ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF
DILUTED MAGNETIC SEMICONDUCTORS Pb_{1-x}V_xTe

E.P. Skipetrov¹, E.A. Zvereva¹, A.E. Primenko¹, O.A. Savelieva¹, N.A. Pichugin¹,
A.N. Golovanov², V.V. Gorbachev², V.P. Zlomanov³, and A.A. Vinokurov³

¹Faculty of Physics, Moscow State University, 1, Leninskie gory, 119992, Moscow, Russia
Tel: +7 (095) 939 44 93, Fax: +7 (095) 932 88 76, e-mail: skip@mig.phys.msu.ru
²Moscow State University of Printing Arts, 127550, Moscow, Russia
³Faculty of Chemistry, Moscow State University, 119992, Moscow, Russia
(Received 23 September 2008)

Abstract

The galvanomagnetic effects, the temperature and magnetic field dependences of magnetization and electron paramagnetic resonance (EPR) in the Pb_{1-x}V_xTe (x ≤ 0.02) alloys under variation of the alloy composition have been investigated. Low temperature activation range of the impurity conductivity on the temperature dependences of the resistivity and the Hall coefficient has been revealed and attributed to the appearance of vanadium-induced deep level in the gap of the alloys. The magnetic susceptibility was found to be a superposition of the matrix diamagnetism and Curie-Weiss paramagnetism provided by vanadium impurity ions. EPR spectra were measured and the g-factor in the temperature range 85-200 K was obtained.

1. Introduction

IV-VI narrow-gap semiconductors doped with rare-earth (Eu, Gd, Yb) or transition metals (Mn, Fe, Cr) are diluted magnetic semiconductors (DMS) whose magnetic properties strongly depend on their electronic structure (energy position of the deep impurity level relative to the band edges and the occupancy of this level with electrons) [1-3]. For example, in Pb_{1-x}Sn_xTe doped with Yb the completely filled ytterbium deep level is situated deep within valence band and the material remains diamagnetic [1]; in Pb_{1-x}Ge_xTe doped with Yb the partially filled Yb impurity level is situated within the gap and the alloys demonstrate a paramagnetic behavior [2]; in Pb_{1-x}Ge_xTe doped with Cr the partially filled Cr impurity level is situated either within the conduction band (x < 0.10) or in the gap (x > 0.10) and alloys are ferromagnetic [3].

It has been found recently that in the PbTe and Pb_{1-x}Mn_xTe alloys vanadium impurity acts as a donor and induces an appearance of the deep impurity states, stabilizing the Fermi level somewhere within the gap [4, 5]. Taking into account the partial filling of 3d shell of vanadium atoms with electrons one can expect that both V^{2+} and V^{3+} ions will be magnetically active in PbTe. So, vanadium doped PbTe-based alloys may demonstrate paramagnetic or ferromagnetic behavior. However, there is no reliable data either on the exact energy position of the vanadium impurity level or on the magnetic properties of the PbTe-based semiconductors yet.

In order to investigate the electronic structure and magnetic properties of new DMS, in the present work the galvanomagnetic properties, the temperature and magnetic field dependences of magnetization and electron paramagnetic resonance in Pb_{1-x}V_xTe (x ≤ 0.02) alloys were studied.
2. Experimental details

Single crystals Pb\(_{1-x}\)V\(_x\)Te were grown using the Bridgman method. The chemical composition was determined using the X-ray fluorescence analysis. The concentration of vanadium changes weakly along the ingots (for example, \(x = 0.0008-0.002\)). X-ray diffraction and scanning electron microscopy have shown that there were no second phases in all our samples.

The temperature dependences of the resistivity \(\rho\) and the Hall coefficient \(R_H\) (\(B \leq 0.1\, \text{T}\), \(4.2 \leq T \leq 300\, \text{K}\)) were measured by four-probe technique on specimens, approximately \(3\times0.7\times0.7\, \text{mm}\) in size and with \((100)\) faces, which were cut from the original crystals using an arc cutting machine. All electrical connections to the samples were made via indium-tinned copper wire 0.05 mm in diameter. Current contacts were soldered to each end of the samples using an alloy of In + 4%Ag + 1%Au. Potential and Hall contacts were attached by spark discharge welding.

For magnetic measurements the samples of the weight 0.1-0.2 g were glued onto a plastic holder. The temperature and magnetic field dependences of the magnetization were measured using vibrating sample magnetometer EG & G PARC M155. The magnetic field up to \(B = 0.5\, \text{T}\) was produced by an electromagnet and determined by means of Hall sensor. For the temperature variation (5 ≤ \(T\) ≤ 300 K) the liquid helium gas-flow cryostat equipped with a heater was used.

Electron paramagnetic resonance in Pb\(_{1-x}\)V\(_x\)Te (\(x \approx 0.007\)) was measured using X-band EPR spectrometer CMS 8400 (ADANI) (\(f = 9.1-9.6\, \text{GHz}\), \(B \leq 0.7\, \text{T}\)) equipped by a low temperature mount with the temperature controller tSTAT335, operating in the range \(T = 80-430\, \text{K}\). The crystal samples for EPR experiments were crushed into powder to decrease the skin effect and to avoid broadening out of the resonance signal caused by the influence of the surface strains.

3. Galvanomagnetic effects

It was found that the temperature dependences of resistivity \(\rho(1/T)\) and Hall coefficient \(R_H(1/T)\) are thermally activated in the whole temperature range investigated (Fig. 1). At high temperatures one can see a beginning of the intrinsic ionization. Upon a decrease of temperature, a distinct activation range is observed, indicating the presence of a vanadium-induced deep level \(E_V\) in the gap near the bottom of conduction band. At the lowest temperatures the resistivity is weakly activated, while the Hall coefficient passes through the maximum. Then the Hall effect signal decreases rapidly and vanishes. This behavior is thought to be associated with a rapid decrease in the Hall mobility of charge carriers, due to a change in the major conductivity mechanism and transition to the hopping conduction via impurity states at low temperatures.

From the slope of the activation range on the \(\rho(1/T)\) dependences in accordance with the relation \(\rho \propto \exp(\Delta E_V/kT)\) we have determined activation energy of the vanadium level \(\Delta E_V\). It is \(\Delta E_V = E_c-E_V \approx 20\, \text{meV}\) and decreases slowly with increasing of vanadium content in the alloy. This could be associated with either broadening out of the impurity level or decreasing of the gap with increase of the vanadium content. The Hall mobility achieves the values as high as \(\mu_H \approx 10^5\, \text{cm}^2\text{V}^{-1}\text{s}^{-1}\) for the samples under study and at \(T>40\, \text{K}\) decreases with temperature as \(\mu_H \propto T^\alpha\), where \(\alpha \approx -(2.1-2.6)\). This behavior is typical of A\(^4\)B\(^6\) semiconductors, where the dominant scattering mechanism at high temperatures is acoustic phonon scattering, while \(\alpha\) differs from the classic value -3/2 due to the temperature dependence of the effective mass, non-parabolicity of the energy bands, and additional polar scattering by the optical phonons [6].
4. Magnetic properties

The temperature dependences of the magnetic susceptibility $\chi(T)$ (Fig. 2) for investigated samples contain two principal shares due to the competition between the temperature independent diamagnetic contribution of the host semiconductor lattice and paramagnetic contribution of the isolated magnetic vanadium ions in the alloys. Estimations of the absolute value of diamagnetic contribution $\chi_0$ show a good agreement in its value with the previously reported data in lead telluride ($\chi_0 = -(4-5) \times 10^{-7}$ emu/g). The paramagnetic contribution becomes prevailing at low temperatures and follows the Curie-Weiss law

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

where $C$ is the Curie constant and $\Theta$ is the Curie temperature, which is about zero for our samples.

The magnetization curves measured at $T = 5$ K are linear that is typical for paramagnets (Fig. 3). Upon an increase in vanadium concentration the paramagnetic response gradually increases, indicating a monotonous increase of the magnetic centers concentration.

5. Electron paramagnetic resonance

EPR spectra were measured in the Pb$_{1-x}$V$_x$Te ($x = 0.007$) sample at $T > 80$ K (Fig. 4). The amplitude of the absorption intensity at $T=86$ K is approximately 20 times more than the one at $T = 200$ K. The center of the absorption line remains practically unchanged upon an increase in temperature, while the EPR spectrum linewidth $\Delta B$ increases from 270 up to 370 G for the temperature range under study. Due to the low concentration of the magnetic ions in the samples, the hyperfine structure was well resolved. At low temperatures the first-derivative of the main absorption line splits into eight components indicating a hyperfine interaction between the electron magnetic moment and nuclear magnetic moment of the isotope $^{51}$V ($I = 7/2$, natural abundance 99.75%). With increasing of the temperature the hyperfine structure disappears, the
amplitude of absorption intensity decreases rapidly. The values of Lande factor $g$ were deduced from the center of the main line of the first-derivative absorption EPR spectra, measured for the sample and the standard organic crystal BDPA with $g = 2.0036$. It was found that $g$-factor is smaller than well-known experimental values for $V^{2+}$ ($g = 1.97$) and $V^{3+}$ ($g = 1.98$) ions in paramagnetic vanadium salts and virtually independent on temperature ($g = 1.904\pm0.010$).

Fig. 2. Temperature dependences of the magnetic susceptibility of Pb$_{1-x}$V$_x$Te single crystals at $B \approx 0.4$ T ($x$: 1–0.001, 2–0.02, 3–0.001, 4–0.002, 5–0.002).

Fig. 3. Magnetization curves at $T = 5$ K for Pb$_{1-x}$V$_x$Te single crystals ($x$: 1–0.001, 2–0.001, 3–0.002, 4–0.02, 5–0.002).

Fig. 4. X-band first-derivative absorption EPR spectra of Pb$_{1-x}$V$_x$Te ($x=0.007$) at various temperatures.

Fig. 5. Results of double integration of the first-derivative absorption EPR spectra for Pb$_{1-x}$V$_x$Te ($x=0.007$).
Figure 5 represents result of double integration of the first-derivative absorption EPR spectra. The main absorption line with the center at about 3490 G is satisfactory described by a Gaussian type curve (see inset in Fig. 5), that is typical for diluted paramagnets. Calculation of the areas $S$ under such curves allows us to estimate the temperature dependence of the magnetic susceptibility in our sample. An analysis of this dependence confirms that the temperature dependence of the magnetic susceptibility $\chi(T)$ follows the Curie-Weiss law (1) in accordance with the data obtained using the vibrating sample magnetometer.

5. Conclusions

Doping of the PbTe alloys with vanadium leads to the appearance of a deep impurity-induced level in the gap. The energy position of the level is about 20 meV under the bottom of conduction band and is likely to depend on the vanadium concentration in the alloy.

The impurity-induced Curie-Weiss paramagnetism in the vanadium doped PbTe was revealed and it was shown that the concentration of magnetic centers increases with increasing vanadium content in the Pb$_{1-x}$V$_x$Te alloys.

From the EPR spectra, the value of Lande factor $g$ and its temperature dependence were obtained; it was shown that the $g$-factor in the Pb$_{1-x}$V$_x$Te alloys is about 1.904 and virtually independent on the temperature.

This research was carried out under financial support of the Russian Foundation for Basic Research (Grant N 08-02-01364).

References