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THE INTRINSIC CARRIER CONCENTRATION IN $Pb_{1-x}Sn_xTe$, $Pb_{1-x}Sn_xSe$ AND $PbS_{1-x}Se_x$

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The results of calculations of the intrinsic carrier concentration in $Pb_{1-x}Sn_xTe$ ($0 \leqslant x \leqslant 0.30$), $Pb_{1-x}Sn_xSe$ ($0 \leqslant x \leqslant 0.14$) and $PbS_{1-x}Se_x$ ($0 \leqslant x \leqslant 1$) for temperature range 30 to 300 K are presented. The calculations have been performed in term of the Kane model.

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1. *Introduction*

The development of the technology of $Pb_{1-x}Sn_xTe$, $Pb_{1-x}Sn_xSe$ and $PbS_{1-x}Se_x$ solid solutions is related to the wide use of those materials in infrared techniques. In wiew of some specific properties characteristic of semiconductors with a small and controlled energy gap (very small effective masses, high carrier mobilities, anomalous values of the dielectric constant, etc.) these compounds have been widely investigated. However, to interpret some of their optic and electric properties it is necessary to know the carrier concentration for various molar compositions x in a wide range of temperatures.

For semiconductors with parabolic energy bands, the intrinsic carrier concentrations is given by [1]

$$n_i = 2\left(\frac{2\pi kT}{h^2}\right)^{3/2} (m_{dn}^* m_{dp}^*)^{3/2} \exp\left(-\frac{E_g}{2kT}\right), \tag{1}$$

where k is Boltzmann's constant, h is Planck's constant, E_g is the energy gap, m_{dn}^* and m_{dp}^* are the density of states effective masses of electrons and holes, respectively. Equation (1) is valid for Boltzmann statistics.

The conduction and valence bands of lead chalcogenides are strongly nonparabolic [2]. In this case, the intrinsic carrier concentration can be calculated using (1) when condition $E_g \gg kT$ is satisfied. In consequence of this limitation, the narrow range of the energy gap 0.04–0.16 eV as well as temperature 50–200 K was used to calculate of $Pb_{1-x}Sn_xTe$

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intrinsic concentration in paper [3]. The effective masses were obtained basing on paper [4] and it was assumed that the effective masses vary proportionally to the width of the energy gap.

So far the intrinsic carrier concentration of $Pb_{1-x}Sn_xSe$ as well as $PbS_{1-x}Se_x$ have not been calculated.

In this paper the intrinsic carrier concentration in $Pb_{1-x}Sn_xTe$, $Pb_{1-x}Sn_xSe$ and $PbS_{1-x}Se_x$ is calculated for the most interesting compositions of this compounds and for temperatures of 30, 50, 77, 100, 150, 200, 250 and 300 K. In the calculations the nonparabolic bands were taken into account according to the Kane's model and the effective masses, and dependence on the composition as well as temperature were assumed after the paper [5]. The results of above mentioned calculations were compared with the results of calculations for the parabolic bands.

2. *Calculations and results*

For intrinsic semiconductors [1]

$$n_i = 2\int_{E_c}^{\infty} \varrho_c(E)f(E)dE = 2\int_{-\infty}^{E_v} \varrho_v(E)\,[1-f(E)]dE, \tag{2}$$

where E_c is the energy of conduction band edge, E_v is the energy of valence band edge, $f(E)$ is the Fermi function, $\varrho_c(E)$ and $\varrho_v(E)$ are the density of states functions for electrons and holes respectively.

The density of states function in the case of the Kane model is [6]:

$$g(E) = \frac{(2m^*_{d0})^{3/2}}{4\pi^2\hbar^3}\left[E\left(1+\frac{E}{E_g}\right)\right]^{1/2}\left(1+\frac{2E}{E_g}\right), \tag{3}$$

where m^*_{d0} is the band edge effective density.

When the Fermi level F is within the gap at least kT below (above) the conduction (valence) band edge, then $f(E)$ can be approximated by

$$f(E) = \exp\left(-\frac{E-F}{kT}\right). \tag{4}$$

This is known as the Boltzmann approximation. The above condition is fulfilled in all range considered compositions of $Pb_{1-x}Sn_xTe$, $Pb_{1-x}Sn_xSe$, and $PbS_{1-x}Se_x$ and temperature range 30 to 300 K.

By substitution of (3) and (4) into (2) for nondegenerate materials ($np = n_i^2$) we obtain:

$$n_i = \frac{1}{2\pi^2\hbar^3}\left(2\sqrt{m^*_{dn}m^*_{dp}}\,kT\right)^{3/2}\exp\left(-\frac{E_g}{2kT}\right)\int_0^{\infty} e^{-z}[z(1+\beta z)]^{1/2}\,(1+2\beta z)dz, \tag{5}$$

where $z = E/kT$ and $\beta = kT/E_g$.

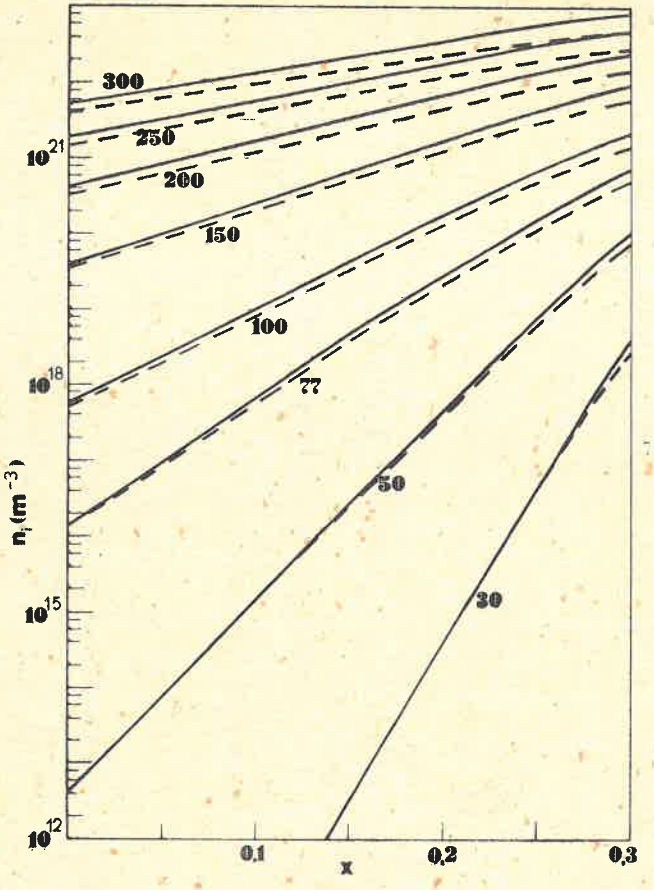

Fig. 1

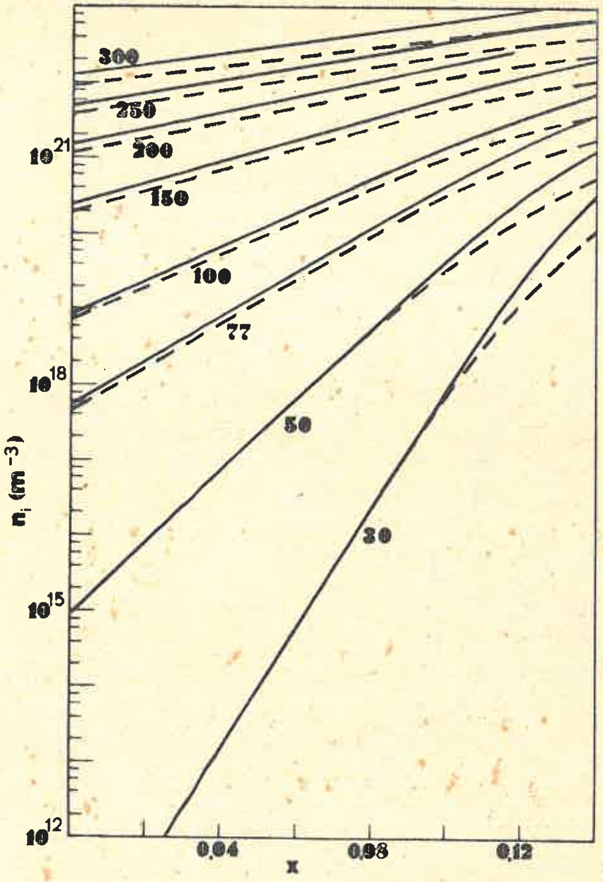

Fig. 2

Fig. 1. Intrinsic carrier concentration in $Pb_{1-x}Sn_xTe$ as a function of composition for various temperatures. The continuous lines are calculated for nonparabolic bands, the dashed lines for parabolic bands

Fig. 2. Intrinsic carrier concentration in $Pb_{1-x}Sn_xSe$ as a function of composition for various temperatures. The continuous lines are calculated for nonparabolic bands, the dashed lines for parabolic bands

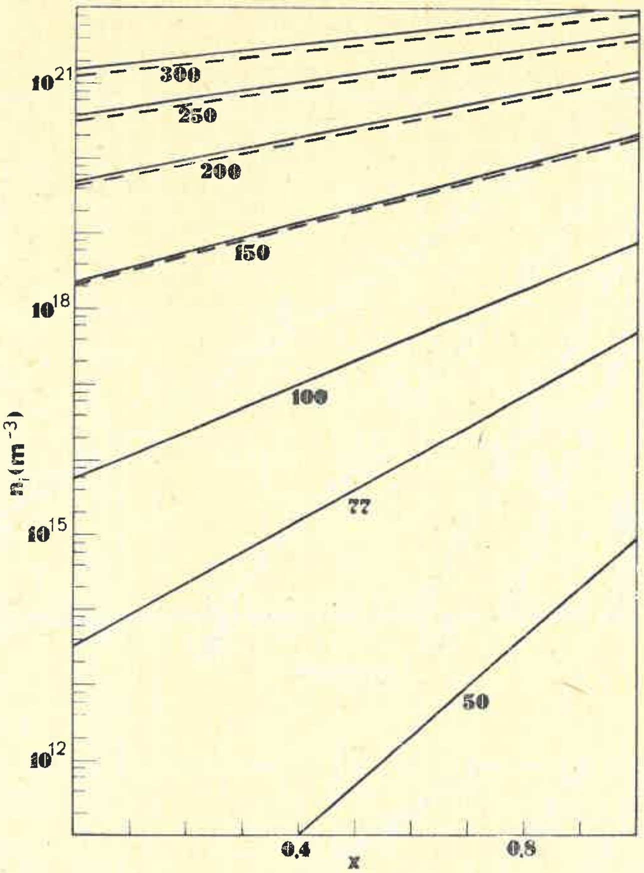

Fig. 3. Intrinsic carrier concentration in $PbS_{1-x}Se_x$ as a function of composition for various temperatures. The continuous lines are calculated for nonparabolic bands, the dashed lines for parabolic bands

The density of states effective mass can be obtained from the longitudinal and transverse mass components according to $m_d^* = N^{2/3}(m_l^* m_t^{*2})^{1/3}$, where $N = 4$ is the number of equivalent band extrema.

In the vicinity of the energy gap in lead chalcogenides we observe a system of three conduction bands and three valence bands. The temperature and x-dependence of the effective masses at the band edges may be expressed by [5]

$$\frac{1}{m^*(x, T)} = \frac{1}{m_{cv}^*} \frac{E_g(0, 0)}{E_g(x, T)} + \frac{1}{m_F^*}, \tag{6}$$

where m_{cv}^* determined a contribution due to the interactions between the nearest extremes of the valence band and conduction band, m_F^* far bands contribution. The functions (6) for the four effective masses: m_{ct}^* (conduction band, transverse), m_{vt}^* (valence band, transverse), m_{cl}^* (conduction band, longitudinal), m_{vl}^* (valence band, longitudinal) were assumed after paper [5].

Exact knowledge $E_g(x, T)$ dependences for the ternary compounds is required for reliable calculations over a wide range. However, different relationships $E_g(x, T)$ can be found in the literature for $Pb_{1-x}Sn_xTe$ [5, 7, 8] and $Pb_{1-x}Sn_xSe$ [5, 9, 10]. On the basis of the study of experimental results for $Pb_{1-x}Sn_xTe$ [11–16], $Pb_{1-x}Sn_xSe$ [16–20] and $PbS_{1-x}Se_x$ [21, 22] good agreement with experimental data was obtained using the following relations [5]:

for $Pb_{1-x}Sn_xTe$ $\quad E_g(x, T) = 171.5-535x+\sqrt{12.8^2+0.19(T+20)^2}$ [meV],

for $Pb_{1-x}Sn_xSe$ $\quad E_g(x, T) = 125-1021x+\sqrt{400+0.256T^2}$ [meV],

for $PbS_{1-x}Se_x$ $\quad E_g(x, T) = 263-138x+\sqrt{400+0.256T^2}$ [meV].

The calculations of the intrinsic carrier concentration were performed basing on the equation (5) and taking into account $m^*(x, T)$ after paper [5] and $E_g(x, T)$ given above. The intrinsic carrier concentration in $Pb_{1-x}Sn_xTe$, $Pb_{1-x}Sn_xSe$ and $PbS_{1-x}Se_x$ as a function of composition x for various temperatures are plotted in Figs 1–3. In those figures, the dashed curves refer to the parabolic bands, are also plotted. As can be seen, the intrinsic concentrations calculated for nonparabolic bands were found to be higher than concentrations calculated for parabolic bands. The discrepancies were found to be large in the range of higher temperature and larger x (smaller energy gap). It can be stated, however, that formula (1) is a good approximation for the evaluation of intrinsic carrier concentration especially in $PbS_{1-x}Se_x$.

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