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ELECTROPHYSICAL PROPERTIES OF NEW SYSTEM [Pb(M)]RETe SEMIMAGNETIC SEMICONDUCTORS

ZAHARI ZLATANOV

Department of General Physics,
Faculty of Physics, St. Kliment Ohridski University of Sofia

Захари Златанов. ЕЛЕКТРОФИЗИЧНИ СВОЙСТВА НА НОВА СИСТЕМА [Pb(M)]RETe ПОЛУМАГНИТНИ ПОЛУПРОВОДНИЦИ

Изследвана е нова система [Pb(M=Bi, Sn, Mn)]RETe полумагнитни полупроводници. Монокристални образци $[Pb_{1-x}Bi_x]_{1-y}Gd_yTe$ са получени чрез Бриджман метода на вертикалната кристализация. Термоелектродвижещата сила, коефициентът на Хол и електропроводимостта са измерени за различни концентрации на примеса Bi. Експерименталните резултати показват донорното действие на Bi. Нивото на Ферми и ефективната маса на плътността на състоянията са разгледани като функция на концентрацията на примесните атоми. Получените резултати могат да се използват, за да се направи извод, че в проводимата зона на PbTe има примесни състояния. Промените на електрофизичните свойства с температурата на образци, легирани с различни количества Bi, биха могли да се свържат с настъпващите промени от присъствието на примесни нива Bi в областта на проводимата зона. Анализът на данните, получени от измерване на термоелетродвижещата сила и електропроводимостта на образци при стайна температура, показва нарастване на електропроводимостта и намаляване на Т.Е.Д. сила с повишаването на примесната концентрация *x*. Изследваните материали са с *n*-тип проводимост.

Zahari Zlatanov. ELECTROPHYSICAL PROPERTIES OF NEW SYSTEM [Pb(M)]RETe SEMIMAGNETIC SEMICONDUCTORS

The new system [Pb(M=Bi, Sn, Mn)]RETe semimagnetic semiconductors have been investigated. Monocrystalline samples $[Pb_{1-x}Bi_x]_{1-y}Gd_yTe$ have been prepared by vertical Bridgeman method. The thermoelectric powers, Hall coefficient, electric conductivity, were measured for different impurity concentrations of Bi. The experimental results show the donor action of Bi. The Fermi level and effective mass of the density of states are studied as a function of the impurity atoms concentration. The results obtained may be used to conclude that impurity states are really present in the PbTe conduction band. The change of the electrophysical properties with the temperatures for samples doped with different amounts of Bi should be attributed to resulting changes, in the region of allowed states in the conduction band, because of the presence of impurity states. The analysis of the data obtained from measurement of the thermoelectric power and the electrical conductivity of samples at room temperature has shown the following: with increasing impurity concentration *x*, the electrical conductivity increases and the thermoelectric power decreases. The samples have a *n*-type conductivity.

***Keiwords*:** semiconductors, structure, magnetic, transport properties
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For contacts: Zahari Zlatanov, Department of General Physics, Faculty of Physics, St. Kliment Ohridski University of Sofia, 5 James Bourchier Blvd.,BG-1164 Sofia, Bulgaria, tel. 0359 2 8161632, E-mail: zaho@phys.uni-sofia.bg

1. INTRODUCTION

Lead telluride is one of the main widely used semiconductor materials. When impurities such as Ag, Bi, Cr, RE (rare-earth elements) are added, its electrophysical properties are improved. One of the possible impurities (Bi) may be added either in PbTe or in lead telluride doping with impurity atoms (as rare earth elements) in atomic form or as a compound BiTe In our case it is atomic form added to PbRETe materials

Gadolinium-doped PbTe and Pb(Gd) semiconductors have been studied recently by several groups [1−7]. These systems are examples of narrow-gap dilute magnetic semiconductors. The interest in this class of compounds centers on the effect caused by the interactions between the carriers and the magnetic moment of the dopands. While the 3*d* dopand Mn has been extensively studied, less is known about the 4*f* dopand Gd. For Gd in PbTe and SnTe, Shubnikov–De Haas oscillations, as well as very high mobilities, are reported in [6]. Measurements of electron paramagnetic resonance (EPR) and of susceptibility have been performed on $Pb_{0.995}Gd_{0.005}Te$ crystals. The EPR spectra consist of two components, one showing the fine structure of Gd^{3+} ions in a cubic environment. The Curie–Weiss temperature in these alloys is small and negative, reflecting a weak antiferro-magnetic exchange interaction between the Gd ions , similar to that of Mn in PbTe [7].

2. EXPERIMENTAL DATA AND DISCUSSI

The impurities Bi is added in atomic form to PbRETe materials, i.e. $Pb_{1-0.005}Gd_{0.005}Te$. In this study was measured initially the thermoelectric power (α) and the electrical conductivity (σ) of samples at room temperature. Of some samples were measured temperature dependence of α and σ (Fig. 1, Fig. 2). The

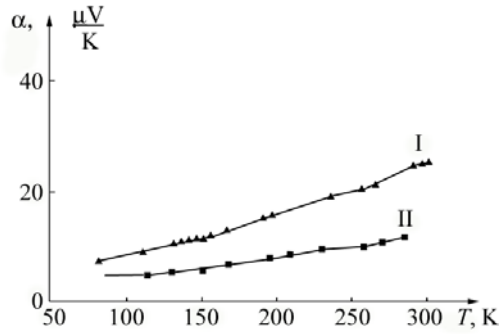

Fig. 1. Temperature dependence of thermoelectric power for samples $[Pb_{1-x}Bi_x]_{1-y}Gd_yTe$ doping with Bi: I) $x = 0.002$; II) $x = 0.003$

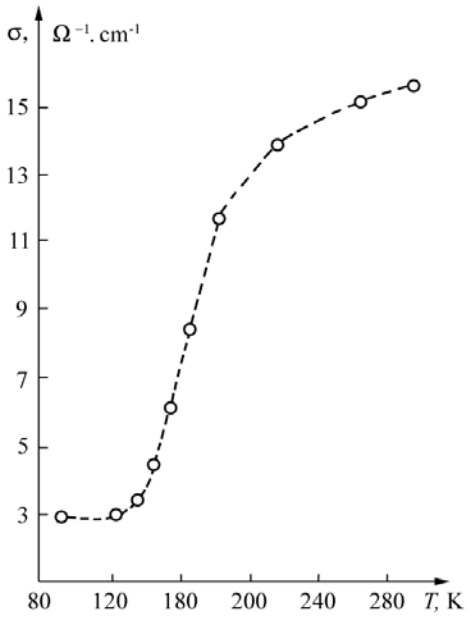

Fig. 2. Temperature dependence of electroconductivity for sample $[Pb_{1-x}Bi_x]_{1-y}Gd_yTe$ with $x = 0.001$

analysis of the data obtained has shown the following: with increasing impurity concentration x, the electrical conductivity increases and the thermoelectric power decreases. The samples have a n-type conductivity. To improve the thermoelectric properties, the samples were annealed in quartz ampoules evacuated down to 10^{-5} Torr at 600^{o} C for the duration of 120 h. The annealing terminated with sharp cooling in an ice bath. The thermoelectric power, electrical conductivity and the Hall coefficient R_x of the annealed samples have been measured at room temperature. The values obtained were used to calculate the current carrier concentration n , carrier mobility μ (see Table). It may be seen that the introduction of small amounts of impurities leads to a increase in electrical conductivity. The thermoelectric power decreases with increasing concentration of Bi (Fig. 1). As far as the current carrier concentration is concerned, the experimental data have shown that it increases with increasing impurity concentration and the reverse dependence is observed simultaneously of the mobility on the Bi concentration (Table).

Table: Dependence of the carrier concentration and mobility of annealed samples on the Bi concentration (x at.%)

x, at.%	$n \times 10^{19}$, cm^{-3}	μ, cm^2 / V.s
0	0.7	1560
0.001	1.3	580
0.002	1.6	470
0.003	1.9	340

The increase in electrical conductivity with increasing amount of impurity may be related to the creation of new carriers as a result of the bismuth donor action.

Small amounts of added impurities produce a sharp increase in the carrier concentration of the doping material as compared with stoichiometric lead telluride. This increase may be explained in terms of the fact that the bismuth atoms take up existing lead vacancies, i.e. hole concentration decreases, and the concentration of the Bi positive ion at the lead sites increases. For low impurity concentrations, the building up crystal lattice is close to that of $Pb_{1-x}Gd_xTe$ system (here x is Gd concentration) and the carrier mobility is high. As a result of the complex action of his current-carrier concentration and mobility, the addition of small amounts of Bi increases the electrical conductivity. With increasing amount of impurity, the number of scattering centers also increases. This leads to decreased carrier mobility (Table). The impurity Gadolinium from the rare-earth elements is characterized by unfilled *d*-electron subshell. Taking into account that the dissolution of the doping impurity is governed by the degree of similarity for the energy characteristics of the valence electrons of the substituting and substituted atom (in our case this is lead), it may be expected that their effect on the properties of the host crystal would be considerable.

This assumption is in agreement with previous studies where have shown that Gd in PbTe (for $Pb_{1-x}Gd_xTe$ system) acts as a donor. When PbTe is doped (at *p*-type PbTe) with Gd in amounts larger than 0.1 at.% the existing lead vacancies would be occupied by the gadolinium ions and electrons are released. This produces a change in the conduction type from p-type samples and the measured concentration of the free electrons is above 8×10^{18} cm^{-3} at 300 K. From the measurements on the temperature dependences of PbTe samples with different amounts of Gd, it was supposed that the impurity levels are present in the PbTe conduction band.

In the presented work are report results from studies on the concentration and temperature dependences of the electrophysical properties of monolithic samples $[Pb_{1-x}Bi_x]_{1-y}Gd_yTe$ from the system Pb(M)]RETe (at fixed concentration of gadolinium y at%, $y = 0.005$).

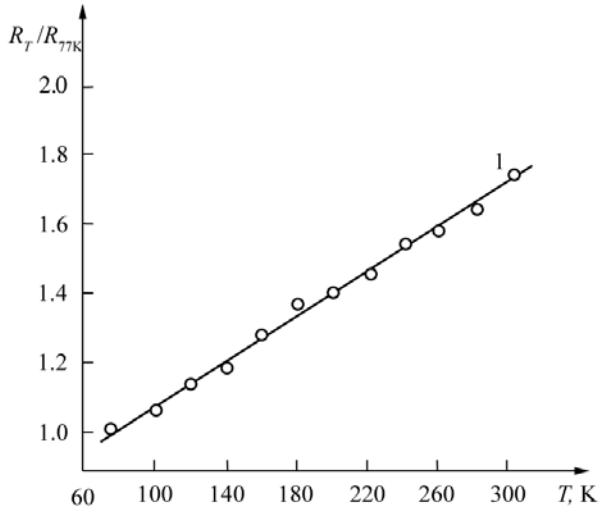

Fig. 3. Temperature dependence of Hall coefficient ($x = 0.002$, $y = 0.005$)

As seen from Fig. 1 and Fig. 3, the thermoelectric power and the Hall coefficient for Bi-doped $Pb_{1-x}Gd_xTe$ samples, i.e. $[Pb_{1-x}Bi_x]_{1-y}Gd_yTe$ (at range of concentration of Bi $x = 0.001$ to $x = 0.003$) reveal a sharp increase with temperature (77−300 K) which is not observed in undoped PbTe samples. The Hall coefficient in PbTe with *n*-type conduction is known [10] to be constant in a rather wide temperature range Even for the most strongly doped samples, the variation of R in the same temperature interval does not exceed 10–15% [9]. The differences are substantial at temperatures higher than 100 K .

As a result of the inclusion of the impurity atoms into the host crystal lattice, the electric conductivity of the doped samples is larger than that of the undoped samples. A field of own conductivity is not observed in the studied temperature range. Hence it may be supposed that the temperature variations of the Hall coefficient reflect the change in the part of ionized impurity atoms with the temperature resulting from the presence of impurity in the PbTe conduction band. Such a strong increase of the Hall coefficient with temperature could hardly be due to the increase in the Hall factor r_H in the dependence:

$$R = \frac{r_H}{e.n} \ , \qquad (1)$$

since the rise starts at much lower temperatures (77 K) [8], when the degeneracy is rather strong and the Hall factor is weakly affected by the energy dependence of the relaxation time [10]. Thus the nature of the change in the electrophysical (kinetic parameters) parameters with temperature for Bi-doped samples ($[Pb_{1-x}Bi_x]_{1-}$

$_y$Gd$_y$Te) is defined by changes in the free carrier concentration. Thus if the impurity electron concentration n_0 in the crystal is assumed to be distributed among the band states – the free carriers in the conduction band n_c and the states localized at the bismuthium impurities n_d – then the following relations would hold

$$n_o = n_c + n_d \,, \qquad (2)$$
$$n_d = N_{Bi} f_d \,,$$

where N_{Bi} is the concentration of the impurity's electroactive states, f_d is the Fermi distribution function. In this case, the Hall coefficient would be defined by an expression such as

$$R = \frac{r_H}{e} . \frac{1}{n_o - N_{Bi} f_d} \,. \qquad (3)$$

In case of degeneracy, r_{H} =1. With increasing temperature $N_{\mathrm{Bi}}f_d$ increases, which produces an increased Hall coefficient. Under the assumption of an impurity band in the allowed state region, containing two states of the impurity atom, using distribution function such as [11]

$$F_d = 2/\{1 + \exp[(E_d - E_F)/K_o T]\} \,, \qquad (4)$$

it was found that the energy separation between this band and the extremum from the conduction band of PbTe at T = 77 K is E_d = 0.08 eV. The rise of the thermoelectric power with increasing temperature for the Bi-doped samples may also be explained from the point of view of impurity states being present in the PbTe conduction band. The effective mass of the density of states in the conduction band extremum has been found when taking into account the non – parabolicity of the PbTe band by the Kane model; the experimental values of the thermoelectric power and the charge carrier concentration were used in this determination.

In the case of elastic scattering, weak magnetic field, impurity conductivity and arbitrary degeneracy, the thermoelectric power and the carrier concentrations are known to be defined by [12] :

$$\alpha = \frac{k_o}{e}\left[\frac{{}^1L^1_{-2}}{{}^oL^1_{-2}} - E^*_F\right], \qquad (5)$$

$$n = \frac{(2m^*_{do}k_oT)^{3/2}}{2\pi^2\hbar^3}\,{}^oL^{3/2}_o(E^*_F,\beta) \,, \qquad (6)$$

where k_0 is the Boltzmann constant; e is the charge of electron; E^*_F is the reduced Fermi level ; ${}^mL^n_k(E^*_F,\beta)$ are generalized Fermi integrals ; β is a coefficient

characterizing the non-parabolicity of the bands ; $\hbar = \frac{h}{2\pi}$ is the Planck constant.

Then, for the effective mass of the density of states in the band extrema the following expression is obtained:

$$m_{d0}^{*} = \frac{(2\pi^2\hbar^3 n)^{2/3}}{2k_o T({}^{o}L_o^{3/2})^{2/3}}. \qquad (7)$$

In brief, the procedure is as follows. From the theoretical relation (4) for the thermoelectric power, from the reduced Fermi level E^*_F, under the assumption of acoustic phonon scattering and accounting for the temperature dependence of the band gap width for different β at :

$$\frac{dE_g}{dT} = 4\times10^{-4} \text{ eV/K}, \qquad (8)$$

can found the Fermi level. The experimental Hall coefficient values were used to find the charge carrier concentration $n = 1/ R.e$, calculating further from relation (6) the effective mass m_{d0}^{*} .

The Fermi level was found from the thermoelectric power and this is justifiable when a single type of carrier contributes to the conductivity and no effect of electron entrapment by phonons is observed as is the case under consideration. The assumption of scattering by acoustic phonon is in compliance with the theory of electromagnetic phenomena [12].

With variable temperature in the 77−300 K , the effective mass changes by the $m_{d0}^{*} \sim T^a$ law, where :

$$a = \frac{T}{E_g}.\frac{dE_g}{dT} = 0.4, \qquad (9)$$

as expected by the theory in the case of PbTe [10].

3. CONCLUSION

This study have shown that regardless of the way of fabrication of $Pb_{1-x}Gd_xTe$ samples doped with Bi , the behavior of their electrophisical properties is defined by the presence of the impurity atoms Bi and the related changes in the region of allowed states in the PbTe electronic spectrum.

The results obtained may be used to conclude that impurity states are really present in the PbTe conduction band. The dependence of the electrical conductivity, thermoelectric power, mobility, current carrier concentration *n* on the amount of Bi has been found. The observed behavior of the studied quantities has

been explained in terms of the impurity incorporation into the PbTe lattice and the related change in the defect ratio. The studies carried out supplement the information on the electrophysical (kinetic) parameters of the $[Pb_{1-x}Bi_x]_{1-y}Gd_yTe$ system and may serve as a basis for further studies.

REFERENCE

[1] Averous, M., B. A. Lombos, C. Fau, E. Ilbnouelchazi, J. C. Tedenac, G. Brun, M. Bartkowski. *Phys. Stat. Solidi B*, 1985, **131**, 759.

[2] Hedgcock, F. T., P. C. Sullivan, M. Bartkowski. Low Temperature Physics, LT17. Elsevier, Amsterdam, The Netherlands, 1984, CQ13.

[3] Hedgcock, F. T., P. C. Sullivan, J. T. Grembowiz, M. Bartko. *Can. J. Phys*., 1986, **64**, 1345.

[4] Bartkowski, M., D. J. Northcott, A. H. Redddoch. *SolidState Commun*., 1985, **56**, 659.

[5] Savage, H. T., J. J. Rhyne. *AIP Conf. Proc*., 1971, **5**, 879.

[6] Han, B. S., O. G. Symco, D. J. Zheng, F. T. Hedgcock. *Materials Research Society. Fall Meeting.* Boston, MA, 1986, Abstract, Q3.3.

[7] Bartkowski, M., A. H. Reddoch, D. F. Williams, G. Lamarche, Z. Korczak. *Solid State Commun*., 1986, **57**, 185.

[8] Borisova, L., L.S. Parfeneva. *Bulg. J. Phys,* 1983, **10**, 338.

[9] Prokofeva, L.V. *Fiz. Tekhn. Poluprov.*, 1970, **4**, 3.

[10] Ravich, J. I., B. A. Efimova, I. A. Smirnov. Methods of investigation of lead chalcogenide semiconductors. Moscow, 1963.

[11] Veis, A.N., B.I. Kaidanov, J. I. Ravich. *Fiz. Tekhn. Poluprov*., 1976, **10**, 104.

[12] Askerov, B. M. Electrophysical effects in the semiconductors. Leningrad,1970.