

## Electron Paramagnetic Resonance Knight Shift in Semimagnetic (Diluted Magnetic) Semiconductors

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The effect of the carrier concentration induced shift of the  $g$  factor (the Knight shift) of the  $\text{Mn}^{2+}$  magnetic moment in PbTe and SnTe semiconducting matrices is experimentally observed and is of different sign for  $n$ - and for  $p$ -type crystals. The analysis of this effect allows for a straightforward determination of both the sign and the magnitude of the free carrier–local moment exchange integrals for holes and electrons in PbTe, as well as for light and heavy holes in SnTe. [S0031-9007(96)01225-2]

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The investigations of the physical properties of magnetic ions diluted in metallic matrices with their local magnetic moments (if formed) coupled to the conducting carriers by  $s$ - $d$  exchange interaction have led to several outstanding experimental and theoretical discoveries. These include, in particular, the Kondo effect, the Anderson virtual bound state (VBS) model, the Ruderman-Kittel-Kasuya-Yosida (RKKY) indirect exchange interaction via free carriers, and the formation of metallic spin glasses. Since the very beginning, electron paramagnetic resonance (EPR) was used as an experimental tool to study these systems. In the pioneering works of Owen, Dyson, and Yosida [1–3] the basic ideas of EPR on local moments in a conducting matrix were developed and quantified in the phenomenological Bloch-Hasegawa equations as reviewed, e.g., by Barnes [4]. One of the standard effects anticipated in these works is the carrier concentration induced shift of the position of the EPR resonance field of the local magnetic moment—the analog of the well known Knight shift in nuclear magnetic resonance. This effect can be expressed as a change of the local moment's  $g$  factor:  $\Delta g = J_{sd}\rho(E_F)g_e$ , where  $J_{sd}$  is the local moment–conducting carrier exchange integral,  $\rho(E_F)$  is the density of states at the Fermi level  $E_F$ , and  $g_e$  is the  $g$  factor of conducting carriers. The change of the  $g$  factor is accompanied by the Korringa contribution to the width of the resonance line:  $\Delta H = (\pi/\hbar)[J_{sd}\rho(E_F)]^2 k_B T$  with a characteristic linear temperature dependence.

The Korringa contribution to the EPR linewidth was identified in a large number of diluted magnetic metallic systems [4] including semimagnetic semiconductors [5–9] with both  $\text{Mn}^{2+}$  as well as  $\text{Gd}^{3+}$ ,  $\text{Eu}^{2+}$ , and  $\text{Fe}^{3+}$  ions. The observation of the carrier concentration induced shift of the resonance field is quite rare and, in fact, is well documented only in strongly paramagnetic metals like Pd:Gd [4]. The experimental observation usually made is to find the resonance at a position different than expected for a given magnetic ion in other (nonconducting) matrices and

assign the difference to the effect of the Knight shift. Also, in metals, a direct experimental proof by the observation of the carrier concentration induced shift scaling with the density of states at the Fermi level is not possible because of the inherent lack of control of the concentration of carriers. In this Letter we will show for the first time that a straightforward proof for the EPR Knight shift can be established for diluted magnetic systems with well controlled semimetallic electron properties. By changing the concentration of carriers in  $\text{PbTe:Mn}^{2+}$ , a strongly degenerated IV-VI semiconductor, we observe the shift of the resonance field being of different sign for holes and for electrons and scaling as a density of states at the Fermi level. This first observation of the EPR Knight shift in semimagnetic semiconductors gives new possibilities to determine experimentally both sign and magnitude of the  $J_{sd}$  exchange integrals. The method is unique in its ability to provide the information in the limit of strong dilution. It also has no limitations brought about by the high mobility required in the (usually applied) magneto-optical methods, so it is, in particular, suitable for disordered systems.

PbTe and SnTe are well known IV-VI semiconductors with narrow energy gaps and nonparabolic energy bands [10,11]. The characteristic intrinsic property of these semiconductors is the tendency to grow slightly nonstoichiometrically. This leads to a high concentration of native defects: metal or nonmetal vacancies which are known to be acceptor or donor centers, respectively, with zero activation energy. Therefore, the IV-VI crystals are usually strongly degenerated with typical carrier concentrations  $n, p = 10^{17} - 10^{19} \text{ cm}^{-3}$  for PbTe and  $p = 10^{20} - 10^{21} \text{ cm}^{-3}$  for SnTe. There is a possibility to control the number of these vacancies (i.e., the concentration of carriers) by annealing. The experimental studies of magnetic properties of  $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ ,  $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$ , and  $\text{Pb}_{1-x-y}\text{Sn}_y\text{Mn}_x\text{Te}$  have revealed that Mn substitutes  $\text{Pb}^{2+}$  or  $\text{Sn}^{2+}$  as a  $\text{Mn}^{2+}$  ion being electrically neutral and possessing the well localized magnetic moment.

In these systems with a sufficiently high content of Mn ( $x \geq 0.01$ ), carrier concentration induced ferromagnetic and spin glass transitions are observed [9,12–15].

We studied bulk monocrystals of  $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$  and  $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$  with  $x = 0.0003$  and  $0.001$  grown by the Bridgman method. To change the concentration of carriers several samples were subsequently annealed. The EPR measurements were performed with a Bruker X-band spectrometer. The magnetic properties of our samples were checked by SQUID measurements of the temperature and magnetic field dependence of magnetization. Hall effect measurements were performed by a standard 4-probe dc technique. As expected, we found our crystals to have semimetallic electrical properties with carrier concentrations being practically temperature independent. The experimental data on magnetic field and temperature dependence of the magnetization can be excellently described by a standard Brillouin function for  $S = 5/2$ . It indicates that our crystals constitute a well defined Curie paramagnet, i.e., a system of localized non-interacting magnetic moments.

The typical EPR spectrum of our PbTe:Mn samples is presented in Fig. 1. The well resolved narrow lines are essential for our further analysis. Because of the metallic conductivity of our crystals, the skin effect limits the penetration depth of microwave radiation to about  $10 \mu\text{m}$  causing the asymmetric (Dysonian) shape of the resonance lines. This spectrum was observed before, both for bulk crystals [5,16] and for epitaxial layers [17]. It consists of the main 6-line structure due to the hyperfine interaction between Mn  $3d^5$  electrons and its nuclear magnetic moment ( $S = 5/2$ , 100% natural abundance) with the

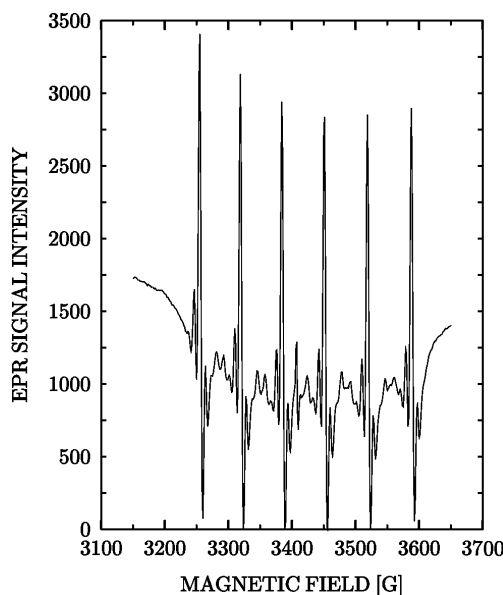


FIG. 1. The EPR spectrum of  $n$ -type  $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$  with electron concentration  $n = 3.48 \times 10^{18} \text{ cm}^{-3}$  and Mn concentration  $x = 0.0003$ . The weak symmetric line in the center of the spectrum is due to the DPPH  $g$ -factor marker.

relevant hyperfine constant  $A_{\text{Mn}} = 61.2 \times 10^{-4} \text{ cm}^{-1}$ . The two satellite lines to each of the six main lines are due to the superhyperfine coupling with the neighboring Te nuclei ( $S = 1/2$ , natural abundance 8%) with the hyperfine constant  $A_{\text{Te}} = 15.4 \times 10^{-4} \text{ cm}^{-1}$ . In our analysis of these spectra we took into account the Dysonian shape of the lines and fitted the spectrum theoretically, taking into account both the first and the second order perturbation theory of hyperfine interactions. We estimate the precision of the determination of the resonance field as equal  $\pm 2 \text{ G}$ . In our experiments the spectra were taken with a small amount of diphenyl-picryl-hydrazyl (DPPH)  $g$ -factor marker. The results of the study of the carrier concentration dependence of  $\text{Mn}^{2+}$   $g$  factor are presented in Fig. 2 both for  $n$ - and for  $p$ -type PbTe. As the symmetry of the wave function of the conducting carriers has mostly  $p$ -type character for electrons and mostly  $s$ -type character for holes, we expected the qualitative difference in the EPR Knight shift in  $n$ -type and in  $p$ -type crystals. The key element of the data is the carrier concentration induced shift of the  $g$  factor, being of different sign for  $n$ - and for  $p$ -type samples. It can be noticed that the observed shift is small and corresponds to about 10 (and less) G. In this respect, we have verified the physical nature of the effect by a simultaneous measurement of two samples with different carrier concentration. Under these identical experimental conditions we observed two, clearly separated, sets of 6-line patterns. Within the accuracy of our experiment we have found no difference between the samples with different Mn concentrations in the range  $0.0003 \leq x \leq 0.001$ . Also, no anisotropy of the spectrum was found for the (110) oriented sample.

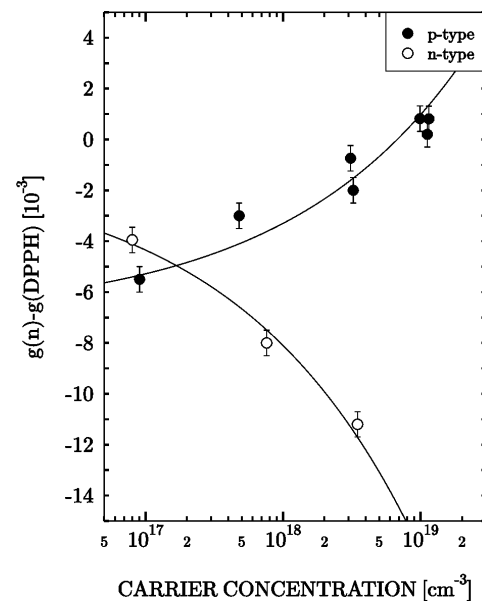


FIG. 2. The carrier concentration dependence of the  $g$  factor of  $\text{Mn}^{2+}$  ions for  $n$ - and  $p$ -type PbTe. The zero level is set at the position of the  $g$  factor of DPPH,  $g = 2.0036$ . The solid lines are calculated based on the  $\Delta g \sim n^{1/3}$  relation.

We have also studied the related SnTe:Mn crystals which always show  $p$ -type conductivity with very high carrier concentrations. The mixed crystals of  $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$  with  $x \geq 0.01$  exhibit the carrier concentration induced ferromagnetic and spin glass transitions driven by the RKKY exchange interaction [13–15]. Both the light and the heavy holes contribute to the interspin RKKY coupling that leads to the thresholdlike carrier concentration dependence of the Curie temperature. By studying the Knight shift in SnTe:Mn we expected to gain the information about the carrier–local moment exchange interaction separately for heavy and for light holes. The carrier concentration dependence of the  $g$  factor of the Mn ion in the SnTe matrix is presented in Fig. 3. The large error bars for the samples with  $p \geq 3 \times 10^{20} \text{ cm}^{-3}$  are due to the unresolved hyperfine structure resulting in a single Dysonian line with the peak-to-peak width of 400 G. The determination of the Knight shift is, in this case, possible due to an order of magnitude larger density of states effective mass in the band of heavy holes as compared to the band of light holes. The hyperfine structure is resolved in SnTe:Mn samples with carrier concentration  $p < 3 \times 10^{20} \text{ cm}^{-3}$ , allowing the determination of the  $g$  factor with an order of magnitude better accuracy.

To draw quantitative conclusions from the experimental data presented above, one has to adapt the expression for the Knight shift for the case of IV-VI semiconductors, taking into account the nonparabolicity, many valley structure, and anisotropy of the band structure of these compounds. It is known from the magneto-optical in-

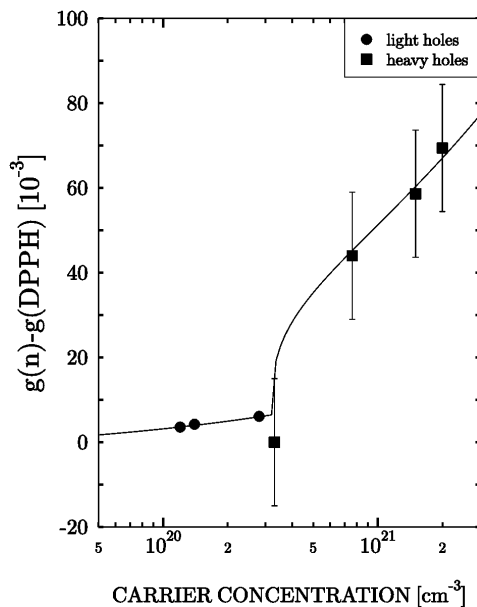


FIG. 3. The carrier concentration dependence of the  $g$  factor of  $\text{Mn}^{2+}$  ion in SnTe. The solid line is calculated assuming the contribution from the light and heavy hole band. The heavy hole band is shifted down from the top of the band of light holes and starts to be populated for  $p \geq 3 \times 10^{20} \text{ cm}^{-3}$ .

vestigations that in PbTe the  $g$  factors of electrons and holes (determined by the Zeeman splitting of conduction and valence band states) can be, by a factor of 20, larger than the  $g$  factor of the free electrons. Moreover, when one wants to extract the sign of the  $s$ - $d$  exchange integrals, it is important to realize that the Zeeman splitting of the conduction band and the valence band states is of reversed order, viz., the effective  $g$  factor for holes is negative and for electrons it is positive [18,19]. The sign of the Knight shift is, therefore, determined by the sign of the product  $J_{sd}g_e$ . The band extrema of IV-VI semiconductors are located at the  $L$  point of the Brillouin zone with four equivalent anisotropic Fermi ellipsoids [10,19]. The analysis of the expression for the magnetization of the electron gas (creating via the  $s$ - $d$  exchange interaction the molecular field acting on local spin and producing the Knight shift) shows that the contributions of all four valleys can be accounted for by using free carriers' effective  $g$  factor,  $g^2 = (1/3)g_l^2 + (2/3)g_t^2$ , where  $g_l$  and  $g_t$  are the  $g$  factors describing the splitting of conduction band and valence band states from the Fermi ellipsoids with the main axis parallel or perpendicular, respectively, to the applied magnetic field. Because of the strong nonparabolicity of the energy bands of IV-VI semiconductors, the conducting carriers'  $g$  factor decreases with increasing Fermi level, whereas the density of states increases faster than in the standard  $E_F^{1/2}$  parabolic band case. It can be shown that within Kane's nonparabolic model of the band structure of PbTe these factors exactly cancel each other leading to simple  $\Delta g \sim n^{1/3}$  behavior both for parabolic and for Kane's energy dispersion relation. Similarly to other magneto-optical and magnetotransport experiments, the  $J_{sd}$  integral measured in the Knight shift experiment is related to microscopic exchange integrals used in the theoretical analysis of the band structure of IV-VI semimagnetic semiconductors in a standard way:  $J_{sd} = a_1 - a_2$  for holes and  $J_{sd} = b_1 - b_2$  for electrons. The parameters  $a_1$ ,  $a_2$ ,  $b_1$ , and  $b_2$  describe the contributions to the exchange coupling due to the two components of the carrier wave functions present because of the spin-orbit mixing in the IV-VI matrices [11].

Our experimental data can be quite well described by  $\Delta g \sim n^{1/3}$  (see solid lines in Figs. 2 and 3) indicating that the observed effect scales with the density of states at the Fermi level. Taking the experimental data on the  $g$  factors of carriers in PbTe,  $g_l = 53$  and  $g_t = 15$  were found from our data  $J_{sd} = a_1 - a_2 = -50 \text{ meV}$  for holes and  $J_{sd} = b_1 - b_2 = -90 \text{ meV}$  for electrons. These values can be compared with the magneto-optical data [ $a_1 - a_2 = -(51-225) \text{ meV}$ , depending on temperature and Mn concentration, and  $b_1 - b_2 = -(41-51) \text{ meV}$  [11]], with the experimental results on the Korringa contribution to the EPR linewidth ( $|J_{sd}| = 70 \text{ meV}$  for holes [5]), and with the theoretical analysis of Dietl ( $a_1 - a_2 = -100 \text{ meV}$  and  $b_1 - b_2 = -90 \text{ meV}$

[20]). It is interesting to notice that, contrary to other experimental methods, our measurements do not indicate any significant temperature or manganese concentration dependence of the exchange integrals. The negative sign of the integrals indicate the dominant role of hybridization mechanisms both for Mn-conducting holes and Mn-conducting electrons exchange coupling, despite the differences in the symmetry of the carrier wave functions. For SnTe the free carriers'  $g$  factors are less precisely known. Taking for light holes the calculated values  $g_l = 35$  and  $g_t = 10$  we found  $J_{sd} = 30$  meV. The heavy holes originate from the band located at the  $\Sigma$  point of the Brillouin zone, where the direct energy gap is large, so we do not expect the  $g$  factor of heavy holes to differ substantially from the  $g = 2$  value. The estimated value of the heavy hole–Mn exchange integral is 20 meV and is in reasonable agreement with the data on the Korringa contribution to the linewidth ( $J_{sd} = 35$  meV for heavy holes [9]). The positive sign of both integrals indicates the different (potential exchange) microscopic mechanism determining the  $s$ - $d$  coupling between the Mn local moment and the conducting holes in SnTe. According to the models of the band structure of IV-VI semiconductors the symmetry of the wave function of conducting holes in SnTe is the same as the symmetry of conducting electrons in PbTe, but the wave function is built mostly from the  $p$ -symmetry orbitals of cation, i.e., is different in PbTe and SnTe. This effect is probably responsible for the different sign of the exchange integrals. The theoretical analysis of this effect presents an interesting challenge for the recently developed theoretical models of the  $s$ - $d$  exchange interactions in IV-VI semimagnetic semiconductors [20].

The lack of any Mn concentration dependence of the Knight shift indicates that PbTe:Mn and SnTe:Mn are not subject to the so-called electron bottleneck effect which may reduce both the Knight shift and the Korringa contribution to the linewidth. This effect is important when the local moments–free carriers relaxation channel provided by the  $s$ - $d$  exchange coupling is not accompanied by the existence of the efficient magnetization relaxation channel between conducting carriers and the crystal lattice [4]. Our conclusion about the nonbottleneck character of EPR of Mn in PbTe and SnTe agrees with previous experimental studies [5,9].

In conclusion, we have observed experimentally the carrier concentration induced shift of the  $g$  factor of  $\text{Mn}^{2+}$  in semiconducting matrices of PbTe and SnTe which is of different sign for  $p$ -type and for  $n$ -type crys-

als. The analysis of the data allows for a straightforward determination of the exchange interaction between the Mn ion and conducting carriers which demonstrates the new opportunity given by measurements of the Knight shift in semimagnetic semiconductors.

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