PHYSICAL REVIEW B VOLUME 38, NUMBER 13 1 NOVEMBER 1988

Magnetic susceptibility and exchange in IV-VI compound diluted magnetic semiconductors

M. Górska* and J. R. Anderson†

Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742

(Received 28 March 1988)

Magnetic susceptibility has been measured in $Pb_{1-x}Mn_xTe$, $Pb_{1-x}Mn_xSe$, and $Pb_{1-x}Gd_xTe$ with values of x from 0 to 0.08. The susceptibility followed the Curie-Weiss behavior with a small paramagnetic Curie temperature that indicated a weak antiferromagnetic exchange coupling between magnetic ions. We analyze our results together with previously published data for $Pb_{1-x}Mn_xS$ and $Pb_{1-x}Eu_xTe$ and present a review of susceptibility parameters in IV-VI compound diluted magnetic semiconductors. We find that the exchange constants obtained from high-temperature susceptibility data in IV-VI diluted magnetic semiconductors are generally an order of magnitude lower than those in II-VI compound diluted magnetic semiconductors. This fact can be explained by assuming that superexchange is the dominant exchange mechanism in all investigated systems. Within this mechanism we estimate the exchange parameters taking into account the crystalline and electronic structure of II-VI and IV-VI semiconductors. Our estimations agree with the experimental results and predict the large difference in exchange parameters between II-VI and IV-VI diluted magnetic semiconductors.

I. INTRODUCTION

Many different types of the II-VI and IV-VI solid solutions containing magnetic impurities, such as manganese, now have been grown and the magnetization has been measured as a function of temperature in such systems.[1,2] These materials appear to be weakly paramagnetic at high temperatures and spin-glass phases have been observed at low temperatures.[3-6] In all the systems it appears to be possible to describe the high-field dependence of the magnetization in terms of the modified Brillouin function phenomenological model.[7-17] Moreover, the high-temperature susceptibility can be fitted to a Curie-Weiss expression from which the Mn-Mn, nearest-neighbor exchange can be estimated.[12-22]

We have observed, that the nearest-neighbor exchange interaction is much smaller in IV-VI compound diluted magnetic semiconductors (DMS) than in II-VI DMS. In this report we present some data on IV-VI DMS systems with Mn and Gd as magnetic impurities. The exchange interaction, $2J/k_B$, in these systems as well as other values that have been published previously are collected here and compared with the cation-anion spacings of the DMS systems. Correlations are observed which support the model of superexchange as the dominant mechanism explaining the magnetic properties of DMS systems.

In order to compare II-VI and IV-VI DMS we look for their similarities and differences. The II-VI alloys that we discuss have either the zinc-blende or wurtzite structure with the cations lying in tetrahedral sites with respect to the anions. The bond angle is 109.6°. The IV-VI alloys, on the other hand, have the rock salt structure and the bond angles are 90° and 180°. Therefore, if one is considering wave-function overlaps, both the bond length and bond angle may be significant. It should also be pointed out that the minimum energy gap in the IV-VI systems is small and at the L point, while in the II-VI systems, the gap varies from zero to large values and occurs at the Γ point.

In Sec. II we describe our experiments. In Sec. III we show data for $Pb_{1-x}Mn_xSe$, $Pb_{1-x}Mn_xTe$, and $Pb_{1-x}Gd_xTe$, and present a compilation of experimental data for many different IV-VI DMS systems. In Sec. IV we present estimates of the interatomic matrix elements and transfer integrals to support our conjectures about the relative strength of exchange interactions in IV-VI and II-VI DMS.

II. EXPERIMENTAL TECHNIQUE

Magnetization measurements from 0.01 to 50 kOe were carried out on single-crystal IV-VI samples using a superconducting quantum-interference device (SQUID) system, that has been described previously.[15,16] The measurements were carried out over a temperature range from 2 to 300 K for low-field (<100 Oe) magnetization and from 2 to 25 K for high-field magnetization.

The samples of $Pb_{1-x}Mn_xSe$, $Pb_{1-x}Mn_xTe$, and $Pb_{1-x}Gd_xTe$ were grown by the Bridgman technique and the x values were determined by electron microprobe and x-ray fluorescence. The x-value range was 0.01–0.08 in $Pb_{1-x}Mn_xSe$ and $Pb_{1-x}Gd_xTe$, and 0.01–0.04 in $Pb_{1-x}Mn_xTe$. The x values were determined with an accuracy of about 0.005 for lower concentrations and 0.01 for higher concentrations.

The $Pb_{1-x}Gd_xTe$ samples were n type with carrier concentrations of 10^{19} to 10^{20} cm^{-3}, while the $Pb_{1-x}Mn_xTe$ and $Pb_{1-x}Mn_xSe$ samples were either n or p type with carrier concentrations of roughly 5×10^{18} cm^{-3}.

In order to interpret the susceptibility measurements, it was necessary to correct for the diamagnetic contribution of the PbTe and PbSe hosts. Therefore, the susceptibility of single crystals of PbTe and PbSe was measured from 2 to 100 K at fields from 1 to 10 kOe. Although the susceptibility was small, the SQUID sensitivity was adequate to make measurements with a precision of at least 2%. As expected, both systems were diamagnetic with susceptibilities of about -3.6×10^{-7} emu/g for PbSe and -3×10^{-7} for PbTe, nearly temperature independent in the range 10–100 K. There was a decrease in magnitude of susceptibility for both compounds below 6 K. To account for the host lattice diamagnetism we corrected all our susceptibility data by the constant values given above.

III. RESULTS

We have investigated several systems which can be described as $A_{1-x}M_xB$, where A is the host cation, M is the magnetic ion, and B is the anion. The high-field magnetization data and most of the low-field magnetization data have been presented in our earlier papers.[14,16,17] Here we show the low-field susceptibility measurements.

The low-field susceptibility values have been fitted to Curie-Weiss expressions of the form

$$\chi=\frac{P_1}{T+\Theta}+\chi_{\mathrm{dia}}\,. \tag{1}$$

Here T is the absolute temperature, χ_{dia} is the susceptibility of the host lattice, e.g., PbTe or PbSe, and P_1 and Θ are fitting parameters. The parameter Θ is the Curie-Weiss parameter. Using the parameter P_1, we may obtain the effective number of magnetic ion spins from the expression

$$\bar{x}=\frac{m_A+m_B}{S(S+1)(g\mu_B)^2N_A/(3k_BP_1)+m_A-m_M}\,, \tag{2}$$

where m_A, m_M, and m_B are the atomic masses of the cation, magnetic ion, and anion, respectively, S is the spin of the magnetic ion, g is the spin-splitting g factor, k_B is the Boltzmann constant, μ_B is the Bohr magneton, and N_A is the Avogadro number. For all the magnetic elements we assume that $g=2$.

The inverse susceptibility χ^{-1} versus temperature is shown in Figs. 1–3 for $\mathrm{Pb}_{1-x}\mathrm{Mn}_x\mathrm{Se}$, $\mathrm{Pb}_{1-x}\mathrm{Mn}_x\mathrm{Te}$, and $\mathrm{Pb}_{1-x}\mathrm{Gd}_x\mathrm{Te}$, respectively. The x values are given in Table I. The data for $\mathrm{Pb}_{1-x}\mathrm{Mn}_x\mathrm{Se}$ and $\mathrm{Pb}_{1-x}\mathrm{Gd}_x\mathrm{Te}$ have been fitted to the Curie-Weiss expression over the temperature range above 20 K; for $\mathrm{Pb}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ fits were carried out from 5 to 25 K. The χ^{-1} is nearly linear with T; the apparent deviation from a straight line in some samples at high temperatures is a result of the host diamagnetic contribution. All the curves extrapolate to small negative temperatures as χ^{-1} goes to zero, implying a weak antiferromagnetic interaction.

In Table I we show the concentration and parameter values for the IV-VI systems that we have studied. The parameter errors depend on the range of temperatures and magnetic fields used in the analysis. In order to present a review of magnetic susceptibilities in IV-VI DMS we also include parameters derived for $\mathrm{Pb}_{1-x}\mathrm{Mn}_x\mathrm{S}$ from data by Karczewski *et al.*[11] and for $\mathrm{Pb}_{1-x}\mathrm{Eu}_x\mathrm{Te}$ from data by Braunstein *et al.*[13]

In all samples Θ is much less than the measurement temperature. Therefore $\Theta_0=\Theta/\bar{x}$ should be approximately constant[20] and can be used to estimate the nearest-neighbor exchange interaction from the relation

TABLE I. Susceptibility parameters for $A_{1-x}M_xB$ IV-VI systems.

Compound	Sample	x	$\bar{x}$	Θ (K)	$\Theta_S=\dfrac{\Theta}{S(S+1)z}$ (K)	$2\dfrac{J}{k_B}$ (K)
$\mathrm{Pb}_{1-x}\mathrm{Mn}_x\mathrm{Se}$	*A*	0.03[a,b]	0.022±0.002	3.0±0.3	2.86×10^{-2}	3.9
	B	0.077[a,b]	0.045±0.005	4.4±0.4	4.19×10^{-2}	2.8
$\mathrm{Pb}_{1-x}\mathrm{Mn}_x\mathrm{Te}$	*A*	0.01[b]	0.009±0.005	0.8±0.2	7.62×10^{-3}	2.41
	B	0.022[b]	0.024±0.005	1.2±0.3	1.14×10^{-2}	1.43
	C	0.04[b]	0.03±0.005	1.3±0.3	1.24×10^{-2}	1.24
$\mathrm{Pb}_{1-x}\mathrm{Gd}_x\mathrm{Te}$	*A*	0.033[a,b]	0.033±0.005	1.7±0.3	8.99×10^{-3}	0.82
	B	0.036[b]	0.041±0.005	1.5±0.1	7.94×10^{-3}	0.58
	C	0.056[a,b]	0.053±0.005	1.8±0.2	9.52×10^{-3}	0.54
	D	0.062[b]	0.063±0.01	3.5±0.6	1.85×10^{-2}	0.87
	E	0.064[b]	0.066±0.01	2.6±0.2	1.38×10^{-2}	0.63
	F	0.066[a,b]	0.07±0.01	3.8±0.4	2.01×10^{-2}	0.86
$\mathrm{Pb}_{1-x}\mathrm{Mn}_x\mathrm{S}$[c]		0.012	0.0169	2.045	1.95×10^{-2}	2.42
		0.02	0.0208	1.145	1.57×10^{-2}	2.13
		0.02	0.0218	1.848	1.76×10^{-2}	2.26
		0.04	0.0378	2.822	2.69×10^{-2}	3.46
$\mathrm{Pb}_{1-x}\mathrm{Eu}_x\mathrm{Te}$[d]		0.042	0.037	0.6	3.18×10^{-3}	0.26
		0.096	0.076	1.0	5.29×10^{-3}	0.21
		0.316	0.320	4.6	2.43×10^{-2}	0.23

[a] Microprobe measurement.

[b] X-ray fluorescence measurement.

[c] From Ref. 11.

[d] From Ref. 13.

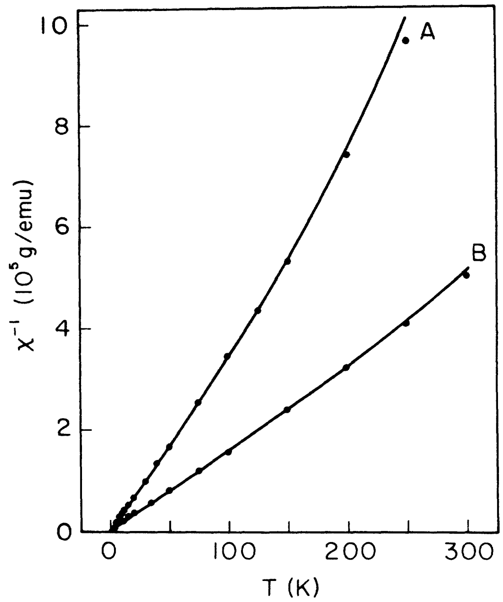

FIG. 1. Inverse susceptibility vs temperature for $Pb_{1-x}Mn_xSe$. The lines are fits to the Curie-Weiss law.

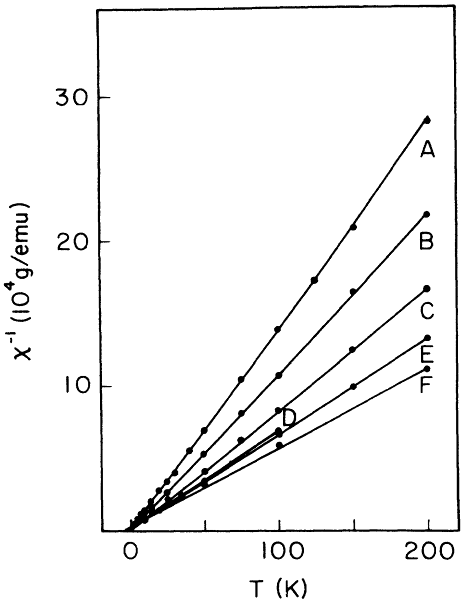

FIG. 3. Inverse susceptibility vs temperature for $Pb_{1-x}Gd_xTe$. The lines are fits to the Curie-Weiss law.

$$\frac{2J}{k_B}=\frac{3\Theta_0}{S(S+1)z}\ , \tag{3}$$

where z is the number of nearest neighbors on cation sites. For all the materials presented here $z=12$.

In this paper we compare systems containing magnetic ions with different spins ($S=2.5$ for Mn and $S=3.5$ for rare-earth elements). Therefore, as a representative parameter for comparisons among different materials we choose the parameter $\Theta_S=\Theta/S(S+1)z$. In the first approximation this parameter should depend linearly on $\bar{x}$, and go to zero as $\bar{x}$ goes to zero. The values of Θ_S are shown in Table I.

In Fig. 4 we present Θ_S versus $\bar{x}$ for all the IV-VI systems that have been investigated. Dashed lines are one-parameter, least-squares fits to a linear dependence of Θ_S

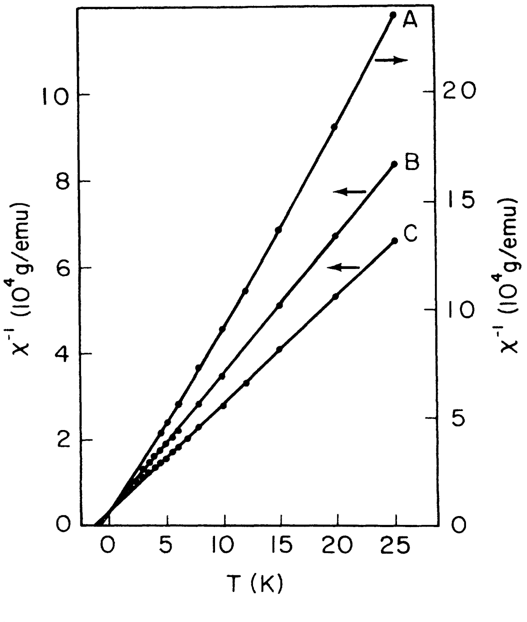

FIG. 2. Inverse susceptibility vs temperature for $Pb_{1-x}Mn_xTe$. The lines are fits to the Curie-Weiss law. *A*—right-hand scale; *B* and *C*—left-hand scale.

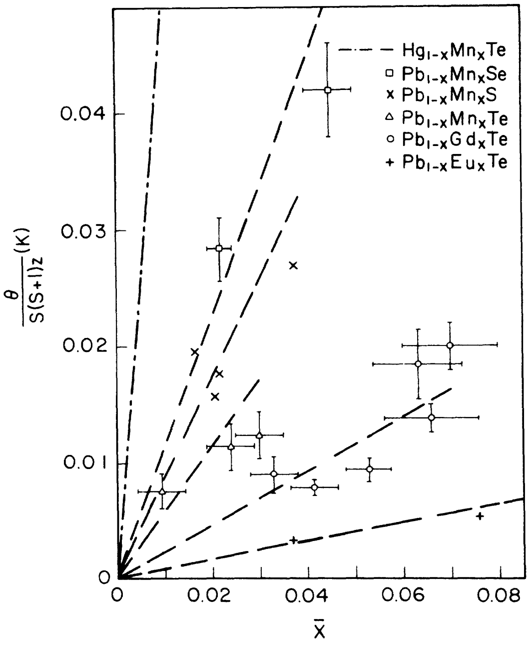

FIG. 4. Θ_s vs effective magnetic ion concentration in IV-VI DMS. Dashed lines are one-parameter, least-squares fits to a straight line. Included is a fitted line for $Hg_{1-x}Mn_xTe$.

on $\bar{x}$. The slope of the fitted line in each system is directly proportional to the average exchange constant $2J/k_B$ in that material. In order to compare the IV-VI with the II-VI DMS we also include a line Θ_S versus $\bar{x}$ derived from our earlier data for $Hg_{1-x}Mn_xTe$.[15] (The experimental values would be far beyond the scale of the figure.)

We see from Fig. 4 that, although there is a significant scatter in the experimental data compared to the straight-line fits, the exchange integrals obtained from these fits for rare-earth-doped IV-VI compounds are less than half those for Mn-doped IV-VI compounds. On the other hand, the line for $Hg_{1-x}Mn_xTe$ has a much higher slope than all lines for IV-VI DMS; the slope would be even higher for other II-VI DMS. This indicates that the values of exchange constants in II-VI DMS are an order of magnitude higher than in IV-VI DMS.

In the last column of Table I we present the values of exchange parameter $2J/k_B$ for all the compounds. (Recently Bruno *et al.*[23] reported a value of J for $Pb_{0.95}Gd_{0.05}Te$ higher than ours, but only from high-field magnetization data.) The average values for each system will be shown and discussed in Sec. IV.

IV. INTERPRETATION OF RESULTS

As we see from the results presented in Sec. III, the exchange constants in a series of IV-VI DMS are an order of magnitude smaller than in II-VI DMS. We are now interested in examining the possible reason for this difference.

Three possible exchange mechanisms in DMS are direct exchange, Bloembergen-Rowland-type exchange, and superexchange. First we note, that CdTe, HgTe, and PbTe have almost the same lattice constants (6.48, 6.46, and 6.45 Å, respectively) in their cubic structures. Therefore, the distance between Mn ions in all the compounds is also the same and there is no reason for a big difference in the direct Mn-Mn exchange interaction in these cases. Moreover, since the Mn-Mn distance is about 4.57 Å while the atomic radius of the Mn d shell is only about 0.755 Å,[24] we may exclude direct exchange as a dominant exchange mechanism in our systems.

The Bloembergen-Rowland-type exchange interaction depends strongly on the value of the energy gap. These energy gaps in most of the HgTe based and PbTe based DMS are in the same range ($\sim$0.2 eV) and therefore exchange constants based on the Bloembergen-Rowland mechanism should also be close. Although the gap occurs at the Γ point in II-VI semiconductors and at the L point in IV-VI semiconductors and this may lead to smaller Bloembergen-Rowland exchange values in the IV-VI compounds, the expected corrections would be too small[25] to explain the large differences observed in the exchange constants.

Superexchange via an anion should depend strongly on the cation-anion distance in DMS. For the same lattice constant a the cation-anion separation in the zinc-blende and wurtzite structure equals $a\sqrt{3}/4$ while in the rock salt structure it equals $0.5a$. As will be shown below, this difference in the cation-anion separation alone can lead to an order of magnitude or more difference in the superexchange interaction parameter J. Consequently, we believe that superexchange is the dominant exchange mechanism in both II-VI and IV-VI DMS. This point of view is also supported by the results of Spalek *et al.*[20] and by Larson *et al.*,[26] who show that the contribution of superexchange to J in II-VI DMS is 95% of the total.

In order to estimate the dependence of the exchange constant J in the superexchange mechanism on the cation-anion separation, we will follow the simple method of estimation used by Spalek *et al.*,[20] which is based on the Anderson theory of the superexchange interaction.[27,28]

We consider the interaction between Mn ions in the II-VI or IV-VI chalcogenide host lattice. The exchange parameter is[27,29]

$$\frac{2J}{k_B}=\frac{2b^2}{4S^2U}\ , \tag{4}$$

where U is the energy to add an extra electron to a neutral Mn atom in the solid, $2S=n$ is the number of unpaired electrons on the magnetic cation d or f shell (five for Mn, seven for Eu and Gd), and b is an interatomic transfer integral connecting the d- and p-electron wave functions. The one-electron transfer integral is[30]

$$H_{i,j}=\langle p_i\,|\,H\,|\,d_j\rangle\ , \tag{5}$$

where the subscripts i and j refer to the p orbitals on an anion and the d orbitals on neighboring magnetic cation, respectively. For the total interaction between a Mn cation and a neighboring anion, the transfer integral is

$$b=\frac{2\sum_{i,j}H_{ij}H_{ji}}{U-\Delta E}\ , \tag{6}$$

where $\Delta E=E_v-E_d$ is the difference in energy between the position of the Mn d level and the p-band (valence band) maximum. The sum goes over three p orbitals on an anion and five d orbitals on a magnetic cation, and a factor of 2 comes from taking into account two electrons on each p orbital. The matrix elements in the transfer integrals may be related to the interatomic matrix elements $V_{ll'm}$ given by Harrison.[31,32] That is

$$\sum_{i,j}H_{ij}H_{ji}=\sum_{m}V_{pdm}^2\ , \tag{7}$$

where $m=-1$ to 1.

In the rock salt structure the transfer integrals become

$$b=\frac{2V_{pd\sigma}^2+4V_{pd\pi}^2}{U-\Delta E}\ . \tag{8}$$

For rare-earth-doped lead chalcogenides we will use transfer integrals of the same form, with $V_{pf\sigma}$ and $V_{pf\pi}$ replacing $V_{pd\sigma}$ and $V_{pd\pi}$, respectively.

Although the s-p hybridization is negligible in the rock salt structure,[33] it is relatively strong in the zinc-blende structure. In a first approximation we will use as an average transfer integral for the zinc-blende structure a sum over one-hybrid matrix elements. (This approximation may underestimate the contribution of p-d matrix elements to the total interaction.) In this structure the coefficient b will be

$$b=\frac{2V_{pd\pi}^2+V_{pd\sigma}^2+V_{sd\sigma}^2}{U-\Delta E} . \tag{9}$$

For the terms $V_{pd\sigma}$, $V_{pd\pi}$, $V_{pf\sigma}$, and $V_{pf\pi}$ we will use the interatomic matrix elements calculated by Harrison and Straub.[32] They are expressed as

$$V_{ll'm}=\eta_{ll'm}(\hbar^2/m_0)[(r_l^{2l-1}r_{l'}^{2l'-1})^{1/2}/d^{l+l'+1}] , \tag{10}$$

where r_l and $r_{l'}$ are distances characteristic of the lth state of the free atom, d is the interatomic nearest cation-anion separation, m_0 is the electron mass, the subscripts l, l', and m are the quantum numbers with $1 \leq l \leq l'$, π corresponds to $m=\pm 1$, and σ to $m=0$. In our case $l=1$ (p shell), and $l'=2$ for d-shell electrons and 3 for f-shell electrons.

The matrix elements entering Eqs. (8) and (9) are

$$V_{pd\sigma}=\eta_{pd\sigma}\frac{\hbar^2}{m_0}\frac{(r_p r_d^3)^{1/2}}{d^4} ,$$

$$V_{pd\pi}=\eta_{pd\pi}\frac{\hbar^2}{m_0}\frac{(r_p r_d^3)^{1/2}}{d^4} ,$$

$$V_{pf\sigma}=\eta_{pf\sigma}\frac{\hbar^2}{m_0}\frac{(r_p r_f^5)^{1/2}}{d^5} , \tag{11}$$

and

$$V_{pf\pi}=\eta_{pf\pi}\frac{\hbar^2}{m_0}\frac{(r_p r_f^5)^{1/2}}{d^5} .$$

The parameters $\eta_{ll'm}$ are $\eta_{pd\sigma}=-3\sqrt{15}/2\pi$, $\eta_{pd\pi}=3\sqrt{5}/2\pi$, $\eta_{pf\sigma}=10\sqrt{21}/\pi$, and $\eta_{pf\pi}=-15\sqrt{7/2}/\pi$. For $V_{sd\sigma}$ we use the parameter determined earlier by Harrison and Froyen:[34]

$$V_{sd\sigma}=3.11\frac{\hbar^2}{m_0}\frac{r^{3/2}}{d^{7/2}} . \tag{12}$$

The interatomic matrix elements $V_{ll'm}$ strongly depend on the interatomic separation d, i.e., $V_{ll'm}\sim d^{-4}$. Since they enter Eq. (4) in the fourth power, the dependence of the superexchange interaction parameter on d becomes very strong (for example, $J\sim d^{-16}$ for $pd\sigma$ and $pd\pi$). This means that even a relatively small change in an interatomic distance can produce a large change in the exchange interaction. It is also interesting to note that the difference between different anions is taken into account in the $V_{ll'm}$ matrix elements (r_p increases in the series S, Se, Te). Consequently the overlap and therefore the exchange interactions are also affected by the anion radius.

For estimation of the exchange constants using Eqs. (4) and (6) we also need to know the energy values U and ΔE, which are not known for most of the materials with which we are dealing. In order to compare a series of DMS alloys, we choose the values for $Cd_{1-x}Mn_xTe$, $U=7$ eV and $\Delta E=3.5$ eV,[35-37] which are obtained from experiment, and apply those values for all our alloys. The r_f, r_d, and r_p atomic radii for all necessary elements are taken from Refs. 24 and 34. The resulting estimates of the exchange parameters in a series of II-VI and IV-VI DMS are given in Table II.

The interatomic distances d in Table II are for host lattices only. The change of d with added Mn and the lattice distortion are not taken into account, however both effects are small compared to the differences in d for different compounds. Except for $Cd_{1-x}Mn_xS$ (Ref. 38) the experimental values for $2J/k_B$ are taken from high-temperature susceptibility measurements, to be consistent with our experimental values. Our high-temperature susceptibility values for $Hg_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xSe$ (Ref. 39) are about the same as in Table II. Other experiments, e.g., magnetization steps or neutron diffraction usually yield lower values for $2J/k_B$. In part, this is because the values from high-temperature susceptibility include most directly exchange interactions with more distant neighbors. The experimental values of $2J/k_B$ for IV-VI DMS systems are average values of those in Table I.

As we see from Table II, the exchange parameters depend strongly on the cation-anion separation, according to our predictions based on the Anderson superexchange interaction theory. The estimated results for Mn-doped IV-VI chalcogenides are in good agreement with the experimental ones; for Mn-doped II-VI semiconductors the estimated results are generally lower than the experimental ones, but of the right order of magnitude. We have mentioned before, that our simple approach to the sp^3 hybrids in the zinc-blende structure may underestimate the total matrix elements. Furthermore, it should be pointed out that the bond angle in the zinc-blende structure (109.6°) is different from that in the rock salt structure (90° or 180°). These differences may also influence the superexchange parameters. Although the bond angles in the rock salt structure are different for nearest and next-nearest neighbors, the distance d is the same for both. Table II also shows that in the rare-earth-doped

TABLE II. Interatomic distances and exchange parameters in II-VI and IV-VI DMS.

Compound	d (Å)	b (eV)	$2J/k_B$ (K) Calc.	Expt.
$Cd_{1-x}Mn_xS$	2.53	0.349	16.14	21.0[a]
$Zn_{1-x}Mn_xSe$	2.45	0.510	34.44	36[b]
$Hg_{1-x}Mn_xSe$	2.63	0.295	11.50	21.8[c]
$Cd_{1-x}Mn_xSe$	2.63	0.295	11.50	21.2[c,d]
$Zn_{1-x}Mn_xTe$	2.64	0.351	16.38	23.7[e]
$Hg_{1-x}Mn_xTe$	2.78	0.235	7.34	14.3[f]
$Cd_{1-x}Mn_xTe$	2.80	0.223	6.56	13.8[c]
$Pb_{1-x}Mn_xS$	2.97	0.136	2.45	2.57[g]
$Pb_{1-x}Mn_xSe$	3.07	0.125	2.07	3.35[h]
$Pb_{1-x}Mn_xTe$	3.225	0.111	1.62	1.69[h]
$Pb_{1-x}Eu_xTe$	3.225	0.0194	0.025	0.23[i]
$Pb_{1-x}Gd_xTe$	3.225	0.0066	0.003	0.72[h]

[a] Reference 38.
[b] Reference 18.
[c] Reference 20.
[d] Reference 39.
[e] Reference 5.
[f] Reference 3.
[g] Reference 11.
[h] This work.
[i] Reference 13.

IV-VI compounds the values of J are small, due to smaller radii of the f shell and stronger dependence of V_{pfm} on d [see Eq. (11)]. In these rare-earth-doped systems, however, our estimated values for J are much less than the experimental values.

Recently we learned that Bruno *et al.*[40] have reevaluated their earlier studies[23] on $Pb_{1-x}Gd_xTe$ and now they suggest that second-nearest-neighbor interactions dominate the exchange. This suggestion is based on studies of the rare-earth chalcogenides, EuTe, GdS, and GdSe, which have the same rock salt structure as $Pb_{1-x}Gd_xTe$. Since the concentration of the magnetic ions in the rare-earth chalcogenides is much higher than the Gd concentration in $Pb_{1-x}Gd_xTe$, it is not clear that the conclusions based on the rare-earth chalcogenides can be carried over to $Pb_{1-x}Gd_xTe$. Moreover, even in rare-earth chalcogenides it is not a general rule that the magnitude of the next-nearest-neighbor exchange interaction is greater than the nearest-neighbor exchange. For example, although the next-nearest-neighbor exchange dominates in EuTe, the opposite is true in EuSe.[41] If, however, next-nearest-neighbor interactions dominate the exchange interaction in $Pb_{1-x}Gd_xTe$ and $Pb_{1-x}Eu_xTe$, the value of $2J/k_B$ that we obtain from experiment would be doubled since there are only six next-nearest neighbors. On the other hand, the cation-anion wave function overlap would be comparable for nearest and next-nearest neighbors even though the bond angles are different. Therefore, because we assume a superexchange model, the strength of the interaction would be similar in the two cases. Since Bruno *et al.* have not calculated the strength of the proposed antiferromagnetic superexchange between next-nearest neighbors, it is not known whether this mechanism is important or not. Therefore, we have considered only nearest-neighbor interactions in making our comparisons in Table II. We might also note in passing that our latest measurements on $Pb_{1-x}Gd_xTe$ to 15 T show that the data at 4.2 K are fitted very well by the modified Brillouin function.[42]

V. CONCLUSIONS

We have measured the magnetization and susceptibility in mixed crystals of lead-manganese chalcogenides and lead-gadolinium telluride. From the high-temperature susceptibility data we determined the nearest-neighbor exchange constants. They are generally of order of 1 K, which is about an order of magnitude smaller than in the II-IV DMS. Furthermore, the exchange constants for the rare-earth doped lead tellurides are two or more times smaller than in the Mn-doped lead chalcogenides.

These results may be explained by assuming that superexchange via an anion is the dominant exchange mechanism in all investigated materials. Simple estimations based on the Anderson superexchange interaction theory and Harrison interatomic matrix elements give results in good agreement with the experiments. They show that the difference in the crystalline structure between II-VI and IV-VI compounds may lead to an order of magnitude difference in the exchange interaction and also predict reasonably well the dependence of J on the carton-anion interatomic distance. The smaller values of the J constants in $Pb_{1-x}Eu_xTe$ and $Pb_{1-x}Gd_xTe$ relative to $Pb_{1-x}Mn_xTe$ may be also explained, in our estimation, by lower r_f values and stronger d dependence of the matrix elements.

ACKNOWLEDGMENTS

We wish to thank Dr. L. J. Azevedo and Dr. E. L. Venturini for their assistance with the experiments and use of the susceptibility system at Sandia Laboratories. We are also grateful for the use of the SQUID facilities at the National Magnet Laboratory and the help of Dr. R. Frankel. We wish to thank Dr. R. Nielsen and Dr. M. Meyerhoff for their x-ray fluorescence and electron-microprobe measurements on the samples. We are indebted to Dr. Z. Golacki, Dr. A. Szczerbakow, and Dr. P. Becla, who prepared the crystals used in our experiments. We thank Dr. J. Spałek for helpful comments. The support of the International Research and Exchanges Board (IREX), which made possible visits by J.R.A. to the Institute of Physics, is gratefully acknowledged. This work was supported in part by the U. S. Department of Defense Advanced Research Projects Agency (DARPA) and the U.S. Army Research Office under Grant No. DAAG 29-85-K-0052.

---

[*] On leave from the Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland.

[†] Present address: Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai 980, Japan.

[1] For a recent review of II-VI DMS, see J. K. Furdyna, J. Vac. Sci. Technol. **A4**, 2002 (1986), and references therein; also J. K. Furdyna, J. Appl. Phys. **53**, 7637 (1982).

[2] For a recent review of IV-VI DMS, see G. Bauer, Mater. Res. Soc. Symp. Proc. **89**, 107 (1987), and references therein.

[3] S. Nagata, R. R. Galazka, D. P. Mullin, H. Akbarzadeh, G. D. Khattak, J. K. Furdyna, and P. H. Keesom, Phys. Rev. B **22**, 3331 (1980); R. R. Galazka, S. Nagata, and P. H. Keesom, *ibid.* **22**, 3344 (1980).

[4] M. A. Novak, O. G. Symko, D. J. Zheng, and S. Oseroff, Physica **126B**, 469 (1984).

[5] S. P. McAlister, J. K. Furdyna, and W. Giriat, Phys. Rev. B **29**, 1310 (1984).

[6] J. L. Tholence, A. Benoît, A. Mauger, M. Escorne, and R. Triboulet, Solid State Commun. **49**, 417 (1984).

[7] J. A. Gaj, R. Planel, and G. Fishman, Solid State Commun. **29**, 435 (1979).

[8] W. Dobrowolski, M. von Ortenberg, A. M. Sandauer, R. R. Galazka, A. Mycielski, and R. Pauthenet, in *Proceedings of the Fourth International Conference on Narrow Gap Semiconductors, Linz, 1981*, in Vol. 152 of *Lecture Notes in Physics*, edited by E. Gornik, H. Heinrich, and L. Palmetshofer (Springer, Berlin, 1982), p. 302.

[9] D. Heiman, Y. Shapira, S. Foner, B. Khazai, R. Kershaw, and

A. Wold, Phys. Rev. B **29**, 5634 (1984).

[10] A. Twardowski, P. Świderski, M. von Ortenberg, and R. Pauthenet, Solid State Commun. **50**, 509 (1984).

[11] G. Karczewski, M. von Ortenberg, Z. Wilamowski, W. Dobrowolski, and J. Niewodniczańska-Zawadzka, Solid State Commun. **55**, 249 (1985).

[12] M. Averous, B. A. Lombos, C. Fau, E. Ilbnouelghazi, J. C. Tedenac, G. Brun, and M. A. Bartkowski, Phys. Status Solidi B **131**, 759 (1985).

[13] G. Braunstein, G. Dresselhaus, J. Heremans, and D. Partin, Phys. Rev. B **35**, 1969 (1987).

[14] J. R. Anderson and M. Górska, Solid State Commun. **52**, 601 (1984).

[15] J. R. Anderson, M. Górska, L. J. Azevedo, and E. L. Venturini, Phys. Rev. B **33**, 4706 (1986).

[16] M. Górska, J. R. Anderson, and Z. Golacki, Mat. Res. Soc. Symp. Proc. **89**, 119 (1987).

[17] M. Górska and J. R. Anderson, Solid State Commun. **63**, 1055 (1987).

[18] Y. Shapira, S. Foner, D. H. Ridgley, K. Dwight, and A. Wold, Phys. Rev. B **30**, 4021 (1984).

[19] Y. Shapira, S. Foner, P. Becla, D. N. Domingues, M. N. Naughton, and J. S. Brooks, Phys. Rev. B **33**, 356 (1986).

[20] J. Spalek, A. Lewicki, Z. Tarnawski, J. K. Furdyna, R. R. Galazka, and Z. Obuszko, Phys. Rev. B **33**, 3407 (1986).

[21] M. Escorne, A. Mauger, J. L. Tholence, and R. Triboulet, Phys. Rev. B **29**, 6306 (1984).

[22] M. Bartkowski, A. H. Reddoch, D. F. Williams, G. Lamarche, and Z. Korczak, Solid State Commun. **57**, 185 (1986).

[23] S. Bruno, J. P. Lascaray, M. Averous, J. M. Broto, J. C. Ousset, and J. F. Dumas, Phys. Rev. B **35**, 2068 (1987).

[24] G. K. Straub and W. A. Harrison, Phys. Rev. B **31**, 7668 (1985).

[25] J. Ginter, J. A. Gaj, and Le Si Dang, Solid State Commun. **48**, 849 (1983).

[26] B. E. Larson, K. C. Haas, and H. Ehrenreich, Solid State Commun. **56**, 347 (1985).

[27] P. W. Anderson, Phys. Rev. **115**, 1 (1959).

[28] P. W. Anderson, in *Solid State Physics*, edited by F. Seitz and F. Turnbull (Academic, New York, 1963), Vol. 14, p. 99.

[29] In our convention the total interaction between two spins is $2J\mathbf{s}_1\cdot\mathbf{s}_2$.

[30] J. B. Goodenough, *Magnetism and The Chemical Bond* (Wiley, New York, 1966), p. 166.

[31] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[32] W. A. Harrison and G. K. Straub, Phys. Rev. B **36**, 2695 (1987).

[33] A. Nakanishi and T. Matsubara, Prog. Theor. Phys. **63**, 1 (1980).

[34] W. A. Harrison and S. Froyen, Phys. Rev. B **21**, 3214 (1980).

[35] P. Lautenschlager, S. Logothetidis, L. Viña, and M. Cardona, Phys. Rev. B **32**, 3811 (1985).

[36] M. Taniguchi, L. Ley, R. L. Johnson, J. Ghijsen, and M. Cardona, Phys. Rev. B **33**, 1206 (1986).

[37] A. Franciosi, A. Wall, S. Chang, P. Philip, R. Reifenberger, F. Pool, and J. K. Furdyna, in *18th International Conference on the Physics of Semiconductors, Stockholm, 1986,* edited by Olof Engström (World-Scientific, Singapore, 1987), Vol. 2, p. 1751.

[38] Y. Shapira and N. F. Oliveira, Jr., Phys. Rev. B **35**, 6888 (1987).

[39] M. Górska and J. R. Anderson (unpublished).

[40] A. Bruno, J. P. Lasearay, M. Averous, G. Fillion, and J. F. Dumas, Phys. Rev. B **37**, 1186 (1988).

[41] See P. Wachter, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Geschneidner and L. Eyring (North-Holland, Amsterdam, 1979).

[42] J. R. Anderson, M. Gorska, G. Kido, and Y. Nishina (unpublished).