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Electron-paramagnetic-resonance study of s - d exchange in $\text{PbSnMnTe}^{\text{a)}$

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Electron-paramagnetic-resonance (EPR) measurements were performed in the temperature range $T = 1.3$ – 100 K in samples of the semimagnetic $\text{Pb}_{1-x-y}\text{Sn}_y\text{Mn}_x\text{Te}$ semiconductor with carrier concentrations $p = 1.6 \times 10^{19}$ – $1.4 \times 10^{21} \text{ cm}^{-3}$. Magnetization and Hall effect were also measured. Compositions in the range $0.12 < y < 0.72$ and $x = 0.02, 0.04$, and 0.06 were studied. We found a strong influence of the carrier concentration on the temperature dependence of the width of EPR line (ΔH). A very rapid increase of ΔH with increasing temperature is observed in the samples with high carrier concentrations: $p = 5.5, 6.8$, and $14 \times 10^{20} \text{ cm}^{-3}$. The magnitude of this effect is strongly reduced in the sample with the carrier concentration $p = 2.85 \times 10^{20} \text{ cm}^{-3}$. In n - and p -type samples with the lowest carrier concentrations ($p \approx 2 \times 10^{19} \text{ cm}^{-3}$), no temperature dependence of ΔH is observed at high temperature. The strong effect of the carrier concentration on ΔH can be understood, in agreement with magnetic measurements, as a result of the two-carrier (light for $p < p_c = 3 \times 10^{20} \text{ cm}^{-3}$ and very heavy, available only for $p > p_c$) Korringa relaxation mechanism.

I. INTRODUCTION

In this paper we present results of electron-paramagnetic-resonance (EPR) experimental studies of a semimagnetic semiconductor $\text{Pb}_{1-x-y}\text{Sn}_y\text{Mn}_x\text{Te}$. This material is a substitutional solid solution, the matrix of which is a semiconducting alloy $\text{Pb}_{1-y}\text{Sn}_y\text{Te}$. Mn^{2+} ions are randomly distributed within the metal sublattice of the rock-salt crystal lattice of this material. PbSnTe itself is a weak diamagnet, and magnetic properties of PbSnMnTe alloys are due to the Mn ions. The characteristic property of these materials is a metallic type of conductivity and relatively high concentrations of carriers, $p = 10^{19}$ – 10^{21} cm^{-3} . The electron properties of the samples with very high concentrations of carriers are influenced by the presence of a heavy-hole band located approximately 0.2 eV below the top of the main band of light holes.¹ The magnetic properties of PbSnMnTe are governed by Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction. Samples in which the carrier concentration exceeds the threshold value $p_c = 3 \times 10^{20} \text{ cm}^{-3}$ are ferromagnetic at helium temperatures, whereas samples with $p < p_c$ are paramagnetic.² This thresholdlike carrier-concentration dependence of the Curie temperature is due to the structure of the valence band of PbSnMnTe mentioned above.³ The threshold concentration corresponds to the Fermi level entering into the band of heavy holes. At higher carrier concentrations, heavy holes start to dominate the RKKY interaction because of the very high density of states in this band. Similar effects have been observed in the SnMnTe alloy.⁴

Conducting carriers play an important role in the magnetic-resonance phenomena in materials closely related to our system such as $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$ (Ref. 5) and $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$.^{6,7} The high-temperature width of the EPR

line is determined by the Korringa relaxation process in which the relaxation of the magnetic moment of Mn^{2+} subsystem is governed by the s - d interaction between localized moments and carriers. Based on the analysis of the temperature dependence of the linewidth, the exchange constants between localized moments and carriers J_{sd} were found to be 70 meV for p -type PbMnTe (Ref. 6) and 180 meV for p -type SnMnTe .⁵ In these papers the effect of the band structure on the Korringa mechanism and possible differences between exchange constants for different types of carriers are not discussed. However, in view of the recent experimental observation of the carrier concentration induced ferromagnetism in PbSnMnTe (Ref. 2) and SnMnTe (Ref. 4) and the important role of the band structure in the interpretation of magnetic properties of these compounds,³ an analysis of the s - d interaction between Mn^{2+} ions and different carriers seems to be essential. For this purpose EPR is particularly useful since this technique is not subject to strong experimental limitations brought about by the high mobility of the samples usually needed in magneto-optical or magnetotransport investigations of s - d exchange constants. The semimagnetic system PbSnMnTe offers the unique possibility to study the s - d exchange interaction between localized magnetic moments and carriers originating from different bands with different Fermi energies.

II. EXPERIMENTAL RESULTS

We performed EPR measurements in $\text{Pb}_{1-x-y}\text{Sn}_y\text{Mn}_x\text{Te}$ samples in the temperature range $T = 1.3$ – 100 K using a Varian X-band spectrometer. The Hall effect and magnetization of these samples were also measured at helium temperatures. Two groups of samples were studied. The first group consists of the low-concentration samples (typically $p \approx 2 \times 10^{19} \text{ cm}^{-3}$) with compositions $x = 0.02, y = 0.12$ (n and p type); $x = 0.04, y = 0.16$; and $x = 0.06, y = 0.16$. All these samples are

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FIG. 1. The temperature dependence of the linewidth and resonance field for $\text{Pb}_{0.8}\text{Sn}_{0.16}\text{Mn}_{0.04}\text{Te}$ with carrier concentration $p = 1.7 \times 10^{19} \text{ cm}^{-3}$.

paramagnetic in the temperature range studied. The second group consists of the samples with composition $x = 0.02$, $y = 0.72$ with different carrier concentrations in the range $p = 2.85 \times 10^{20} - 10^{21} \text{ cm}^{-3}$. From magnetic measurements we found that samples with $p > p_c = 3 \times 10^{20} \text{ cm}^{-3}$ are ferromagnetic below $T_c \approx 3 \text{ K}$. The sample with carrier concentration $p = 2.85 \times 10^{20} \text{ cm}^{-3}$ is paramagnetic with a paramagnetic Curie temperature $\Theta = 0.5 \text{ K}$. Our samples are crystalline in the form of a thin flat plate. Because of the high conductivity of our crystals, the observed EPR line has a Dysonian shape. We determined the resonance field H_R and the linewidth ΔH by fitting the observed resonance line numerically using Dyson's theory. Only one broad line was observed.

All low-carrier-concentration samples of PbSnMnTe exhibit qualitatively the same temperature dependence of the linewidth and resonant field (Fig. 1). At high temperatures ($T > 4 \text{ K}$) ΔH is practically temperature independent and has typically the value $\Delta H = (425 \pm 50) \text{ G s}$ for different samples. In this temperature range the resonance field is also constant with a g -factor close to $g = 2.0$. With temperature decreasing below $T = 4 \text{ K}$, a relatively rapid increase of ΔH is observed. This effect is accompanying by the continuous decrease of H_R . The experimental results for high-carrier-concentration samples are presented in Fig. 2. The EPR linewidth increases very rapidly with increasing temperature. This effect is observed in the samples with carrier concentrations $p = 5.5, 6.8$, and $14 \times 10^{20} \text{ cm}^{-3}$. In the sample with a carrier concentration $p = 2.85 \times 10^{20} \text{ cm}^{-3}$, the temperature coefficient of the linewidth is strongly reduced.

III. DISCUSSION AND CONCLUSIONS

We interpret the observed temperature and carrier-concentration dependence of the EPR linewidth within the framework of the Korringa relaxation mechanism. This mechanism is based on the s - d exchange interaction between carriers and magnetic impurities. The line-

FIG. 2. Linewidth of $\text{Pb}_{0.25}\text{Sn}_{0.72}\text{Mn}_{0.02}\text{Te}$ with two concentrations of carriers: solid dots: $p = 5.5 \times 10^{20} \text{ cm}^{-3}$; open dots: $p = 2.85 \times 10^{20} \text{ cm}^{-3}$.

width due to Korringa relaxation depends on temperature, exchange constant J_{sd} , and carrier concentration $\Delta H_K \sim [\rho(E_F)J_{sd}]^2 kT$.⁸ Here, $\rho(E_F)$ is the density of electron states at the Fermi level. The strong difference in the temperature dependence of the width of the EPR line of PbSnMnTe observed in the samples with carrier concentration $p = 2.85 \times 10^{20}$ and $p = 5.5 \times 10^{20} \text{ cm}^{-3}$ cannot be due to the relatively small difference in the concentration of carriers in one band. The expected difference in the density of states is much too low to account for the observed effect. It can be understood, however, in the framework of the two-valence-band description of the magnetic properties of PbSnMnTe alloys. In PbSnMnTe samples with a carrier concentration $p < p_c$, only light holes are present. The density of states associated with this band is too low to produce a Korringa-type contribution to the linewidth comparable with the relatively broad residual width. So a very weak increase of ΔH in the case of the sample with $p = 2.85 \times 10^{20} \text{ cm}^{-3}$ and no temperature dependence of ΔH in the samples with the lowest carrier concentrations is observed. In these compounds, however, the Korringa temperature coefficient may be reduced as a result of the effect of a bottleneck mechanism, as will be discussed later on. In samples with carrier concentration $p > p_c$, the Korringa relaxation is due to mostly heavy holes. As the density of states associated with this band is about 20 times larger than the density of state in the band of light holes, this mechanism is strongly enhanced. An analysis of the exchange constant is somehow obscured, however, because of the fact that the observed temperature dependence deviates from the linear increase predicted by the simple Korringa mechanism. The origin of this effect is not understood.

The effect of increase of ΔH and decrease of H_R observed at low temperatures ($T < 4 \text{ K}$) in low-carrier-concentration samples is usually attributed to the d - d exchange interaction and a possible magnetic phase transition at lower temperature.⁸ Magnetic data do not reveal any magnetic transition in the temperature range studied ($T > 1.5 \text{ K}$). However, the negative values of the paramagnetic Curie temperature (e.g., $\Theta = -1.4 \text{ K}$ for sample with $x = 0.06$) suggests that such an interaction exists and can be responsible for the observed behavior. Recently, a different mechanism was proposed to be responsible for the increase of ΔH with decreasing tempera-

ture in PbMnTe.⁹ It originates from the temperature-dependent narrowing of the residual linewidth and is effective only in systems in which a bottleneck effect is observed and the EPR line is inhomogeneously broadened. This mechanism may play a role in the samples with lowest carrier concentrations, as will be discussed later on. The shift of H_R is partially caused by demagnetization field. However, the observed effect is too large to be explained by this mechanism. Also, we do not observe significant differences in H_R in the situation when the external magnetic field is parallel or perpendicular to the surface of samples.

Finally, we would like to discuss the role of the bottleneck effect in the EPR studies of PbSnMnTe alloys. This effect influences the effective Korringa relaxation and limits the precision of determination of the J_{sd} exchange constants. No bottleneck effect was observed in SnMnTe.⁵ In the case of PbMnTe, two contradictory results are reported. In Ref. 6 the bottleneck effect was not observed, and in Ref. 7 this effect was found to be very important. We can offer a possible explanation for these results. The effect of electron bottleneck is important when the relaxation rate of the magnetization of carriers to the lattice $\delta_{eL} \sim \rho(E_F)c_{imp}V_{s0}^2$ is not fast enough as compared to the backflow relaxation channel from carriers to localized magnetic moments: $\delta_{ei} \sim J_{sd}^2\rho(E_F)x$.¹⁸ In these equations c_{imp} is the concentration of scattering centers effective in the relaxation of the magnetic moment of electrons and V_{s0} is a scattering potential. We suggest that vacancies, which are the main defect in PbSnMnTe alloys and generate the carrier concentration in these materials, can be responsible for the electron-lattice relaxation. In this model the electron-lattice relaxation rate increases with increasing carrier concentration faster than backflow relaxation ($\delta_{eL} \sim p^{4/3}$ and $\delta_{ei} \sim xp^{1/3}$ in the parabolic band approximation). In samples of SnMnTe in which the carrier concentration is always very high and therefore δ_{eL} is large, EPR is not bottlenecked. In the case of PbMnTe where the number of carriers (i.e., the number of vacancies) is one to two orders of magnitude smaller, the bottleneck effect may be important in samples with a high concentration of mag-

FIG. 3. A schematic presentation of the role of the bottleneck effect in the EPR studies of PbSnMnTe alloys. The condition for nonbottlenecked resonance is $\delta_{eL} > \delta_{ei}$, where δ_{eL} is the relaxation rate for the electron-lattice relaxation process and δ_{ei} is the relaxation rate of the electron-localized spin-relaxation process. The shaded areas present the range of the concentration of Mn ions and carriers where EPR measurements were performed (Refs. 5-7).

netic ions, as is actually observed,⁷ or absent in diluted samples⁶ (Fig. 3).

In conclusion, we found that the effect of the carrier concentration on the temperature dependence of the EPR linewidth can be understood based on the two-band description of the magnetic properties of PbSnMnTe alloys. The observed behavior provides experimental evidence for the effective s - d interaction between heavy holes and Mn ions.

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