YU ISSN 0015—3206
FZKAAA 18 (1) 65 (1986)

THE EFFECT OF MANGANESE ON ELECTRICAL PROPERTIES OF $Hg_{1-x}Mn_xSe$

BORKO STOŠIĆ[+], MIODRAG STOJIĆ[+], BRANKA BABIĆ-STOJIĆ[+] and OLGA ŽIŽIĆ[++]

[+]*Boris Kidrič Institute of Nuclear Sciences,*
P. O. Box 522, 11000 Belgrade, Yugoslavia
[++]*Faculty of Mechanical Engineering,*
11000 Belgrade, Yugoslavia

Received 26 December 1985
UDC 538.93
Original scientific paper

Electrical resistivity and Hall effect measurements have been performed on the $Hg_{1-x}Mn_xSe$ mixed crystals with manganese concentration $x = 0.09$, 0.11, 0.15 and 0.18 in the temperature range 77—300 K. It was established that the electrical resistivity is an increasing function of temperature and the free carrier concentration, of the order 10^{17} cm^{-3}, is almost temperature independent in all the crystals investigated. The two scattering mechanisms, the spin scattering and phonon scattering, dominate the transport properties of the system and both are dependent on manganese concentration and temperature.

1. Introduction

In recently published literature there has been much interest for ternary compounds of $A^{II}_{1-x}Mn_xB^{VI}$ type. They represent a new class of semiconducting materials which fills the gap between the ordinary non-magnetic and magnetic semiconductors, and are thus called »semimagnetic semiconductors«.

The $Hg_{1-x}Mn_xSe$ compound, solid solution of HgSe and MnSe, exists up to the concentration $x = 0.385$[1]. Mercury selenide has tetrahedral coordination with zincblende structure and shows semimetallic character with a negative value of the energy gap (— 0.10 eV). Manganese selenide, with octahedral coordination and rock-salt structure, is an insulator with the energy gap 2.5 eV, and shows antiferromagnetic ordering below 247 K[2]. The HgSe-MnSe solid solution retains zincblende structure, the lattice constant being a decreasing function of manganese concentration[1].

Magnetic properties of this semimagnetic semiconductor are of particular interest. It was established[3] that the temperature dependence of the inverse magnetic susceptibility is linear for $x < 0.1$ and a line with two slopes for $x > 0.1$, which suggests two mechanisms of magnetic behaviour. The critical temperature was found to be concentration dependent, varying from 30 to 50 K. The authors suggest an interpretation of these results on the basis of spin-glass and micromagnet model. The values of these critical temperatures are comparable with those found from EPR measurements[4]. For manganese concentration exceeding $\sim 20\%$ no EPR signal was detected below corresponding temperatures, varying from 60 to 80 K, a fact which was ascribed to a paramagnetic-antiferromagnetic phase transition. Some authors however suggest[5] that the disappearance of the resonance can be explained as a transition to the spin-glass phase.

Up to now only a few papers concerning the determination of band parameters, including exchange parameters, on the basis of magnetoabsorption measurements[6] and measurements of the anomalous temperature dependence of the Shubnikov-de Haas effect in weak[7] and strong magnetic fields[8] have been published. It was found that the energy gap for $x < 0.2$ depends linearly on manganese concentration[7]:

$$E_0 = (-0.27 + 4.4x)\ \text{eV}.$$

The band structure was also confirmed to be strongly dependent on the exchange interaction between Mn^{2+} ions and mobile charge carriers. For interpretation of experimental data all of these papers use the modified Pidgeon-Brown model[9].

In this work the electrical resistivity and Hall effect measurements were performed on several $Hg_{1-x}Mn_xSe$ crystals, with $x = 0.09$, 0.11, 0.15 and 0.18, in order to obtain some information about the electronic transport properties of these materials and particularly how the magnetic interactions influence the transport phenomena.

2. *Experimental*

Monocrystalline samples, prepared at the Institute of Physics of the Polish Academy of Sciences, were cut in a rectangular form (typically $0.5 \times 3 \times 6\ \text{mm}^3$) perpendicularly to the ingot axis. Electrical contacts, made of silver paste, were shown to be non-rectifying and mechanically stable. Electrical resistivity and Hall voltage were measured in helium atmosphere by a standard dc potentiometric method, in the temperature range 77—300 K. The temperature of the samples was measured by a chromel-alumel thermocouple. Measurements were erformed in magnetic fields up to 0.7 T.

3. *Results and discussion*

The results of electrical resistivity measurements on the $Hg_{1-x}Mn_xSe$ crystals with $x = 0.09$, 0.11, 0.15 and 0.18 manganese concentration are presented in Fig. 1. The curves $\varrho\,(T)$ show that the electrical resistivity of these samples is an increasing function of temperature in the temperature range measured, 77—300 K.

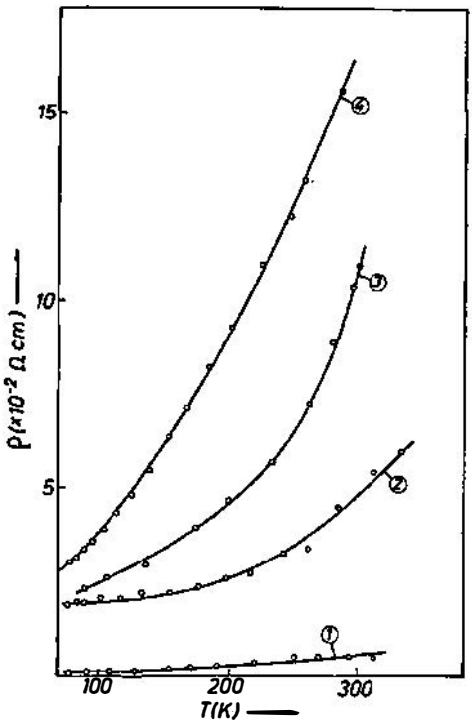

Fig. 1. Temperature dependence of the electrical resistivity of $Hg_{1-x}Mn_xSe$: curves 1, 2, 3, and 4 correspond to $x = 0.09$, 0.15, 0.11 and 0.18, respectively.

The Hall resistivity of $Hg_{1-x}Mn_xSe$ crystals was also measured as a function of temperature and manganese concentration. In the paramagnetic phase of magnetic materials the Hall resistivity, defined as the Hall electric field per unit longitudinal current density, is given by the following empirical expression[10]:

$$\varrho_H/H = R_0 + 4\pi\chi^* [R_s + R_0 (1 - N)] \tag{1}$$

where H is the applied magnetic field, N is the demagnetisation factor, R_0 is the ordinary and R_s the anomalous Hall coefficient, and $\chi^* = \chi/(1 + 4\pi N\chi)$ is the effective magnetic susceptibility.

In accordance with expression (1) the measured Hall resistivity as a function of applied magnetic field exhibits a linear dependence[11] for all the samples studied in the whole observed temperature range. By a special numerical procedure it was shown[11] that the anomalous Hall effect is much smaller than the normal Hall effect, $(\varrho_H/H - R_0)/R_0 < 0.02$, and thus can be neglected.

The concentration of the free charge carriers and the Hall mobility were then evaluated according to the relations:

$$n = 1/R_0\, e \tag{3}$$

and

$$\mu_H = R_0\, \sigma \tag{3}$$

where e is the electron charge and σ is the electrical conductivity. The temperature dependence of these transport parameters for one of the samples, with $x = 0.11$, is shown in Fig. 2. As can be seen the concentration of the free charge carriers is

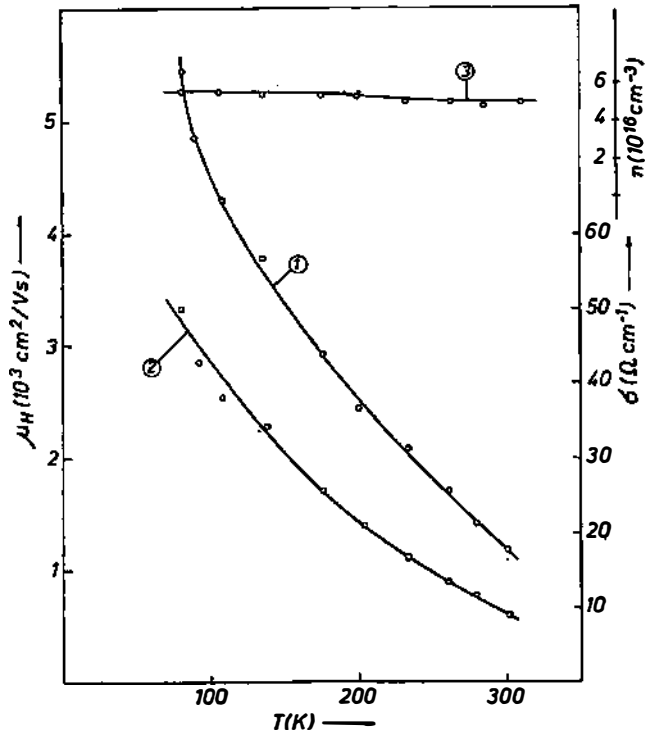

Fig. 2. Temperature dependence of the Hall mobility (curve 1), electrical conductivity (curve 2) and free carrier concentration (curve 3) for the sample with $x = 0.11$.

practically temperature independent, while the Hall mobility decreases with increasing temperature. The variation of the parameters σ and μ_H with manganese concentration at $T = 300$ K is presented in Table 1. The free carrier concentration is of the order of 10^{17} cm^{-3} and shows a tendency to decrease with increasing

TABLE 1.

x	$\sigma/(\Omega\,\mathrm{cm})^{-1}$	$n/(10^{17}\,\mathrm{cm}^{-3})$	$\mu_H/(10^3\,\mathrm{cm}^2/\mathrm{Vs})$
0.09	217.0	3.3	4.1
0.11	9.4	0.5	1.2
0.15	20.0	1.3	0.9
0.18	6.4	1.0	0.4

manganese concentration except for the $x = 0.11$ sample indicating that this quantity strongly depends on the conditions in which the crystal was grown. In fact, the small value of the parameter n in this sample explains the reversed order of curves $\varrho(T)$ in Fig. 1, the electrical resistivity of the sample $x = 0.11$ being higher than that for $x = 0.15$.

The temperature dependence of the Hall mobility for all the $Hg_{1-x}Mn_xSe$ samples is presented in Fig. 3. It is seen that the mobility monotonically decreases with increasing temperature in the whole range measured.

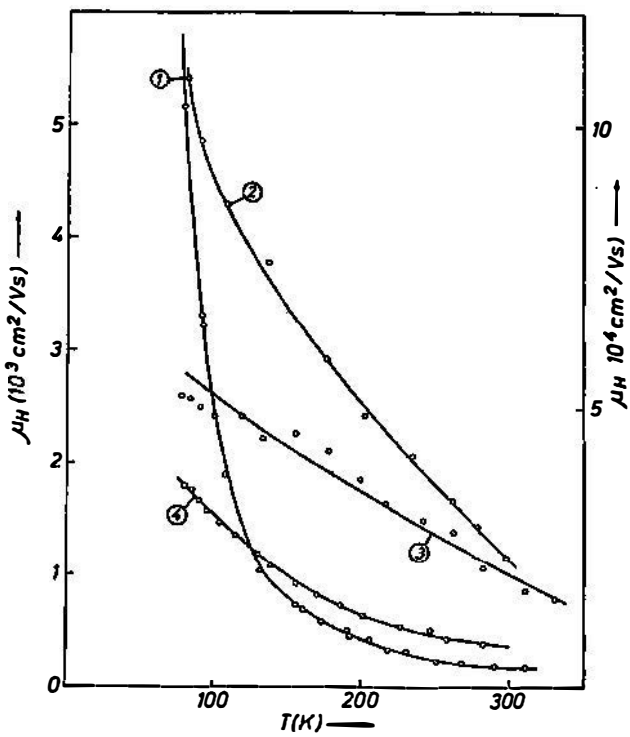

Fig. 3. Temperature dependence of the Hall mobility: the sample with $x = 0.09$ (curve 1) — right hand scale; the samples with $x = 0.11$, 0.15 and 0.18 (curves 2, 3 and 4, respectively) — left hand scale.

In Fig. 4 the Hall mobility is plotted as a function of manganese concentration for three different temperatures. These data show a drastic decrease of the Hall mobility with increasing x up to $x \approx 0.1$ and gradual decrease for $x > 0.1$.

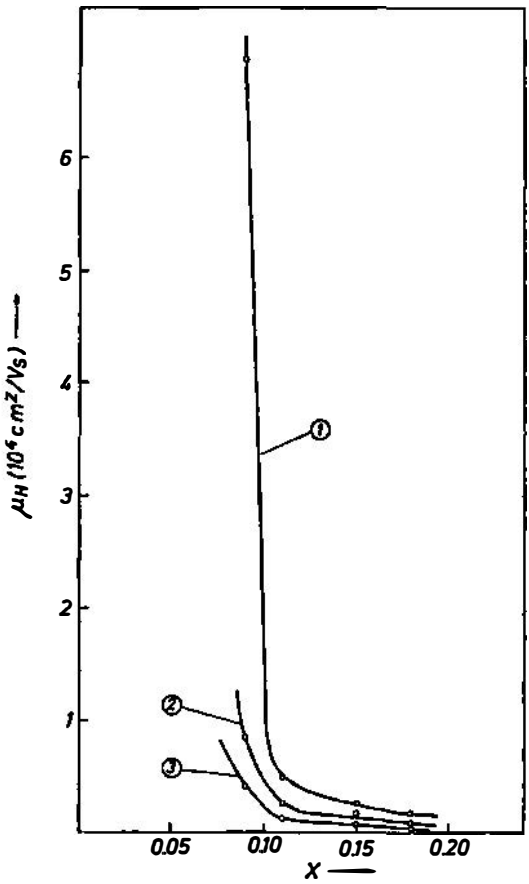

Fig. 4. Hall mobility as a function of manganese concentration for three different temperatures: 90 K (curve 1), 200 K (curve 2) and 300 K (curve 3).

The observed Hall mobility was fitted to the form

$$\mu_H = AT^{-\alpha}. \tag{4}$$

The best-fit results are given in Table 2.

It is known that different scattering mechanisms lead to a different temperature dependence of the free carrier mobility. In the regular, nondegenerated semiconductors for example the free carrier mobility is described by the above expression with the value of the parameter $\alpha = 1.5$ if the carriers are scattered on the acoustic and nonpolar optical phonons, and $\alpha = -1.5$ in the case of ionized impurity scattering.

TABLE 2.

x	a	A
0.09	2.90	3.2×10^{10}
0.11	0.95	3.6×10^{5}
0.15	0.55	3.0×10^{4}
0.18	1.10	2.3×10^{5}

Although the $Hg_{1-x}Mn_xSe$ is a complicated alloy system, the following analysis of the experimental data, presented in this work, has been done.

In the temperature range 77—300 K, where the $Hg_{1-x}Mn_xSe$ system has paramagnetic properties, the two scattering mechanisms of the free charge carriers can be expected to be dominant, the spin scattering and phonon scattering. The spin scattering, i. e. the scattering of the free charge carriers on localised spins of Mn^{2+} ions, becomes stronger with increasing manganese concentration because the density of localised spins as effective scattering centers is increased. This fact could explain the observed tendency of the parameter a to decrease with increasing x (Table 2) and also the rapid decrease of the Hall mobility as a function of manganese concentration (Fig. 4). The strong dependence of the Hall mobility on the manganese concentration seems to arise from the existence of the clusters of Mn^{2+} ions which are formed in real magnetic crystals of this type[12]. Moreover, the observed variation of the parameter a indicates that the spin scattering component might be also temperature dependent. Such behaviour is possible if the spin fluctuations become larger with increasing temperature.

The phonon scattering is dependent on temperature and manganese concentration. It has been established that the substitution of Hg ions by Mn ions in the $Hg_{1-x}Mn_xSe$ system manifests itself by a lattice parameter contraction[1] shifting the low-lying vibrational modes to much higher frequencies[12]. If these vibrational modes are excited at higher temperatures, such perturbations of phonon spectrum, caused by the presence of manganese ions in the mercury sublattice, should result in more effective phonon scattering. So, at higher temperatures one may expect the significant influence of the phonon spectrum perturbations on the total free carrier mobility.

References

1) A. Pajaczkowska and A. Rabenau, Mater. Res. Bull. **12** (1977) 183;
2) D. L. Decker and R. L. Wild, Phys. Rev. **B4** (1971) 3425;
3) A. Pajaczkowska and R. Pauthenet, J. Mang. Magn. Mater. **10** (1979) 84;
4) K. Leibler, A. Sienkiewicz, K. Checinski, R. Galazka and A. Pajaczkowska, Proc. of 3rd Int. Conf. on Physics of Narrow-Gap Semiconductors (1977) 199;
5) D. P. Mullin, R. R. Galazka and J. K. Furdyna, Phys. Rev. **B24** (1981) 355;
6) M. Dobrowolska, W. Dobrowolski, R. R. Galazka and A. Mycielski, Phys. Stat. Sol. (b) **105** (1981) 477;
7) S. Takeyama and R. Galazka, Phys. Stat. Sol. (b) **96** (1979) 413;
8) P. Byszewski, M. Z. Cieplak and A. Mongird-Gorska, J. Phys. C: Solid State Phys. **13** (1980) 5383;

9) G. Bastard, C. Rigaux, Y. Guldner, J. Mycielski and A. Mycielski J. Phys. Paris **39** (1978) 87;
10) C. M. Hurd, *The Hall Effect in Metals and Alloys*, Plenum Press, New York-London, 1972;
11) O. Žižić, M. Stojić and B. Stošić, Phys. Stat. Sol. (a) **88** (1985) K 191;
12) S. Nagata, R. R. Galazka, D. P. Mullin, H. Akbarzadeh, G. D. Khattak, J. K. Furdyna and P. H. Keesom, Phys. Rev. **B 22** (1980) 3331.

UTICAJ MANGANA NA ELEKTRIČNE OSOBINE $Hg_{1-x}Mn_xSe$

BORKO STOŠIĆ[+], MIODRAG STOJIĆ[+], BRANKA BABIĆ-STOJIĆ[+] i OLGA ŽIŽIĆ[++]

[+]*Institut za nuklearne nauke »Boris Kidrič«, P. fah 522, 11000 Beograd, Jugoslavija*

[++]*Mašinski fakultet, 11000 Beograd, Jugoslavija*

UDK 538.93

Originalan naučni rad

Izvršena su merenja električne otpornosti i Hall-ovog efekta na kristalima $Hg_{1-x}Mn_xSe$ sa koncentracijom mangana x 0,09, 0,11, 0,15 i 0,18 u temperaturskom intervalu 77—300 K. Ustanovljeno je da električna otpornost raste sa porastom temperature, a da je koncentracija slobodnih nosilaca reda 10^{17} cm^{-3} i gotovo ne zavisi od temperature u svim ispitivanim kristalima. Dva mehanizma rasejanja, spinsko rasejanje i fononsko rasejanje imaju dominantan uticaj na transportne osobine sistema i oba zavise kako od koncentracije mangana, tako i od temperature.