Carrier-Concentration–Induced Ferromagnetism in PbSnMnTe

T. Story and R. R. Gałązka
Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland

and

R. B. Frankel and P. A. Wolff
Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
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The influence of charge-carrier concentration on the magnetic properties of the semimagnetic semiconductor $[(PbTe)_{1-x}(SnTe)_x]_{1-y}[MnTe]_y$ ($x = 0.72$, $y = 0.03$) is reported. Magnetization, magnetic susceptibility, and specific heat have been measured. For carrier concentrations below $p = 3\times10^{20}$ cm^{-3} the alloy is paramagnetic. For $p \geqslant 3\times10^{20}$ cm^{-3} an abrupt transition to a ferromagnetic phase is observed at helium temperatures. The ferromagnetic transition temperature increases with increasing p. This is the first demonstration of the effect of carrier concentration on the magnetic properties of semimagnetic semiconductors.

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The alloys of IV-VI semiconductors and MnTe are a group of semimagnetic materials with very interesting magnetic properties. Ferromagnetic ordering was observed by Escorne, Ghazalli, and Leroux-Hugon[1] in $Sn_{1-x}Mn_xTe$, by Cochrane, Plischke, and Strom-Olsen[2] in $Ge_{1-x}Mn_xTe$, and by Hamasaki[3] in PbGeMnTe, for $x > 0.005$. Because of the deviation from stoichiometry, these semiconductors are very strongly degenerated with carrier (hole) concentration $p = 10^{20}$–10^{21} cm^{-3}. In $Pb_{1-x}Mn_xTe$ a much lower carrier concentration is usually observed, $p = 10^{17}$–10^{19} cm^{-3}, and this material is a paramagnet down to helium temperatures. Recently, indications of a spin-glass phase below $T = 1$ K have been established.[4] The carrier-concentration range studied in the former alloys is relatively narrow: $p = (1\text{–}2)\times10^{21}$ cm^{-3} in GeMnTe,[2] $p = (3\text{–}8)\times10^{20}$ cm^{-3}, $p = (6\text{–}10)\times10^{20}$ cm^{-3}, and $p = (1\text{–}4)\times10^{20}$ cm^{-3} in SnMnTe.[1,5] In all the above-mentioned semiconducting alloys only slight shifts of the ferromagnetic ordering temperature with changes in the carrier concentration were observed. A more pronounced influence of carrier concentration on the magnetic properties has been observed by Holtzberg *et al.*[6] in the magnetic semiconductors $Eu_{1-x}Gd_xSe$ and $Eu_{1-x}Gd_xTe$. The values of the paramagnetic Curie temperatures of these magnetic alloys are strongly gadolinium-content dependent. This effect is interpreted as the influence of electron concentration via Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction (carriers are generated as a result of Gd^{3+}-Eu^{2+} substitution).

Recently, the influence of optically induced carriers on the magnetic properties of HgMnTe was observed by Krenn, Zawadzki, and Bauer.[7]

The $[(PbTe)_{1-x}(SnTe)_x]_{1-y}[MnTe]_y$ alloy, like $Sn_{1-x}Mn_xTe$ and $Pb_{1-x}Mn_xTe$, is a substitutional solid solution in which magnetic ions are randomly distributed in a metal fcc sublattice of the rock-salt crystal lattice. Materials can be grown with arbitrary tin content and with a wide range of manganese concentration (probably up to 15–20 at.%). Isothermal annealing in an appropriate atmosphere controls the number of metal vacancies and thereby the number of conducting holes. These technological properties of PbSnMnTe allow one to obtain samples with desired magnetic ion and tin concentrations, with the possibility of changing the carrier concentration in each sample over more than 1 order of magnitude. PbSnMnTe is thus the first semimagnetic semiconductor material in which the effect of the free-carrier concentration on the magnetic properties can be studied. In this Letter we present the magnetic properties of PbSnMnTe with $x = 0.72$ and $y = 0.03$, for carrier concentrations from $p = 1\times10^{20}$ cm^{-3} to $p = 1.4\times10^{21}$ cm^{-3}. For carrier concentration $p < 3\times10^{20}$ cm^{-3}, the alloy is paramagnetic to below 4 K. For $p \geqslant 3\times10^{20}$ cm^{-3}, there is an abrupt transition to a ferromagnetic state at about 4 K. The base compounds PbTe and SnTe are diamagnets.

The alloy was grown by the Bridgman method. Electron microprobe analysis revealed good homogeneity of both the manganese and tin atom distributions in the sample. No second-phase inclusions were observed in x-ray measurements. Carrier concentrations were increased or decreased by thermal annealing in Te-rich or Sn-rich atmospheres, respectively.

Magnetization, magnetic susceptibility, specific heat, and the Hall effect were measured in the temperature region 1.5–300 K. According to Hall-effect measurements the hole concentration is constant below $T = 100$ K and monotonically decreases at higher temperatures.[8] For samples with low carrier concentration, $p < 3\times10^{20}$ cm^{-3}, a typical paramagnetic

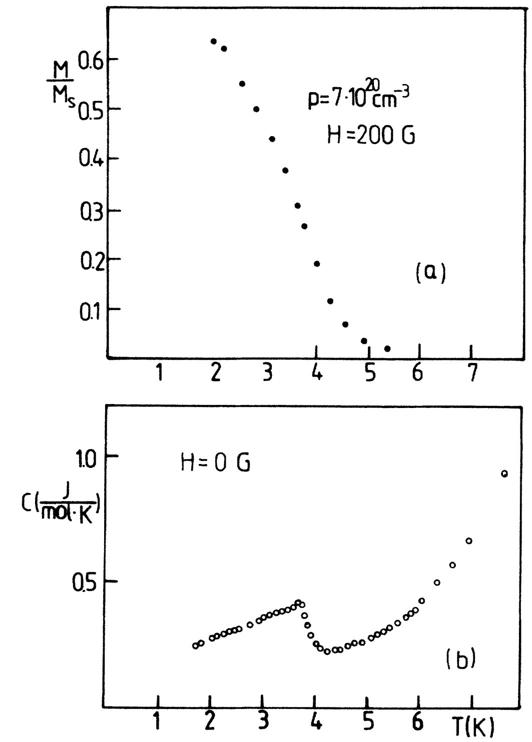

FIG. 1. Temperature dependence of (a) the magnetization and (b) specific heat of PbSnMnTe in the critical temperature region.

behavior is observed over the entire temperature range. The magnetic susceptibility follows the Curie law $\chi \sim 1/T$, and the magnetic field dependence of the magnetization is described by the Brillouin function for $S=\frac{5}{2}$. Annealing the same sample in a Te-rich atmosphere, which increases the carrier concentration, drastically changes the low-temperature magnetic properties. The magnetic susceptibility follows a Curie-Weiss law, $\chi \sim 1/(T-\theta)$, with the paramagnetic Curie temperature $\theta = 3$–5 K, indicating ferromagnetic coupling between magnetic ions. The magnetization in a low magnetic field increases over 2 orders of magnitude with decreasing temperature below 4.1 K [Fig. 1(a)]. Simultaneously an asymmetric peak is observed in the temperature dependence of the specific heat [Fig. 1(b)]. The ferromagnetic Curie temperature obtained from magnetic measurements, $T_C = 4.1$ K, is slightly higher than the specific-heat maximum, $T_C = 3.8$ K.

A narrow ($H_c = 1$ G) hysteresis loop is observed in high–carrier-concentration samples below the critical temperature. The rapid saturation of the magnetization with applied field observed below the Curie temperature is shown in Fig. 2. The experimentally observed value of the saturation magnetization agrees within experimental error with that theoretically calculated for $S=\frac{5}{2}$.

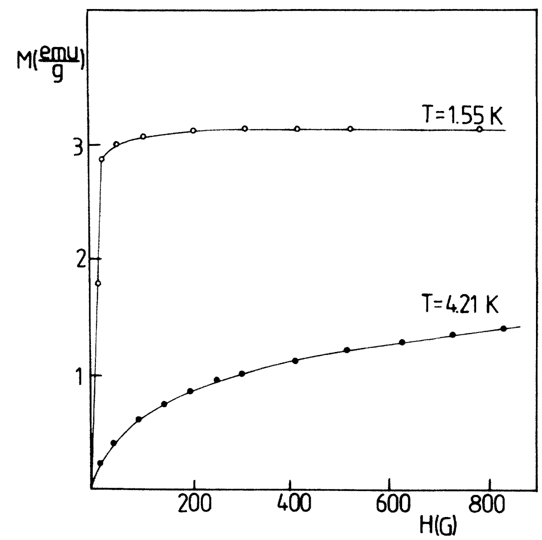

FIG. 2. Magnetization isotherms for the sample with $T_C = 4.1$ K. Theoretical saturation magnetization for 3-at.% alloy ($S=\frac{5}{2}$) is 3.1 emu/g.

All these experimental facts are clear evidence of a magnetic phase transition from a paramagnetic to a ferromagnetic state in high–carrier-concentration samples at helium temperatures. Figure 3 shows in double logarithmic coordinates the temperature dependence of the magnetic susceptibility for low and high carrier concentrations in the same sample. A strong qualitative and quantitative difference between the two car-

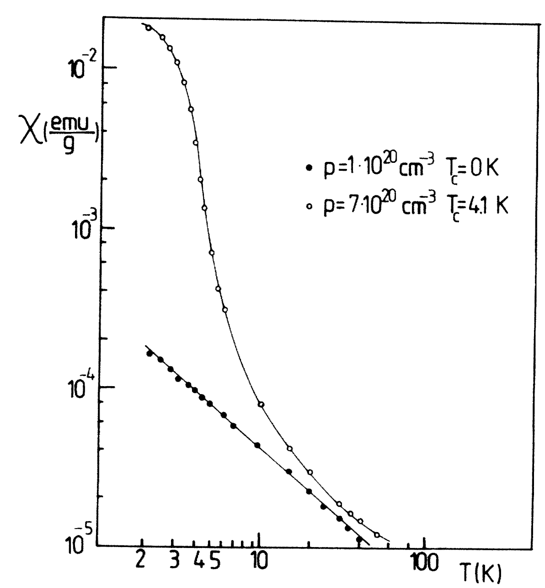

FIG. 3. dc magnetic susceptibility vs temperature for PbSnMnTe samples with different hole concentrations.

rier concentrations is easily observed. If one subsequently reanneals the same sample in an Sn-rich atmosphere, which decreases the number of holes, the ferromagnetism of the sample is completely destroyed and the sample remains paramagnetic below 4 K.

By control of the annealing conditions the carrier-concentration dependence of the paramagnetic and ferromagnetic Curie temperatures can be studied. The results are presented in Fig. 4, where the threshold at $p = 3\times10^{20}$ cm^{-3} in both paramagnetic and ferromagnetic Curie temperatures can be seen. The Curie temperature appears to decrease slightly with carrier concentration above $p = 10^{21}$ cm^{-3}.

According to the Curie-constant and magnetic-saturation measurements, the manganese ions conserve their spin magnetic moment of 5 bohr magnetons in the crystal lattice of PbSnMnTe and this value is not disturbed during isothermal annealing.

Low-temperature ferromagnetism of dilute magnetic alloys is a well-known phenomenon in metallic alloys of transition metals.[9] So-called giant moments are often observed in such ferromagnets. Giant-moment formation does not take place in PbSnMnTe or other IV-VI-MnTe alloys because of diamagnetism of the host crystal. According to the theory of dilute metallic alloys the magnetic-ion concentration practically determines the magnetic properties of the alloy. A similar situation is observed in dilute semiconducting magnetic alloys. In PbSnMnTe the situation is quite different. The magnetic properties are determined by both the magnetic-ion concentration and by charge-carrier concentration, and the *magnetic-phase diagram includes carrier concentration as a parameter*. It is clear from our experiments that the mechanism responsible for manganese-ion coupling in PbSnMnTe is carrier-concentration sensitive and long ranged (average interspin distance in the alloy with $y = 0.03$ is approximately 13 Å).

Among known exchange mechanisms only indirect exchange via carriers (RKKY interaction) seems to be sufficiently long ranged and effective in the high–carrier-concentration samples to account for the ferromagnetism of PbSnMnTe. Nevertheless, within the framework of the RKKY interaction alone, the thresholdlike dependence of the Curie temperature on carrier concentration is difficult to understand. Further experimental and theoretical investigations are necessary to clear up the problem.

In conclusion we want to emphasize the extreme sensitivity of the magnetic properties of PbSnMnTe alloys to carrier concentration, and the unique possibility of generating ferromagnetic ordering by changes in the hole concentration alone.

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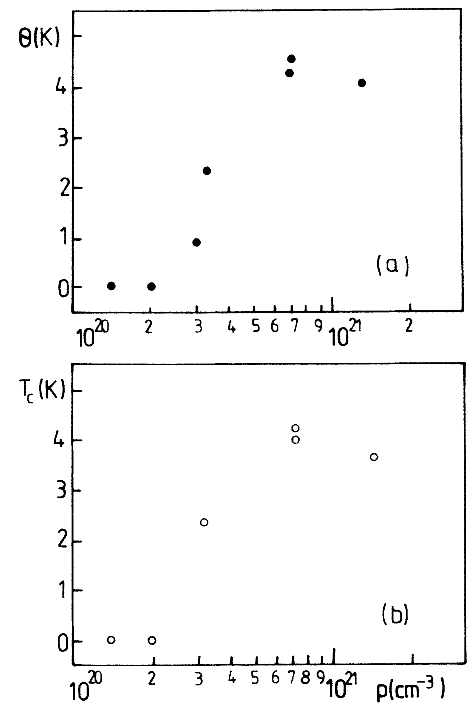

FIG. 4. Carrier-concentration dependence of (a) paramagnetic and (b) ferromagnetic Curie temperatures of PbSnMnTe.

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