Semiconductors, Vol. 35, No. 11, 2001, pp. 1249–1251. Translated from Fizika i Tekhnika Poluprovodnikov, Vol. 35, No. 11, 2001, pp. 1306–1308.

ELECTRONIC AND OPTICAL PROPERTIES OF SEMICONDUCTORS

Magnetic Properties of $Pb_{1-x}Ge_xTe$ Alloys Doped with Ytterbium

E. P. Skipetrov*, N. A. Chernova*, L. A. Skipetrova*, A. V. Golubev*, and E. I. Slyn'ko**

** Moscow State University, Vorob'evy gory, Moscow, 119899 Russia*
e-mail: skip@mig.phys.msu.su
*** Institute of Material Science Problems, Chernovtsy, 274001 Ukraine*
Submitted February 14, 2001; accepted for publication April 2, 2001

Abstract—Temperature dependences of magnetic susceptibility and as a function of magnetic-field dependences of magnetization in the $Pb_{1-x-y}Ge_xYb_yTe$ ($0 \le x \le 0.02$, $y \le 0.065$) solid solutions were studied. It was found that diamagnetic response was replaced by the Curie–Weiss paramagnetic response as temperature decreased. This indicates that $Yb^{3+}(4f^{13})$ magnetic ions are present in the alloys. The magnetic ion concentration and the occupancy of the Yb-induced impurity band were determined from the experimental data. © *2001 MAIK "Nauka/Interperiodica".*

Doping of the IV–VI compounds and the corresponding alloys with variable-valence impurities radically affects the energy spectrum of the charge carriers. This circumstance gives rise to deep impurity levels (impurity bands) the energy position of which depends on the type of impurity, the alloy composition, temperature, pressure, and magnetic field [1, 2]. Due to this fact, a number of new physical effects are observed in the IV–VI doped semiconductors (Fermi-level pinning by the impurity level, slow relaxation of the nonequilibrium charge carriers, metal–insulator transitions in a quantizing magnetic field and under pressure, and others) which allow one to include them in a specific class of doped semiconductor materials. Initially only Group III elements (Al, Ga, In, and Tl) represented impurities with a variable valence. However, in recent years, this group of impurities was significantly expanded due to inclusion of the Cr, Yb, Eu, Gd, and Ce transition elements. Doping with these elements transforms IV–VI semiconductors into semimagnetic semiconductors [3–7].

Ytterbium holds a special place among all the impurities mentioned above. The reason for this is that the *f*-shell of Yb atoms is completely filled with electrons. Ytterbium ions substituting for the metal atoms in a crystal lattice can be both in magnetic and nonmagnetic states. The magnetic activity of these ions is directly related to their charge state and is controlled by the energy position of the deep impurity level relative to the band edges of the energy spectrum. The Yb ions in the Yb^{2+} ($4f^{14}5s^25p^6$) state, which form impurity levels occupied by electrons, are nonmagnetic and electrically neutral relative to the metal sublattice. At the same time the Yb ions in the Yb^{3+} ($4f^{13}5s^25p^6$) state with unoccupied impurity levels are electrically active, and they have a localized magnetic moment. On the other hand, the degree of the impurity state occupation by electrons can vary due to redistribution of electrons between the level and the band as the alloy composition varies, as well as under the effect of external factors [8]. Therefore, the main aim of this study was to determine the concentration of the magnetic ions and the impurity band occupancy in the $Pb_{1-x}Ge_xTe$:Yb alloys with different Yb and Ge content. It was assumed that Ge concentration variation will enable us to change the impurity band position relative to the valence-band top, and that the variation in the Yb content will make it possible to change the position and total capacity of the impurity band.

Single crystal $Pb_{1-x-y}Ge_xYb_yTe$ ingots ($0 \le x \le 0.02$, $y \le 0.065$) were synthesized by the Bridgman–Stockbarger method. The germanium and ytterbium content was measured by X-ray fluorescence analysis. Samples in the shape of thick disks weighing 0.7–0.8 g were studied using an EG&G PARC M155 vibration-coil magnetometer. Temperature dependences of magnetic susceptibility χ and magnetic-field dependences of magnetization M were measured for each sample at temperatures of $5 \le T \le 300$ K in the magnetic fields as high as 0.5 T.

Typical temperature dependences of magnetic susceptibility for the alloys with different Yb content are shown in Fig. 1. Alloy magnetic susceptibility is a sum of two components: a diamagnetic χ_0 component, which, apparently, is temperature-independent (curve *1*), and a paramagnetic component, which rapidly increases as temperature decreases. The diamagnetic contribution, which is usually related to the susceptibility of the crystal lattice, is in good agreement with the well-known experimental data for undoped PbTe and $Pb_{1-x}Sn_xTe$ [9, 10] and decreases steadily with increasing Yb content. Such a decrease in the diamagnetic contribution

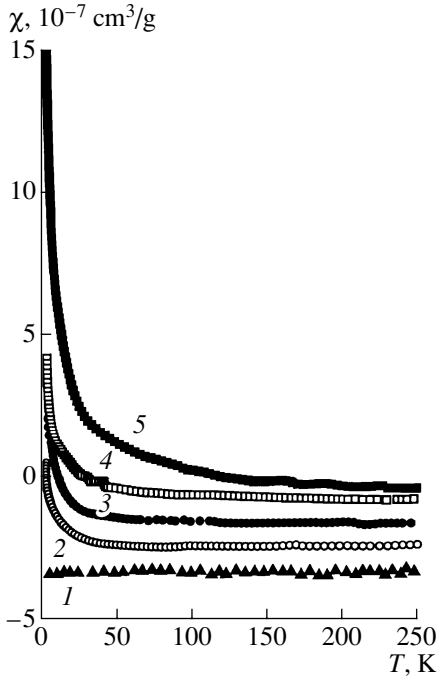

Fig. 1. The temperature dependences of magnetic susceptibility in $Pb_{1-y}Yb_yTe$ with Yb content y = (*1*) 0.0003, (*2*) 0.005, (*3*) 0.008, (*4*) 0.015, and (*5*) 0.065.

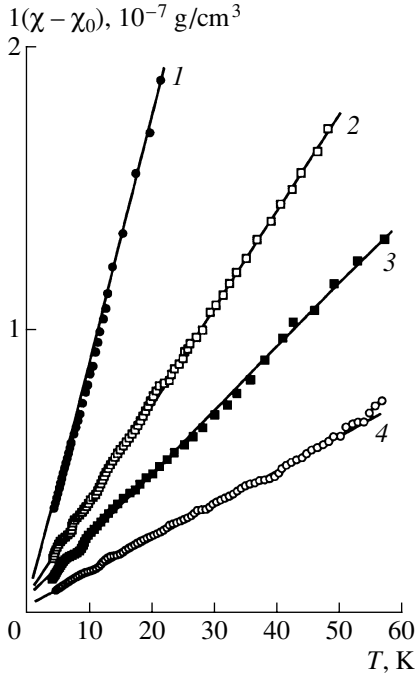

Fig. 2. Temperature dependences of reciprocal magnetic susceptibility of $Pb_{1-x-y}Ge_xYb_yTe$ (x = 0.02) with Yb content y = (*1*) 0.007, (*2*) 0.01, (*3*) 0.014, and (*4*) 0.019.

with increasing impurity concentration can be caused by an increase in the density of electron states in the impurity band, which stabilizes the Fermi level in the investigated alloys. In this case, an additional paramagnetic contribution to the magnetic susceptibility of the impurity band electrons is controlled by the density of states at the Fermi level located within the impurity band [11]. Previously, a similar decrease in the diamagnetic response has been observed, for example, when the Fermi level was brought into the impurity band of thallium as the hole concentration in PbTe doped with Tl increased [9].

Parameters of the $Pb_{1-x-y}Ge_xYb_yTe$ samples

Sample no.	x	y	$N_{Yb^{3+}}$, 10^{19} cm^{-3}	N_{Yb}, 10^{20} cm^{-3}	$N_{Yb^{3+}}/N_{Yb}$
1	0	0.0003		0.044	–
2	0	0.005	1.1	0.80	0.14
3	0	0.008	1.7	1.2	0.13
4	0	0.015	2.4	2.2	0.11
5	0	0.030	6.6	4.6	0.14
6	0	0.065	8.4	9.6	0.09
7	0.02	0.007	0.97	1.0	0.09
8	0.02	0.010	2.4	1.5	0.16
9	0.02	0.014	3.7	2.1	0.18
10	0.02	0.019	7.6	2.8	0.27

At low temperatures, a linear increase in magnetization typical of paramagnets is observed in weak magnetic fields. In this case, the magnetic susceptibility temperature dependences obey the Curie–Weiss law (Fig. 2):

$$\chi = \chi_0 + C/(T - \Theta), \quad (1)$$

where C is the Curie–Weiss constant, and Θ is the Curie temperature. Experimental data shown in Fig. 2 can be extrapolated by straight lines which intersect the abscissa at a small negative temperature ($\Theta \approx -2$ K). This indicates the existence of weak antiferromagnetic interaction between the magnetic centers. The Curie constant values calculated from the line slopes were used to estimate the magnetic center concentration. In this case, we assume that individual Yb^{3+} ions are the magnetic centers in the alloys under study. The ground electron state of these centers in the cubic crystalline field is the Γ_6 doublet. According to electron spin resonance data, the g-factor of this state is equal to 2.52 and the effective spin S = 1/2 [12]. In this case, the magnetic ion concentration $N_{Yb^{3+}}$ can be calculated from the Curie constant C obtained from the experiment:

$$N_{Yb^{3+}} = 3k_BC/(g^2\mu_B^2S(S+1)), \quad (2)$$

where k_B is the Boltzmann constant, and μ_B is the Bohr magneton.

Calculated concentrations $N_{Yb^{3+}}$ are listed in the table. Total concentrations of the ytterbium atoms N_{Yb} in the alloys were determined from the X-ray fluorescence analysis and are also given in the table. Comparison of these data shows that a fraction of the magnetic ions $N_{Yb^{3+}}/N_{Yb}$ in $Pb_{1-x}Yb_xTe$ is equal to 10–15% of the total Yb content, and is almost independent of the alloy composition. In Ge-containing alloys, the fraction of the magnetic ions is somewhat greater than in $Pb_{1-y}Yb_yTe$, and it increases with Yb concentration. At the same time, the magnetic center concentration increases steadily as the Yb concentration in the alloys increases.

In terms of the energy-band diagram of the Yb-doped $Pb_{1-x}Yb_xTe$ alloys, the magnetically active Yb^{3+} ion concentration corresponds to the concentration of unoccupied electron states in the Yb impurity band. In $Pb_{1-y}Yb_yTe$ crystals with a relatively low Yb concentration ($y \lesssim 0.03$), the impurity band is located in the valence band, and at low temperatures it pins the Fermi level near its edge [8]. As Yb concentration increases, the impurity band apparently approaches the valence band edge, crosses it, and enters the band gap. A similar transformation of the energy spectrum also occurs as the Ge concentration in $Pb_{1-x-y}Ge_xYb_yTe$ increases, so that the impurity band is located in the band gap for any Yb concentration in the alloys with $x = 0.02$. In these conditions, the unoccupied states in the impurity band are obviously caused by the electron transitions from this band to the unoccupied states of the valence band. Concentration of these states is controlled mainly by the native structure defects of the acceptor type associated with the deviation from stoichiometry.

In the context of this model, an increase in the fraction of unoccupied electron states in the impurity band as Ge concentration increases is quite understandable because all unoccupied states of the $Pb_{1-x-y}Ge_xYb_yTe$ ($x = 0.02$) valence band are occupied by electrons from the impurity band. In $Pb_{1-y}Yb_yTe$, only the states below the Fermi level located in the valence band are occupied. A steady increase in the magnetic Yb ion concentration (concentration of the unoccupied states in the impurity band) indicates that the deviation from the stoichiometric composition increases as the impurity concentration increases. Therefore, we may conclude that doping with Yb (as well as in other doped IV–VI semiconductors [13]) gives rise to self-compensation, i.e., the fractional compensation of the donor effect of the impurity by the native structure defects.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, project no. 00-15-96784.

REFERENCES

1. V. I. Kaœdanov and Yu. I. Ravich, Usp. Fiz. Nauk **145**, 51 (1985) [Sov. Phys. Usp. **28**, 31 (1985)].
2. B. A. Akimov, A. V. Dmitriev, D. R. Khokhlov, and L. I. Ryabova, Phys. Status Solidi A **137**, 9 (1993).
3. T. Story, Z. Wilamowski, E. Grodzicka, *et al.*, Acta Phys. Pol. A **84**, 773 (1993).
4. E. Grodzicka, W. Dobrowolski, T. Story, *et al.*, Acta Phys. Pol. A **90**, 801 (1996).
5. R. Denecke, L. Ley, G. Springholz, and G. Bauer, Phys. Rev. B **53**, 4534 (1996).
6. T. Story, M. Gorska, A. Lusakowski, *et al.*, Phys. Rev. Lett. **77**, 3447 (1996).
7. X. Gratens, S. Charar, M. Averous, *et al.*, Phys. Rev. B **56**, 8199 (1997).
8. E. P. Skipetrov, N. A. Chernova, E. L. Slyn'ko, and Yu. K. Vygranenko, Phys. Rev. B **59**, 12928 (1999).
9. K. I. Andronik, M. P. Boœko, and A. V. Luzhkovskiœ, Fiz. Tekh. Poluprovodn. (Leningrad) **22**, 1878 (1988) [Sov. Phys. Semicond. **22**, 1190 (1988)].
10. L. A. Fal'kovskiœ, A. V. Brodovoœ, and G. V. Lashkarev, Zh. Éksp. Teor. Fiz. **80**, 334 (1981) [Sov. Phys. JETP **53**, 170 (1981)].
11. S. V. Vonsovskiœ, *Magnetism* (Nauka, Moscow, 1971; Wiley, New York, 1974).
12. S. Isber, S. Charar, X. Gratens, *et al.*, Phys. Rev. B **54**, 7634 (1996).
13. V. I. Kaœdanov, S. A. Nemov, and Yu. I. Ravich, Fiz. Tekh. Poluprovodn. (St. Petersburg) **28**, 369 (1994) [Semiconductors **28**, 223 (1994)].

Translated by I. Kucherenko