

THE EFFECT OF MANGANESE ON THE ENERGY GAP  
 OF THE SEMICONDUCTING ALLOY  $Hg_{1-x}Mn_xSe$

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In the range of 50-5000  $cm^{-1}$  reflection and absorption spectra of semimagnetic semiconductors  $Hg_{1-x}Mn_xSe$  ( $x=0.09, 0.11, 0.15$  and  $0.18$ ) at 300K were registered. By the analysis of curves  $R(\nu)$  and  $R(\nu)$  their energy gap  $E_g$  was evaluated. It was found that for  $x < 0.15$ ,  $E_g$  is a linear function of the concentration of  $Mn^{2+}$  ions. The obtained dependence  $E_g(x)$  was compared to the same at 10K which is obtained by Takeyama and Galazka /2/ for magneto-optical measurements.

INTRODUCTION

The semiconducting alloy  $Hg_{1-x}Mn_xSe$  is a solid solution of HgSe, zero gap of the semiconductor with the inverted band structure ( $E_g = -0.10eV$ ) /1/ and the magnetic semiconductor MnSe ( $E_g = 2.5eV$ ) /1/.

By substituting the manganese in the sublattice of mercury the band structure of HgSe is modified. The relative position of the level  $\Gamma_6$  and  $\Gamma_8$ , and thereby the energy difference  $E(\Gamma_6) - E(\Gamma_8) \cong E_g$ , changes with the change of the content of Mn ions. The dependence of energy gap on the alloy content  $Hg_{1-x}Mn_xSe$  is known only in the region of lower temperatures ( $T \leq 10K$ ) /2,3,4/. From the magneto-optical measurements at  $T=10K$  Takeyama and Galazka /2/ found that energy gap, for  $x < 0.20$ , changes according to the law

$$E_g (eV) = -0.270 + 0.044x (\%)$$

For  $x < 0.06$  these alloys have the characteristics of the semimetals ( $E_g < 0$ ), for  $x > 0.06$  - characteristics of semiconductors with small energy gap ( $E_g > 0$ ).

It is unknown to the authors that the dependence  $E_g(x)$  of this crystal at higher temperatures was determined by any procedure.

If we take that the activation energy is a good measure of the energy gap at higher temperatures, too, then  $E_g$  can be evaluated from reflection and absorption spectra, from the curves  $R(\nu)$  and  $T(\nu)$ . The data of this type of experiments for semiconducting alloys  $Hg_{1-x}Mn_xSe$  are non-existent.

This paper presents the first preliminary measurements of  $R(\nu)$  and  $T(\nu)$  in order to estimate  $E_g(x)$  in  $Hg_{1-x}Mn_xSe$ .

System  $Hg_{1-x}Mn_xSe$  is a solid solution till  $x=0.385$ , with the crystal structure of sphalerite. The lattice constant decays with the increase of the content of manganese, it changes according to linear Vegard's law [5].

## EXPERIMENTAL

Crystals were prepared in the Institute of Physics of the Polish Academy of Sciences. Their homogeneity and composition were verified by X-ray powder technique [6]. Thin polycrystalline (sinterized) samples were obtained by cutting the ingot normally at its axis. According to the paper Stošić et al. [7] crystals  $Hg_{1-x}Mn_xSe$  ( $x=0.09, 0.11, 0.15, \text{ and } 0.18$ ) are semiconductors of the n-type with the carrier concentration of  $n=(0.5-3.3)\times 10^{17} \text{ cm}^{-3}$ .

In order to get the reflection spectra the samples were prepared in the form of thin well polished slabs. For the preparation of samples for absorption spectra two techniques were used: radiation by neutrons and pellet technique. It was found that by the first procedure the "optical" thickness of the sample decreases sufficiently so that the same becomes "transparent". In the second case the sample powder was diluted with KBr or CsI, so that the so-obtained mixture, by a standard procedure was pressed into a pellet.

The IR absorption and reflection spectra were recorded on Perkin - Elmer 983 G and Bruker 113 V FTIR spectrophotometers in the region from  $50 - 5000 \text{ cm}^{-1}$ . The measurements were performed at 300 K, on samples with the following concentrations:  $x = 0.09, 0.11, 0.15 \text{ and } 0.18$ .

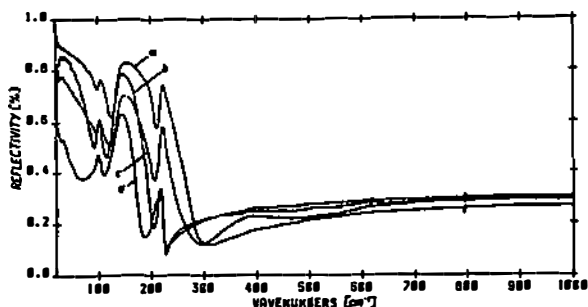
## RESULTS AND DISCUSSION

Figure 1 shows the reflection spectra of  $Hg_{1-x}Mn_xSe$  with

various manganese composition, in the region from 50 - 1000  $\text{cm}^{-1}$ . More significant changes in spectra are noticeable below 500  $\text{cm}^{-1}$ , in the region where LO and TO lattice vibrations are to be anticipated. In paper /6/ two bands at about 101  $\text{cm}^{-1}$  and 137  $\text{cm}^{-1}$  were identified as TO modes of HgSe. The third band at about 215  $\text{cm}^{-1}$ , whose position in the spectrum is sensitive to the composition of  $\text{Mn}^{2+}$  in the sample, is ascribed to TO mode  $\beta$ -MnSe. The band at about 400  $\text{cm}^{-1}$  probably stems from the interband electron transitions in  $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$  /6/.

The reflection spectrum  $\text{Hg}_{0.82}\text{Mn}_{0.18}\text{Se}$ , in the region from 500 - 5000  $\text{cm}^{-1}$  is shown in Fig.2.

Fig. 1. Reflection spectra  $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$  for:  
 b)  $x = 0.09$ , a)  $x = 0.11$   
 c)  $x = 0.15$ , d)  $x = 0.18$



The reflection spectrum  $\text{Hg}_{0.82}\text{Mn}_{0.18}\text{Se}$ , in the region 500 - 5000  $\text{cm}^{-1}$  is shown in Fig.2.

A part of the reflection curve which is of importance for the evaluation of the energy gap of this crystal is given in the insert. The absorption spectrum of the same sample in the region from 2700 - 4000  $\text{cm}^{-1}$  is plotted in Fig.3.

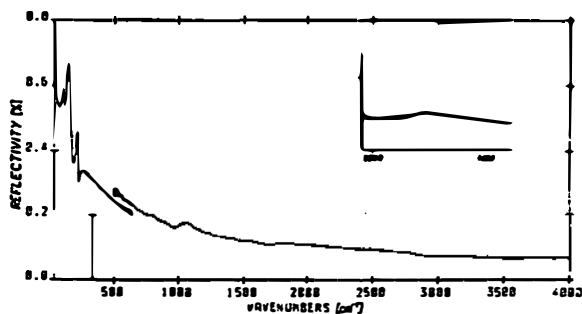
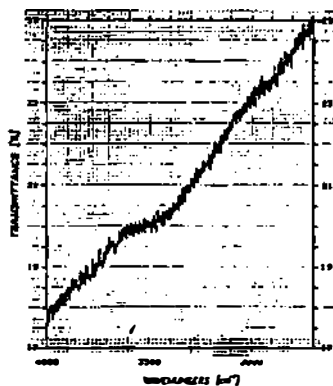


Fig.2. The reflection spectrum  $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$  ( $x = 0.18$ )

Fig.3. The absorption spectrum  $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$  ( $x = 0.18$ ). The sample in KBr



Knowing the following data for the system  $\text{Hg}_{1-x}\text{Mn}_x\text{Se}; E_g(x)$  at 10 K [2,3],  $E_g(300\text{ K})$  for the pure  $\text{HgSe}$  [1], the dependence  $E_g(x)$  at 300 K for similar three-component compounds, we have evaluated the regions of wave numbers wherein the change  $T$  (i.e.  $R$ ) can be connected to  $E_g$  of these crystals. Let us notice (Figure 2) that in a large region around these characteristic wave numbers we have a constant coefficient  $R$  (the same is valid for  $T$ , too).

The results obtained through the analysis of curves  $T(\nu)$  and  $R(\nu)$  with four samples  $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$  are shown in Table 1 and in figure 4 (points denote the data from  $T(\nu)$ , crosses the data from  $R(\nu)$ ).

Table 1

COMPOSITION $x$ (%)	$E_g$ (meV) at 300K	
	from $T(\nu)$	from $R(\nu)$
0	290	
11	375	
15	471	406
18	510	462
0	$E_g(300) = -0.10\text{ eV}/1\%$	

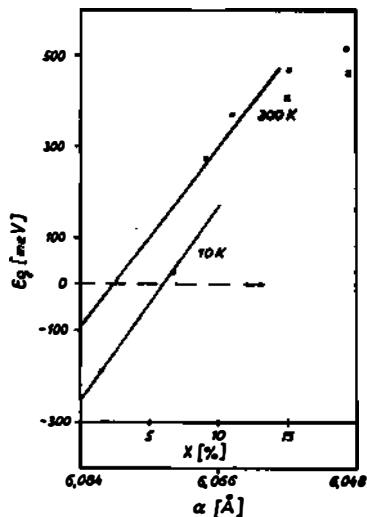


Fig. 4. The dependence of  $E_g$  on the composition and lattice constant at 300K (our measurement) and 10K (data from reference [2]). Dependence  $a(x)$  is given from reference [5].

If we can speak about the linear dependence  $E_g(x)$  at 300 K then it could possibly be only for  $x < 0.15$ . In that case the dependence  $E_g(x)$  determined by the method of least squares can be written in the form

$$E_g(\text{eV}) = -0.094 + 0.036 x (\%)$$

For greater concentrations the deviation from the linearity occurs. We have to have in view that  $E_g(x)$  in principle is not a linear function for composite semiconducting compounds. Obviously, for a more precise determination of  $E_g(x)$  a bigger number of measurements of samples in the regions of concentrations smaller and greater than those involved here is necessary.

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