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## TEMPERATURE AND COMPOSITION DEPENDENCE OF PHOTOVOLTAIC SPECTRA OF $Pb_{1-x}Mn_xSe$ DIODES

LE-VAN-KHOI, A. SZCZERBAKOW, G. KARCZEWSKI AND R.R. GALĄZKA

Institute of Physics, Polish Academy of Sciences, Al.Lotnikow 32/46, 02-668 Warszawa, Poland

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Photovoltaic spectra of  $Pb_{1-x}Mn_xSe$  homojunctions have been measured in the infrared spectral region within the temperature range 15-300 K. The junctions have been formed by cadmium diffusion into the *p*-type  $Pb_{1-x}Mn_xSe$  crystals with manganese content  $0 \le x \le 0.08$ . From the positions of the photovoltaic maxima the energy band gap of the diode material has been determined. A phenomenological expression describing the energy band gap of  $Pb_{1-x}Mn_xSe$  as a function of temperature and crystal composition has been proposed. In diodes containing high manganese content x = 0.06 and x = 0.08 a second photovoltaic maximum caused by indirect optical transitions between the main conduction band and the secondary valence band located along the  $\Sigma$ -axis of the Brillouin zone has been observed.

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 $Pb_{1-x}Mn_xSe$  solid solutions have been recently studied in view of their possible semimagnetic properties [1-3], but the temperature and the composition dependence of the energy band gap in this material have not been determined. The aim of this work was to determine the energy band gap of  $Pb_{1-x}Mn_xSe$  by photovoltaic effect measurements on p-n diodes. This method gives the correct band gap values with an accuracy about 5 meV [4].

## I. Experimental technique

The diodes were prepared from  $Pb_{1-x}Mn_xSe$  single crystals grown by the Bridgman method with manganese molar fraction  $x = 0 \div 0.08$ . The as-grown *p*-type crystals with carrier concentration of the order of  $10^{19}$  cm<sup>-3</sup> at 77 K were cleaved along [100] surfaces and annealed by two-zone technique in Se atmosphere

to establish a constant carrier concentration of  $5 \times 10^{18}$  cm<sup>-3</sup> at 77 K. The mobility of the holes in these samples reached  $3 \times 10^3$  cm<sup>2</sup> /Vs at 77 K. The *p*-*n* junctions were prepared by the two-zone technique as well. However, the source consisted here of cadmium dissolved in indium (2 at. %) in order to decrease the Cd-vapour pressure. The temperature of the crystal was 510°C and the temperature of the source was 300°C during 2 hours. After the diffusion procedure the wafers having an *n*-type "skin" were cleaved to obtain samples containing *p*-*n* junctions. The ohmic contacts were formed by soldering indium to the *n*-type surface and by covering the *p*-type surface with gold. The diode size was about  $500 \times 500 \times 200 \,\mu\text{m}^3$ . Neither protective nor antireflecting coating were applied.



Fig. 1. (a) Photovoltaic spectra of Pb<sub>0.96</sub> Mn<sub>0.02</sub>Se diode at different temperatures: (1) T = 130 K, (2) T = 90 K, (3) T = 50 K, (4) T = 30 K. The amplitudes of the photovoltaic maxima have been normalized. (b) Temperature dependence of the energy band gap of Pb<sub>1-x</sub>Mn<sub>x</sub>Se: (1) x = 0.00; (2) x = 0.007; (3) x = 0.01; (4) x = 0.02; (5) x = 0.05; (6) x = 0.06.

The optical measurements were carried out using a thermal infrared source and a SPM-2 Zeiss monochromator with LiF or NaCl prisms. The chopping frequency was 810 Hz. The photovoltaic response locked in by the LOCK-IN amplifier NEM 212 was compared with that of thermocouple signal at the chopping frequency of 8 Hz.

The temperature was continuously stabilized by controlling He-flow in a continuous-flow He dewar and measured with a calibrated Au(Fe)-Chromel thermocouple soldered on the ceramic wafer carrying the diodes. The photovoltaic measurements were carried out in the temperature range of 15-300 K.

## **II.** Experimental results and discussion

The zero bias photovoltaic responses of the  $p-n \operatorname{Pb}_{1-x} \operatorname{Mn}_x \operatorname{Se}$  diodes were measured. The photovoltaic spectra of the  $Pb_{1-x}Mn_xSe$  diodes with x = 0.02obtained at several temperatures are shown in Fig. 1a. The shapes of these spectra are characteristic for all investigated diodes. The photovoltaic spectrum of the diodes shows a sharp maximum vanishing rapidly on the longer-wavelength side. This maximum shifts towards shorter wavelengths with increasing temperature. Chambouleyron [4] has related the energy gap of the diode material to the photon energy at which the photovoltaic response reaches its maximum. Since the photons of energy  $E_{g}$  are directly absorbed in the junction region giving electron-hole pairs, their dissociation causes the voltage rise in the circuit. By assuming that the value of the energy gap is equal to the photon energy corresponding to the photovoltaic maximum, the energy gap values of  $Pb_{1-x}Mn_xSe$  as a function of temperature for the samples with several manganese contents was determined and are shown in Fig. 1b. The slope of each plotted line,  $dE_g/dT$ , decreases with the manganese content. These coefficients are equal to 0.460; 0.425; 0.420; 0.400; 0.320; 0.300 meV/K for the alloy compositions x = 0; 0.075; 0.01; 0.02; 0.05; 0.06, respectively. One can see from the Fig. 1b that the energy gap of  $Pb_{1-x}Mn_xSe$  diodes increases with the increasing manganese content.

The results of the measurements presented above can be expressed in term of a phenomenological formula describing the energy gap of  $Pb_{1-x}Mn_xSe$  alloy system as a function of both the temperature and manganese content:

$$E_{g}[\text{meV}] = 130 + 28x + [(0.442 - 0.022x)^{2}T^{2} + 400]^{1/2},$$
$$x = 0 \div 6\%, \ T = 30 \div 300 \text{ K}.$$

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For diodes with the high manganese content  $x = 0.06 \div 0.08$  the photovoltaic spectrum of the diode at low temperature shows one distinct maximum at the wavelength, which corresponds to the band gap energy of the diode material and a second weak maximum in the region of higher energies (Fig. 2). When the temperature increases the first maximum shifts towards the direction of higher energy and the magnitude of detectivity decreases, whereas the second maximum remains at the same wavelength (Fig. 2). The magnitudes of both maxima become comparable at the temperature of about 120 K and further temperature increase leads to domination of the second maximum. The behavior of the photovoltaic spectrum of the diodes  $Pb_{1-x}Mn_xSe$  with  $x = 0.06 \div 0.08$  is in good agreement with the two valence zone model given in [5] for PbTe, which states that the valence band consists in reality of two subbands (one associated with the *L*-point of the Brillouin zone and the second – with the  $\Sigma$ -point).



Fig. 2. Photovoltaic spectra of  $Pb_{0.92}Mn_{0.08}Se$  diode at two temperatures, showing two maxima of the photovoltaic response.

Considering the model [5] the energy difference between the valence subbands  $\Delta E_v$  is equal to 0.095 meV and 0.090 meV at 30 K for x = 0.06; 0.08, respectively. When the temperature increases, these energy differences decrease with coefficients -0.30 meV/K; -0.43 meV/K for x = 0.06; 0.08, respectively.

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