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CONDUCTION BAND PROPERTIES OF $Hg_{1-x}Mn_xSe$

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The energy at the Fermi level, the effective mass of the conduction electrons and the coefficients of the electron wave function in $Hg_{1-x}Mn_xSe$ were calculated within the Kane three band model. The electron concentration was taken in the range $1 \cdot 10^{17} \leq n \leq 1 \cdot 10^{19}$ cm^{-3}, the composition in the range $0 \leq x \leq 0.12$ and temperatures from 4.2 to 77 K. The electron mobility for scattering by ionized impurities was also calculated as a function of composition of the material. The efficiency of various scattering mechanisms is discussed.

1. Introduction

$Hg_{1-x}Mn_xSe$ belongs to the class of $A^{II}_{1-x}Mn_xB^{VI}$ semimagnetic semiconductors. It forms a single phase solid solution of the zincblende structure up to $x = 0.38$[1]. The manganese ions substitute the mercury ions and are randomly distributed in the cation sublattice. The lattice parameter and band parameters change in a continuous manner by varying the composition of the material. The lattice parameter obeys Vegard's law[2]. The energy gap is also a linear function of manganese content[3,4]. For lower values of x ($x < 0.06$ at 4.2 K) $Hg_{1-x}Mn_xSe$ is a zero gap semiconductor with the »inverted« band structure[5]. For higher values of x it is a positive gap semiconductor with the normal band ordering[5]. The electron concentration in $Hg_{1-x}Mn_xSe$ is relatively high[3,6] even at low temperatures. The existence of donors is associated with the stoichiometric defects in the crystal lattice.

In the present paper the energy of the conduction electrons, the electron effective mass and the coefficients of the electron wave function in $Hg_{1-x}Mn_xSe$ are calculated and discussed as a function of electron concentration, temperature and composition of the material. The electron mobility for scattering by ionized impurities was also calculated as a function of composition. The electron concentration is taken in the range $1 \cdot 10^{17} \leq n \leq 1 \cdot 10^{19}$ cm^{-3}, temperatures from 4.2 to 77 K and composition in the range $0 \leq x \leq 0.12$.

2. *Theory*

The conduction band energy in $Hg_{1-x}Mn_xSe$ is described by the Kane three band model[5]. The interaction with higher bands is also taken into account in the spherical approximation:

$$E = E' + \frac{\hbar^2 \cdot k^2}{2m_0}\left[1 + a^2A' + b^2M + c^2L' + 0.2\,(b^2 - 2c^2)\,(L' - M - N')\right] \tag{1}$$

where E' is the solution of the equation:

$$E'\,(E' + \Delta)\,(E' - E_g) - k^2P^2\left(E' + \frac{2}{3}\Delta\right) = 0. \tag{2}$$

On the energy scale denoted by E, the zero of energy is at the Γ_8 band edge. In the above equation k is the wave number, P is the s-p momentum matrix element, E_g is the energy gap, Δ is the energy of spin-orbit splitting, A', M, L' and N' are the higher band parameters, a is the coefficient which describes the contribution of s-type function to the total electron wave function, whereas b and c determine the amount of different components of p-type functions to the total electron wave function. These coefficients are defined by the following relations[5]:

$$a^2 = \frac{1}{D}\left(\Delta + \frac{3}{2}E'\right)(\Delta + E')\,E'$$

$$b^2 = \frac{\Delta^2}{3D}\,(E' - E_g) \tag{3}$$

$$c^2 = \frac{2}{3D}\left(\Delta + \frac{3}{2}E'\right)^2(E' - E_g)$$

where:

$$D = \left(\Delta + \frac{3}{2}E'\right)(\Delta + E')\,E' + (\Delta + E')^2\,(E' - E_g) + \frac{1}{2}\,(E' - E_g)\,E'^2.$$

The higher band parameters and spin-orbit splitting energy are assumed to be temperature and composition independent and equal to the values determined for HgSe: $A' = -0.25$, $M = -2.7$, $L' = -0.5$, $L' - M - N' = 4$ and $\Delta = 0.39$ eV[3,7]. On the other hand, the energy gap in $Hg_{1-x}Mn_xSe$ exhibits a linear dependence on composition in the composition range $0 \leq x \leq 0.115$[3,4]. The temperature dependence of the energy gap is assumed to be the same as in HgSe, which is approximately a linear function in the temperature range $10 \leq T \leq 80\,K$[7], with the temperature coefficient $dE_g/dT = 8.98 \cdot 10^{-4}$ eV/K. Therefore, the energy gap in $Hg_{1-x}Mn_xSe$ in the studied composition and temperature range is taken in the form:

$$E_g(x, T) = -0.279 + 4.4x + 8.98 \cdot 10^{-4} \cdot T\,(\text{eV}). \tag{4}$$

The s-p momentum matrix element P in $Hg_{1-x}Mn_xSe$ exhibits also a pronounced dependence on composition[4]. In the present work the matrix element P is calculated including also a weak dependence on temperature which is taken to be the same as in HgSe[8]:

$$P(x, T) = 7.20 \cdot 10^{-8} - 11.73 \cdot 10^{-8} \cdot x + 2 \cdot 10^{-11} \cdot T\,(\text{eV cm}). \tag{5}$$

The energy dependent effective mass is defined by the expression[5]:

$$m^* = \hbar^2 \cdot k \cdot \left(\frac{\partial \varepsilon}{\partial k}\right)^{-1}. \tag{6}$$

The zero of energy denoted by ε is at the Γ_6 band edge, so that $\varepsilon = E - E_g$.

Performing the derivation in the above expression, one obtains:

$$m^* = \frac{\hbar^2 \left[3\varepsilon^2 + 2(2E_g + \Delta)\varepsilon + E_g(E_g + \Delta) - k^2P^2\right]}{2P^2\left[\varepsilon + E_g + \frac{2}{3}\Delta\right]}. \tag{7}$$

3. *Results and discussion*

Calculated energy at the Fermi level as a function of composition is presented in Fig. 1. for three different values of electron concentration. For $n = 1 \cdot 10^{18}$ cm^{-3} the Fermi energy versus composition is also shown at three different temperatures. The Fermi energy is referred to the bottom of the conduction band and this band is of Γ_8 symmetry in the inverted band structure ($E_g = E_{\Gamma 6} - E_{\Gamma 8} < 0$) and of Γ_6 symmetry in the normal band ordering ($E_g > 0$). It was found that the higher band correction of energy is small compared with E' (Eq. (1)), and it can be completely neglected in the normal band ordering. As can be seen from Fig. 1., a pronounced maximum of the energy appears for all electron concentrations at a place where the energy gap goes through zero.

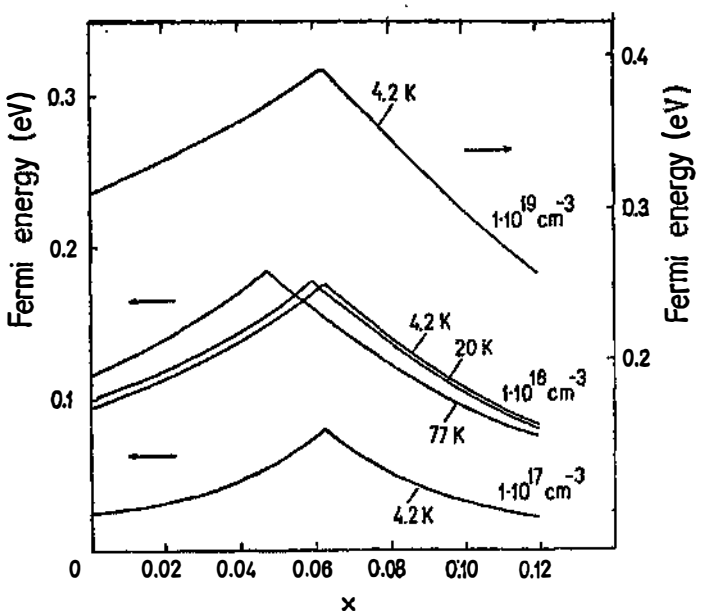

Fig. 1. Electron energy at the Fermi level in $Hg_{1-x}Mn_xSe$ calculated as a function of composition for three values of electron concentration, $n = 1 \cdot 10^{17}$, $1 \cdot 10^{18}$ and $1 \cdot 10^{19}$ cm^{-3}. The Fermi energy for $n = 1 \cdot 10^{18}$ cm^{-3} also is shown at three different temperatures.

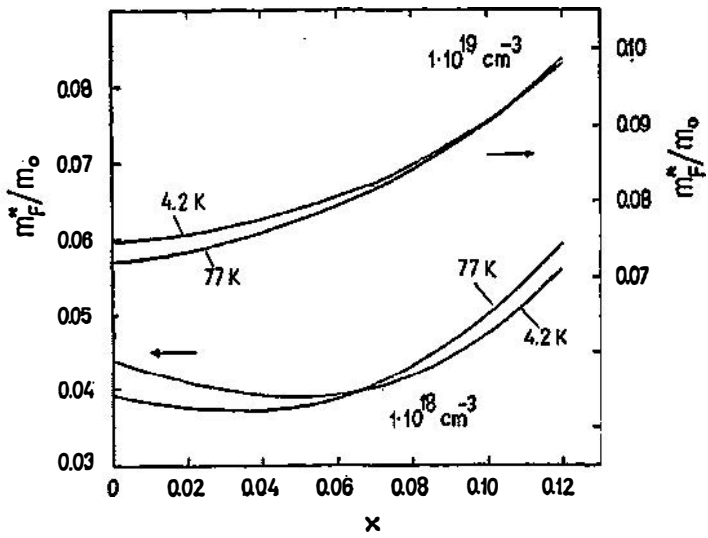

Fig. 2. Electron effective mass at the Fermi level in $Hg_{1-x}Mn_xSe$ calculated as a function of composition for two values of electron concentration, $n = 1 \cdot 10^{18}$ and $1 \cdot 10^{19}$ cm^{-3} at temperatures 4.2 and 77 K. The effective mass is presented as a ratio of the calculated effective mass to the free electron mass m_0.

The electron effective mass at the Fermi level is also calculated and presented as a function of composition in Fig. 2. for two values of electron concentration, $1 \cdot 10^{18}$ and $1 \cdot 10^{19}$ cm^{-3}. It was established that a minimum of the function $m_F^*(x)$ exists for $n < 7 \cdot 10^{18}$ cm^{-3} and its position depends on the electron concentration. In fact, the effective mass decreases with increasing x through the energy ε and increases with increasing x through the energy gap E_g and the matrix element P (Eq. (7)). For lower values of electron concentration ($n < 7 \cdot 10^{18}$ cm^{-3}) and for lower values of x the negative increment of the effective mass due to energy ε becomes larger than the positive increment of the effective mass due to E_g and P, and a minimum appears at a certain value of x. For higher values of n, $n \geq 7 \cdot 10^{18}$ cm^{-3}, the increase of the effective mass due to E_g and P is larger than the diminution due to energy in the whole composition range and the effective mass monotonically increases with increasing composition of the material.

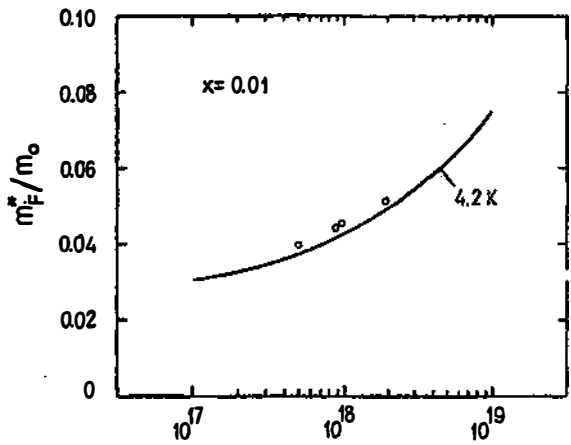

Fig. 3. Electron effective mass at the Fermi level in $Hg_{1-x}Mn_xSe$ calculated as a function of electron concentration for the composition $x = 0.01$ at $T = 4.2$ K. Circles are experimental values of the effective mass deduced from Shubnikov-de Haas experiment[3] on the $Hg_{1-x}Mn_xSe$ sample with $x = 0.01$ at $T = 11.5$ K.

In Fig. 3. the electron effective mass is presented versus electron concentration for $x = 0.01$ at $T = 4.2$ K and compared with the experimental values of Takeyama and Galazka[3] which were deduced from Shubnikov-de Hass effect at low temperatures. The agreement between the theory and experiment is satisfactorily good.

The squares of the coefficients a, b and c versus composition are presented in Fig. 4 for electron concentration $n = 1 \cdot 10^{18}$ cm^{-3} at $T = 4.2$ K. It is seen that a mixing of the s-type and p-type electron functions occurs. In the inverted band structure ($x < 0.06$ at 4.2 K) and for small x the electron wave function is mainly of the p-type. In the normal band ordering the s-type component is larger than the p-type component, and for $x = 0.12$ it amounts about 80% of the total electron wave function.

The electron concentrations in the range $1 \cdot 10^{17}$—$1 \cdot 10^{19}\,\mathrm{cm}^{-3}$ are the concentrations which are usually observed in the real crystals of $Hg_{1-x}Mn_xSe$ and are much larger than the intrinsic free carrier concentration in the studied temperature and composition range. These electrons, with concentration which does not depend on temperature, originate from the ionized donors which are, at the same time, the principal source of electron scattering at lower temperatures, $T < 77$ K, in HgSe[8,9] and in $Hg_{1-x}Cd_xSe$[10,11]. An analysis of the temperature dependent electrical conductivity in a sample of $Hg_{1-x}Mn_xSe$ with $x = 0.09$[12] also has shown that the dominant scattering mechanism in this semimagnetic semiconductor is ionized impurity scattering in the temperature range studied, 20—54 K.

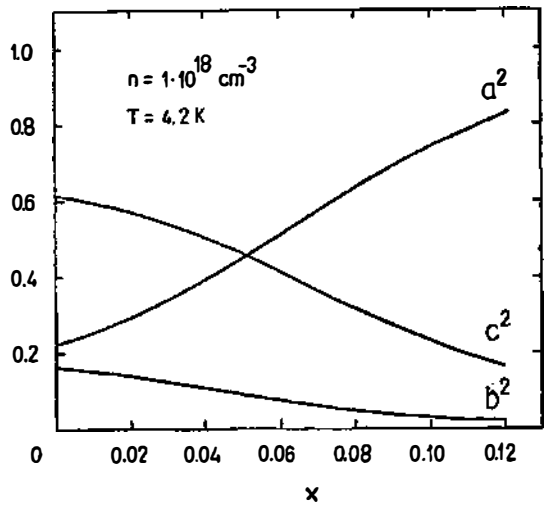

Fig. 4. Squares of the coefficients a, b and c in $Hg_{1-x}Mn_xSe$ calculated as a function of composition for the electron concentration $n = 1 \cdot 10^{18}\,\mathrm{cm}^{-3}$ at $T = 4.2$ K.

In the present paper the electron mobility for scattering by ionized impurities in $Hg_{1-x}Mn_xSe$ was calculated as a function of composition at $T = 20$ K and for electron concentrations $1 \cdot 10^{17}$ and $1 \cdot 10^{18}\,\mathrm{cm}^{-3}$ (Fig. 5). These calculations were performed according to the expression[5]:

$$\mu_I = \frac{\hbar^3 \cdot \varkappa_s^2 \cdot k^3}{2\pi \cdot e^3 \cdot N_I \cdot Z_I^2 \cdot m^{*2} \cdot F_I} \tag{8}$$

where $\varkappa_s$ is the static dielectric function defined in Ref. 5; the wave number of the conduction electrons was determined from $k = k_F = (3\pi^2 n)^{1/3}$, the concentration of ionized impurities N_I was put equal to the electron concentration n, their charge in electron units was taken $Z_I = 1$, the effective mass of the conduction electrons was determined from Eq. (7) and F_I is a function defined in Ref. 5. A maximum in the mobility versus composition appears due to effective mass dependence $m_F^*(x)$ which has a minimum for electron concentrations $n <$

$< 7 \cdot 10^{18}$ cm^{-3}. The calculated electron mobility for scattering by single ionized donors is compared with some experimental values of the mobility obtained for HgSe[8] and for $Hg_{1-x}Mn_xSe$[12]. The experimental values of the electron mobility depend also on the annealing history of the samples, since the thermal treatment changes the electron concentration in the crystal. Generally, the experimental values of the electron mobility in HgSe at low temperatures are somewhat lower than that calculated for single ionized donor scattering[9]. Such behaviour was attributed to the existence of neutral defects or to some acceptor type impurities in this zero gap semiconductor[8,9].

The experimental value of the electron mobility in the $Hg_{1-x}Mn_xSe$ sample with $x = 0.09$ at 20 K is about 40% lower than that calculated for single ionized donor scattering (Fig. 5). The remaining scattering is probably connected with the presence of neutral defects[12], although some acceptor type impurities cannot be completely ruled out.

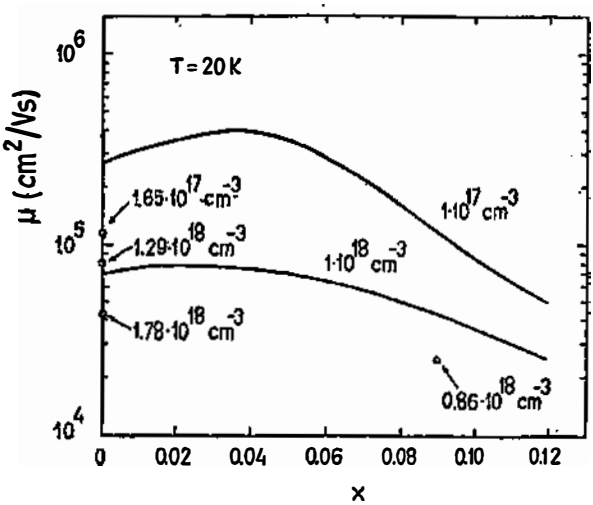

Fig. 5. Electron mobility for scattering by ionized impurities in $Hg_{1-x}Mn_xSe$ calculated as a function of composition for two values of electron concentration, $n = 1 \cdot 10^{17}$ and $1 \cdot 10^{18}$ cm^{-3} at $T = 20$ K. Also are shown the experimental values of electron mobility for $x = 0$[8]: sample with $n = 1.65 \cdot 10^{17}$ cm^{-3} annealed in selenium vapour, sample with $n = 1.29 \cdot 10^{18}$ cm^{-3} annealed in mercury vapour, sample with $n = 1.78 \cdot 10^{18}$ cm^{-3} is »as grown« crystal; experimental value for the composition $x = 0.09$[12] was obtained on the sample with $n = 0.86 \cdot 10^{18}$ cm^{-3}.

Compositional disorder scattering, in our opinion, has no significant influence on the electron transport and scattering in $Hg_{1-x}Mn_xSe$ in the studied composition and temperature range. De Broglie wavelength of the conduction electrons is of the order $\lambda_B \cong 10$ nm and it is much larger than the size of manganese ion clusters in $Hg_{1-x}Mn_xSe$ for lower manganese content, $x \leq 0.12$[13].

Spin disorder scattering in $Hg_{1-x}Mn_xSe$ seems to play a significant role at higher temperatures. An analysis of the electron scattering mechanisms in the sample with $x = 0.09$ has suggested that the spin disorder scattering at $T \cong 20$ K is still very small, but progressively increases with increasing temperature[12].

In the physics of the electron transport in $Hg_{1-x}Mn_xSe$ there are several unsolved problems. First is the problem of the neutral scattering potential. If the neutrals exist, which seems very likely, then their scattering potential should be of long range, not of short range, because the wavelength of the conduction electrons is relatively large. Second is the problem of the spin disorder scattering in $Hg_{1-x}Mn_xSe$ and also in other semimagnetic semiconductors. Theoretical expression for the relaxation time for the spin disorder scattering in a parabolic band was evaluated[14]. However, there is some evidence that the spin disorder scattering in $Hg_{1-x}Mn_xSe$[12] and in $Hg_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xSe$[15] occurs mainly through the inelastic collisions. Further studies of the electron transport properties in $Hg_{1-x}Mn_xSe$ is in progress.

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OSOBINE PROVODNE ZONE $Hg_{1-x}Mn_xSe$

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Izvršena su izračunavanja energije na Fermijevom nivou, efektivne mase provodnih elektrona i koeficijenata elektronske talasne funkcije u $Hg_{1-x}Mn_xSe$ u okviru Kejnovog (Kane) trozonskog modela. Koncentracija elektrona je uzeta u opsegu $1 \cdot 10^{17} \leq n \leq 1 \cdot 10^{19}\ cm^{-3}$, sastav u intervalu $0 \leq x \leq 0.12$ i temperature od 4,2 do 77 K. Takođe je izračunata pokretljivost elektrona usled rasejanja na jonizovanim primesama u zavisnosti od sastava materijala. U radu se diskutuje efikasnost pojedinih mehanizama rasejanja.