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Magnetic properties of lead salts and their ternary compounds

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We make a careful analysis of the Knight shift, magnetic susceptibility, and the effective g factor in lead salts and their ternary compounds and present our results for these quantities. The results compare well with experiment where available.

Lead salt binary semiconductors (PbTe, PbSe, and PbS) form an important class of semiconductors. These are narrow-band-gap semiconductors, and hence their usefulness as infrared lasers and detectors emphasizes their importance in technology.[1,2] However, their unusual characteristics with respect to other semiconductors have made the physics of these semiconductors interesting. For example, the temperature dependence of energy gaps, the high values of static dielectric constants, and the electronic structure of some of the alloys of these compounds show anomalous characteristics compared with the conventional behavior of the diamond- and zinc-blende-structure semiconductors.[3]

During the past few years, we have undertaken extensive investigations of the magnetic properties of these semiconductors, particularly the Knight shift,[4-6] magnetic susceptibility,[7,8] and effective g factors[9] in PbTe and $Pb_{1-x}Sn_xTe$, because there is a considerable amount of experimental data[10] concerning these quantities in these systems. In this Brief Report we present the results of our calculations of these quantities in PbSe, PbS, and some ternary compounds of the lead salt group and compare them with experimental results where available. This report may be viewed as a continuation of our work on lead salts,[4-9] and therefore we avoid mathematical and procedural details which have already been published.[4,5]

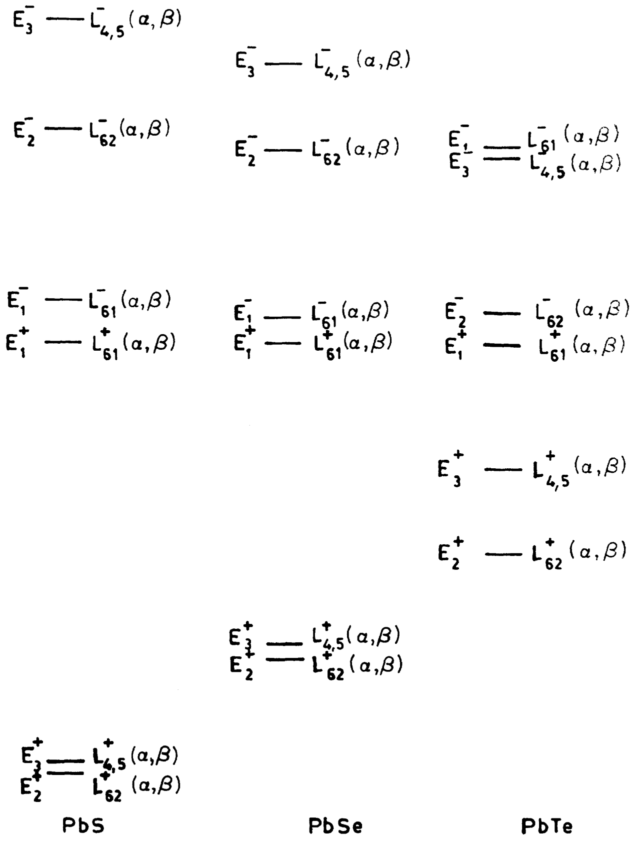

FIG. 1. Schematic picture of the electronic structure of PbS, PbSe, and PbTe at the L point.

In the lead salts the minimum-energy gap occurs at the L point of the Brillouin zone. In addition to the band-edge states, two more conduction and valence bands contribute to a $\mathbf{k}\cdot\mathbf{\Pi}$ band model (Fig. 1). While the interaction between the band-edge states is considered exactly, the interaction of far bands is considered using second-order perturbation theory. The details of the formulation of this model are given in Refs. 4 and 5. It may be noted that, unlike in metals where one needs to define the Bloch functions at a number of $\mathbf{k}$ points in the Brillouin zone, the effective-mass representation,[11] which gives rise to the $\mathbf{k}\cdot\mathbf{\Pi}$ band model, is quite adequate for calculating the different properties of semiconductors. The basis functions are used from the work of Mitchell and Wallis,[12] and the energy levels at the L point are taken from the empirical-pseudopotential-model (EPM) calculation for lead salts by Bernick and Kleinman.[13]

The Knight shift at the jth site is calculated using the general expression derived by Tripathi *et al.*:[4]

$$K_j = K_{js} + K_{jo} + K_{j\text{s.o.}} , \tag{1}$$

where K_{js}, K_{jo}, and $K_{j\text{s.o.}}$ are the spin, orbital, and spin-orbit contributions to the Knight shift, and these are expressed in terms of the matrix elements of momentum $\mathbf{\Pi}$, spin $\boldsymbol{\sigma}$, and hyperfine interaction operators. The νth component of the hyperfine-interaction operator is given by

$$X_j^\nu = X_j^{0\nu} + X_j^{1\nu} , \tag{2}$$

where

$$X_j^{0\nu} = \frac{8\pi}{3}\sigma^\nu \delta(\mathbf{r}_j) + \frac{3(\boldsymbol{\sigma}\cdot\hat{\mathbf{r}}_j)\hat{r}_j^\nu - \sigma^\nu}{r_j^3} \tag{3}$$

and

TABLE I. Single-group momentum-matrix elements used for the lead salts (in atomic units, $e=\hbar=m=1$, $c=137.03$).

	PbTe	PbSe	PbS
p_{11}	0.237	0.261	0.285
p_{13}	0.481	0.501	0.513
p_{31}	0.476	0.479	0.490
p_{21}	0.181	0.186	0.189
p_{22}	0.284	0.305	0.317

$$X_j^{1\nu}=2\epsilon_{\nu\mu\eta}\frac{\hat{\mathbf{r}}_j^{\mu}(\Pi+\hbar\kappa)^{\eta}}{\hbar r_j^2}\ . \tag{4}$$

Equation (3) is a sum of contact and dipolar hyperfine vertices, and Eq. (4) represents the orbital hyperfine vertex. $\epsilon_{\nu\mu\eta}$, the Levi-Civitá tensor, is the completely antisymmetric tensor of third rank, and we follow the Einstein summation convention over the repeated indices. $\mathbf{r}_j$ is the electron coordinate with respect to the jth nucleus. $\boldsymbol{\kappa}$ is the wave vector in the presence of a magnetic field.[4]

The single-group momentum-matrix elements used[14] are listed in Table I. The effect of temperature is considered through the temperature dependence of the minimum-energy gap and through the Fermi function occurring in the expressions for the different contributions to K. The variation of the energy gap with x in $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Se}$ and $\mathrm{Pb}_{1-x}\mathrm{Ge}_x\mathrm{Te}$ for different temperatures are taken from Bauer's work.[15] It may be noted that, unlike the case of $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Te}$,[10] there are no mathematical expressions for the variation of energy gaps as a function of tin and Ge concentrations in $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Ge}$ and $\mathrm{Pb}_{1-x}\mathrm{Ge}_x\mathrm{Te}$, and hence we obtained the energy gaps from a graphical analysis. The hyperfine matrix elements are taken from Ref. 10 for PbTe and from Ref. 16 for PbSe. The **k**-space integrations were done numerically, using the cylindrical coordinate system.

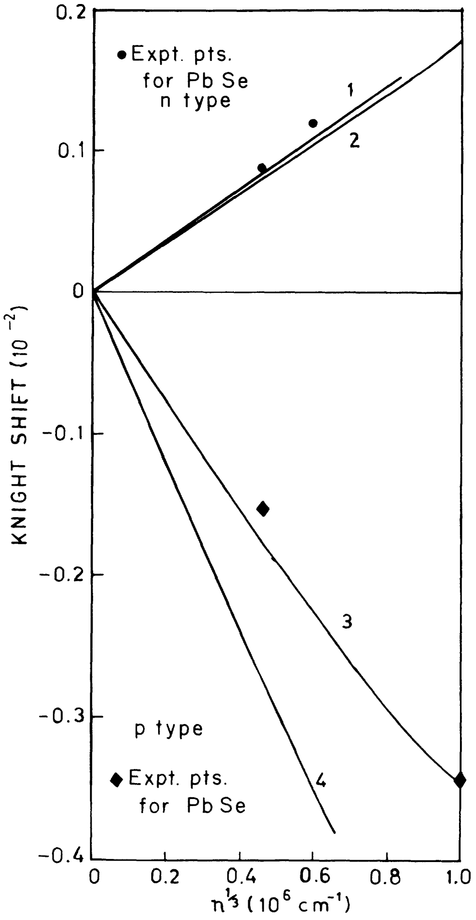

FIG. 2. Knight shift of ^{207}Pb in n- and p-type PbTe and PbSe at 0 K: 1, n-type PbTe; 2, n-type PbSe; 3, p-type PbSe; and 4, p-type PbTe.

We plot our results for the Knight shift of ^{207}Pb in n- and p-type PbSe in Fig. 2. The agreement between our results and the experiment[16] is good. The results for the Knight shift in the ternary compounds are given in Table II. From Table II it is clearly seen that the spin contribution K_s is the dominant contribution. While K_o is small, with an increase in carrier density, $K_{\mathrm{s.o.}}$ becomes important. The differences in magnitude between the n- and p-type systems are due to the following reasons. The spatial parts of the double-group basis functions for the

TABLE II. Details of the Knight-shift calculations in $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Se}$ and $\mathrm{Pb}_{1-x}\mathrm{Ge}_x\mathrm{Te}$.

System	T (K)	x	Carrier density (cm^{-3})	$\mu/(2\ \mathrm{Ry})$	K_s	K_o	$K_{\mathrm{s.o.}}$	K_{tot}
p-type $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Se}$	12							
		0.05	3×10^{17}	0.328×10^{-3}	-0.18×10^{-2}	-0.95×10^{-7}	-0.21×10^{-3}	-0.20×10^{-2}
		0.05	4×10^{18}	0.125×10^{-2}	-0.26×10^{-2}	-0.20×10^{-5}	-0.10×10^{-2}	-0.36×10^{-2}
		0.05	3×10^{17}	0.285×10^{-3}	0.82×10^{-3}	0.25×10^{-6}	0.82×10^{-4}	0.90×10^{-3}
n-type $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Se}$	12							
		0.05	4×10^{18}	0.988×10^{-3}	0.14×10^{-2}	0.11×10^{-5}	0.46×10^{-3}	0.19×10^{-2}
		0.12	3×10^{17}	0.63×10^{-3}	-0.37×10^{-2}	-0.98×10^{-6}	-0.76×10^{-3}	-0.45×10^{-2}
p-type $\mathrm{Pb}_{1-x}\mathrm{Ge}_x\mathrm{Te}$	4.2							
		0.12	10^{18}	0.13×10^{-2}	-0.41×10^{-2}	-0.54×10^{-5}	-0.17×10^{-2}	-0.58×10^{-2}
		0.12	3×10^{17}	0.60×10^{-3}	0.12×10^{-2}	0.58×10^{-6}	0.24×10^{-3}	0.14×10^{-2}
n-type $\mathrm{Pb}_{1-x}\mathrm{Ge}_x\mathrm{Te}$	4.2							
		0.12	10^{18}	0.13×10^{-2}	0.146×10^{-2}	0.109×10^{-5}	0.69×10^{-3}	0.21×10^{-2}

TABLE III. Details of magnetic-susceptibility calculations of the valence band in PbSe in cgs Vol. units.

χ_o^l	χ_o^t	$\chi_{\text{s.o.}}^l$	$\chi_{\text{s.o.}}^t$	χ_o	$\chi_{\text{s.o.}}$	χ
−0.645	0.880	−1.625	−3.288	0.371	−2.734	−9.45

valence band in the lead salts transform like lead S orbitals, and hence the maximum contribution to K in a p-type semiconductor comes from the contact hyperfine interaction, which is usually the dominant one. Since spatial parts of the conduction-band wave functions transform like lead P orbitals, the Knight shift with n-type systems are due mainly to the orbital and dipolar hyperfine interactions occurring in K_s and K_o through $\mathbf{X}_j$. However, the orders of magnitude in both the systems indicate that the orbital hyperfine interaction gives a shift comparable with the contact Knight shift, which is one of the remarkable features of these systems. It may be pertinent here to note that the contribution from the orbital hyperfine interaction appearing in K_s and $K_{\text{s.o.}}$, which accounts for the observed shifts in n-type systems, is different from K_o, the orbital contribution, which is small. This point is more clearly described in one of our recent works on the Knight shift in n-type PbTe.[6]

Apart from the Knight Shift, the other quantity, which is of importance for studying the magnetic properties of lead salt semiconductors, is the zero-field magnetic susceptibility. While there have been some calculations of this quantity for PbTe,[7,8] PbSe has not received much attention. We make an attempt here to fill this gap and present our results for the magnetic susceptibility (χ) of PbSe and some ternary compounds of the lead salts. The magnetic susceptibility is calculated from the formula

$$\chi=\chi_s+\chi_o+\chi_{\text{s.o.}} , \tag{5}$$

where χ_s is the exchange-enhance spin susceptibility,[17]

$$\chi_s=\sum_{\mathbf{k}}\frac{\chi_s^0(\mathbf{k})}{1-\alpha(\mathbf{k})} , \tag{6}$$

where $\alpha(\mathbf{k})$ is the exchange-enhanced function, and in the absence of the electron-electron interaction, χ_s reduces to χ_s^0, where

$$\chi_s^0=\sum_{\mathbf{k}}\chi_s^0(\mathbf{k}) .$$

χ_o is the orbital susceptibility, and $\chi_{\text{s.o.}}$ is the spin-orbit contribution to the susceptibility. Besides $\chi_{\text{s.o.}}$, the effect of spin-orbit interaction also contributes through χ_s via the effective g factor. χ_o is expressed as a sum: $\chi_o=\chi_{\text{LP}}+\chi_{\text{IB}}$, where χ_{LP} is the Landau-Peierls susceptibility[18] and χ_{IB} is due mainly to the interband effects. For a full valence band, both χ_s and χ_{LP} vanish and the susceptibility is accounted for by χ_{IB} and $\chi_{\text{s.o.}}$. The full valence-band contribution to the magnetic susceptibility of PbSe is calculated using a two-band model, where the interaction of the bands is considered exactly. The $\mathbf{k}$ summation was carried out by assuming the Brillouin zone as consisting of four equal spheres and then integrated over the volume of each sphere. The carrier susceptibility is calculated following the procedure used for the calculation of the Knight shift. Our results for the magnetic susceptibility are presented in Tables III and IV. It is seen from Table III that the spin-orbit contribution $\chi_{\text{s.o.}}$ gives a diamagnetic contribution which is about one order more than χ_o, which, in this cases, gives a paramagnetic contribution. This is in contrast to PbTe, where both χ_o and $\chi_{\text{s.o.}}$ are diamagnetic.[19] However, PbSe is more diamagnetic than PbTe owing perhaps to its smaller energy gap compared with PbTe. Our results for the carrier susceptibility are presented in Table IV. For each of the compounds considered, we give our results for two typical values of the carrier density. In every case the susceptibility increases with an increase in carrier density. The increase in the carrier susceptibility while passing from PbSe to PbSnSe is due to the decrease in the energy gap. The opposite behavior in case of $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ is attributed to the increase in the energy gap. Thus the energy gap plays a crucial role in these properties. While the physical processes contributing to

TABLE IV. Orbital, spin, and spin-orbit contributions to the susceptibility (10^{-6} cgs Vol. units).

System	T (K)	Carrier density (cm^{-3})	x	χ_o	χ_s	$\dfrac{\chi_s}{\chi_s^0}$	$\chi_{\text{s.o.}}$	χ_{tot}
p-type PbSe	0	2×10^{17}		−0.202	0.269	1.000 109 1	0.041	0.108
		9×10^{17}		−0.249	0.291	1.000 185 1	0.093	0.135
p-type $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$	12	2×10^{17}	0.05	−0.175	0.241		0.026	0.092
		1.5×10^{18}	0.05	−0.242	0.295		0.082	0.135
p-type $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$	4.2	2×10^{17}	0.12	−0.304	0.387		0.065	0.148
		8×10^{17}	0.12	−0.347	0.376		0.126	0.155

TABLE V. Details of effective g-factor calculations (magnitudes of effective g factors).

System	Carrier concentration (cm^{-3})	x	T (K)	g^l	g^t	g^l (expt)	g^t (expt)	g_{theor}	g_{expt}
PbTe	valence-band edge	0	4.2	49.21	13.64	51±8		25.5	
p-type PbTe	3×10^{18}	0	0	42.07	9.14	32±2	7±2	20.12	
$\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Te}$	band edge	0.27	4.2	231.69	60.08			117.29	120
PbSe	valence-band edge	0	0	37.32	28.79	32±7		31.63	
p-type PbSe	8×10^{17}	0	0	30.16	16.65			21.15	
n-type PbSe	conduction-band edge	0	0	36.26	31.04	27±7		32.78	
n-type PbSe	1.5×10^{18}	0	0	26.99	15.02			19.01	
PbS	valence-band edge	0	0	18.07	16.89	13±3		17.28	
p-type PbS	9×10^{17}	0	0	16.43	13.28			14.33	
PbS	conduction-band edge	0	0	16.96	19.33	12±3		18.54	
p-type $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Se}$	7×10^{17}	0.05	12	32.7	20.45			24.86	
n-type $\mathrm{Pb}_{1-x}\mathrm{Ge}_x\mathrm{Te}$	10^{18}	0.12	4.2	42.27	9.96			20.73	

both χ and K are same, there is one remarkable difference. While K_o is very small compared to K_s, χ_o is appreciable and is of the order of χ_s. This is because of the presence of the χ_{LP} in χ_o, which accounts for the maximum contribution in χ_o, and a counterpart of this contribution is absent in K_o and, hence, the difference. The exchange enhancement of the spin susceptibility is given for two values of carrier concentrations in case of p-type PbSe, and it is seen that the exchange enhancement increases with an increase in carrier density. This trend appears to be right in the sense that the exchange enhancement is appreciable only in metallic density, which is orders of magnitude higher than the carrier densities considered here. There are not enough experimental data with which to compare our results. However, since the trends and behavior found are in conformity with that found in case of PbTe and in the case of the Knight shift where these are supported by experimental results, we believe that the results obtained are meaningful.

Since both the Knight shift and magnetic susceptibility are expressed as functions of the effective g factor, we also calculate the effective g factors for some compounds of this group of semiconductors, using the formulas given in Ref. 9 and present our results in Table V. Our theoretical results compare well with experiment[10] where available.

In conclusion, we believe that we have made a careful analysis of some of the magnetic properties of the lead salt semiconductors by considering several competing and important mechanisms. We believe we have succeeded in making extensive and thorough investigations of these properties. Despite limitations, the results obtained show a broad agreement with the experiment and bring out similarities and contrasts between the Knight shift and magnetic susceptibility.

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