency band which overlaps the conduction band by 0.003 eV [4]. HgSe is a semi-metal with a conduction band overlap of 0.07 eV [4], but it is not yet established whether the energy gap between the Γ_6 and Γ_8 bands is positive or negative. The results for HgS are incomplete and contradictory.

The aim of the present work is to elucidate the band structure and properties of HgS, which exists in two modifications: α–HgS (cynabar) with a stable hexagonal structure at room temperature, and β–HgS (metacynabar) with a sphalerite structure stable above 345° C [5] which reverts to the α-form on cooling. α–HgS is a semiconductor with an energy gap of 2.0 eV at room temperature [6] and 2.2 eV at 77° K [7]. It is probable that β-HgS would be a semi-metal [8, 9] and in order to produce a stable material at room temperature it was studied as a solid solution in HgTe which has a sphalerite structure even with a high concentration of HgS [10, 11].

2. Preparation of the Alloys

Nikolskaia and Regel [10] have obtained ternary solid solutions in the HgS_xTe_{1-x} and HgS_xSe_{1-x} systems by diffusion at 350 or 800° C. The solid solution of HgS_xTe_{1-x} produced by this method is not quite homogeneous due to the difference of 27% in the tetrahedral radii of the substituting elements S and Te. In the case of the HgS_xSe_{1-x} system the radii difference is only 10% and it is possible to obtain, even by diffusion at low temperatures, homogeneous solid solutions.

Solid solutions in this present work have been obtained up to temperatures of 1200° C (depending on the HgS content) by maintaining them at this temperature for several hours, followed by a quick cooling to 700° C and holding for 2 h to obtain a good homogenisation. Due to the high Hg and S vapour pressure, resulting from the dissociation of HgS at relatively low temperatures it was impossible to obtain solid solutions with x greater than 0.20 without an external pressure of 150 atm. Massive homogeneous polycrystalline ingots, which were single-phase were obtained. Attempts to produce solid solutions at lower temperatures or slower cooling rates produced two-phase alloys.

3. Structural Properties

X-ray and metallographic analysis indicated that the materials were homogeneous solid solutions with a sphalerite structure. The variation of the lattice parameter, determined with a large Debye-Scherrer camera, is found to be linear with composition within an experimental error of ± 0.002 Å. Fig. 1 shows that the HgS_xTe_{1-x} system obeys Vegard's law, the present data being indicated by (●) and that of Kharakhorin

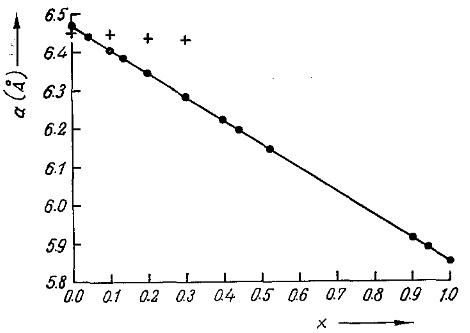

Figure 1 Lattice parameter of HgS_xTe_{1-x} solid solutions in terms of x. ●, present values; +, values from [12].

et al [12] by (+). The result for the β-HgS is in excellent agreement with that previously [13] observed. The deviation in the lattice parameter reported by Kharakhorin [12] is probably due to the loss of S during the preparation of the alloy. Similar losses of S were observed in the present work unless special precautions were taken.

4. Results and Discussions

The measurements of the conductivity and Hall coefficient were performed by a conventional method using DC and a direct magnetic field. At temperatures above 500° K some irreversible effects were observed so the upper experimental temperature was limited to 450° K. The temperature-dependence of the electrical conductivity is given in fig. 2. It is obvious that there are two distinct groups of curves at low temperatures, one group with a variation of conductivity similar to semiconductors (for $x \leqslant 0.20$), and the second group with a variation of conductivity similar to metals ($x \geqslant 0.30$). This indicates the semi-metal character of the band structure of β-HgS, with an overlap between the valency and conduction bands which is higher than that in HgTe, and gives rise to the metallic dependence on temperature of the electrical conductivity for HgS-rich solid solutions. The Hall coefficient measurements (at 2000 Oe) as shown in fig. 3, again suggest two groups of materials, those typically n-type ($x \geqslant 0.30$) and those typically p-type with large electron-hole mobility ratio ($x \leqslant 0.20$).

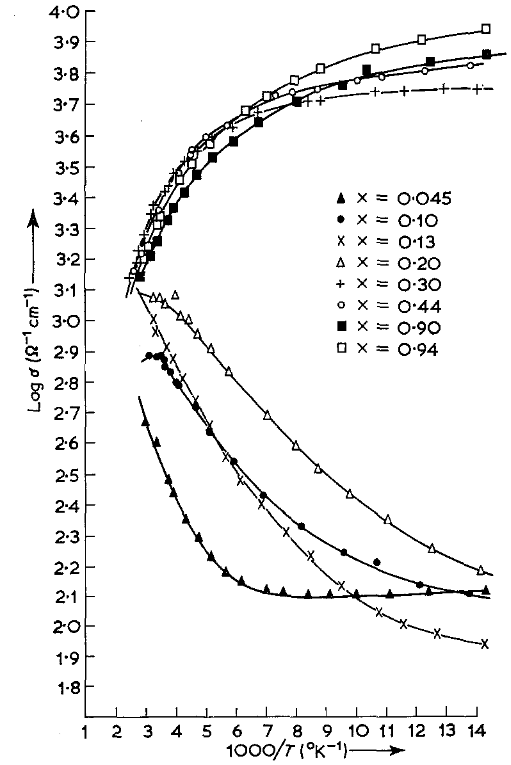

Figure 2 Temperature-dependence of the electrical conductivity of the HgS_xTe_{1-x} system.

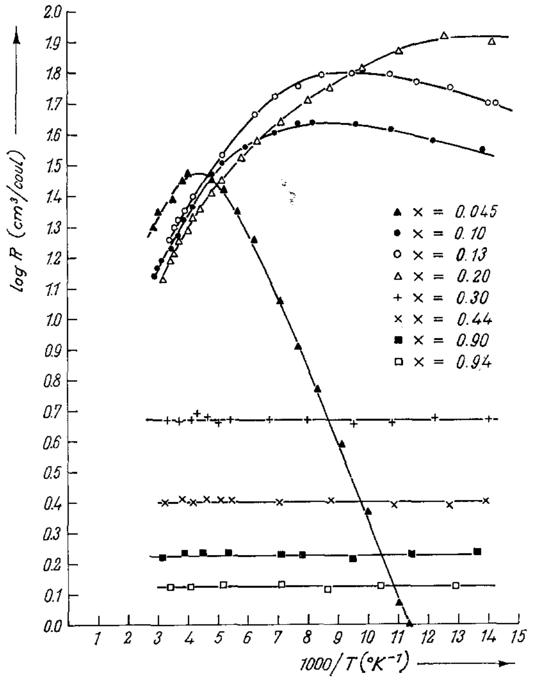

Figure 3 Temperature-dependence of the Hall coefficient.

The p-type of conductivity for the HgTe-rich samples is due to the presence of mercury vacancies introducing acceptor levels [14]. Increasing the HgS concentration, decreases the concentration of acceptors due to the mercury vacancies being filled by S atoms, but also increases the overlap of the conduction and valency bands.

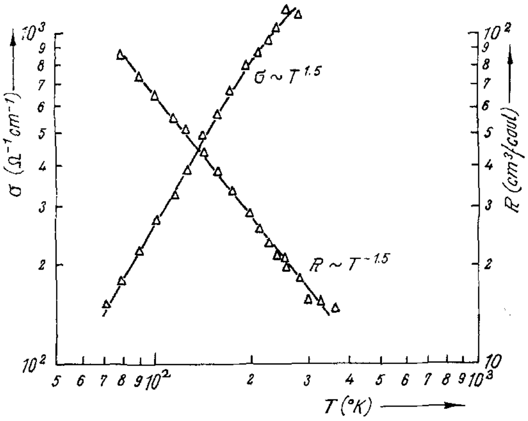

Figure 4 Temperature-dependence of the electrical conductivity and of the Hall coefficient for the sample with $x = 0.2$.

The sample with $x = 0.20$ has the characteristics of an intrinsic sample, the variation of the conductivity and Hall coefficient with temperature being shown in fig. 4. The dependence of the Hall coefficient follows a $T^{-3/2}$ law, which is also found to be true for both α–Sn and HgTe. This temperature relationship can be derived from the normal equation for intrinsic conduction

$$n_1 = K_1 T^{3/2}\, e^{-K_2/kT}$$

if it is noted that, K_2 is negligible for semi-metals and the K_1 term has a very small variation with temperature, due to the small temperature-dependence of the effective mass. Two hypotheses have been proposed for the intrinsic conductivity of HgTe, namely a parabolic band coupled with constant energy gap [15] and a non-parabolic band together with a negative variation of E_g with temperature [16]. In the second case the increase in the effective mass with the non-parabolic band is compensated by the decrease in the effective mass at the bottom band with increasing temperature.

In order to obtain materials with intrinsic conduction at other compositions, the samples with $x = 0.30$ were annealed in Hg and S atmospheres (fig. 5). As a result of the annealing in an S atmosphere the electron concentration was lowered from 1.37×10^{18} cm^{-3} to 10^{18} cm^{-3} suggesting that sulphur vacancies are responsible for the existence of donor sites. After annealing

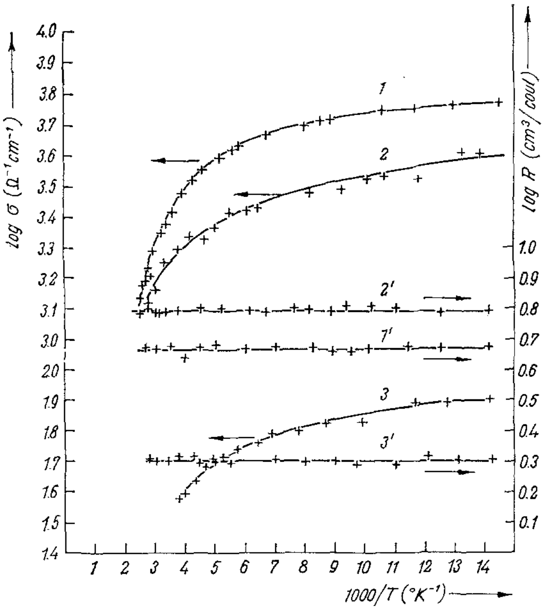

Figure 5 Temperature-dependence of the electrical conductivity and of the Hall coefficient for the sample with $x = 0.3$: 1, 1′, undoped; 2, 2′, S-doped; 3, 3′, Hg-doped.

in an Hg atmosphere, the electron concentration increased to 2.9×10^{18}, confirming that the number of mercury vacancies is reduced.

The small changes in carrier concentration produced by doping may be explained, as in the case of HgSe [17], by noting that the large electron concentration is due to valence-

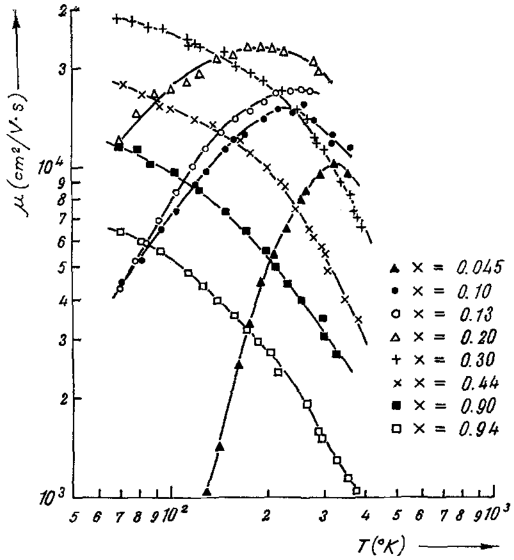

Figure 6 Temperature-dependence of the electron mobility for the HgS_xTe_{1-x} system.

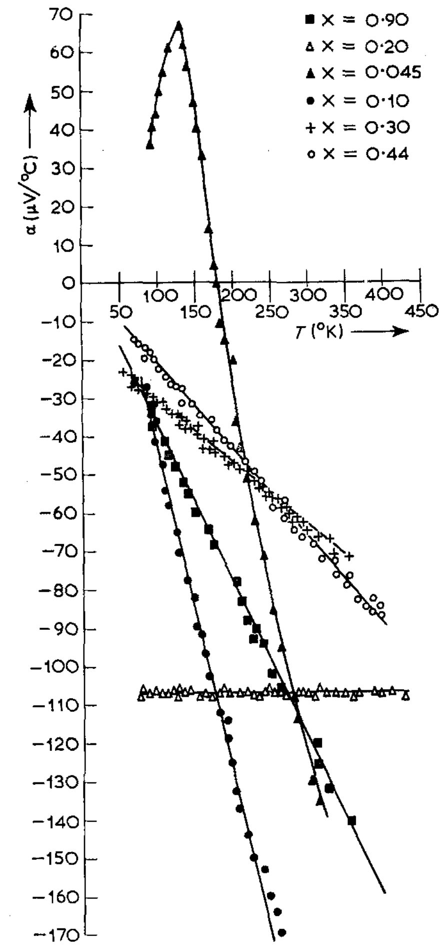

Figure 7 Temperature-dependence of the Seebeck coefficient for the HgS_xTe_{1-x} solid solutions.

conduction band overlap and not to deviations from stoichiometry.

The Hall mobility has been calculated from the formula $\mu = R\sigma$; typical results are shown in fig. 6. The slope of $\mu(T)$ curves near room temperature is negative, varying from 1.0 for HgTe to 1.8 for the sulphur-rich samples. This negative value of the slope suggests that lattice scattering is the dominant mechanism even for sulphur-rich samples down to 77° K. In the case of the tellurium-rich samples the slope is positive at low temperatures due to the onset of either impurity scattering or hole conduction.

The variation in the thermoelectric power with temperature is indicated in fig. 7, and shows clearly the difference between the p-type sample ($x = 0.045$) and the n-type samples. The thermoelectric power of the intrinsic sample ($x = 0.20$) is constant at $108\,\mu V\ grd^{-1}$.

In the present work it was not possible to estimate the effective electron mass due to an inexact knowledge of the relaxation times and scattering mechanisms.

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