Theory of spin, orbital, and spin-orbit Knight shifts of ^{207}Pb in n-type PbTe

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We make a careful analysis of the various contributing mechanisms to the Knight shift of ^{207}Pb in n-type PbTe, and show that it is one of the few examples for which the orbital hyperfine interaction gives a shift comparable to the strengths of the usual dominant contact Knight shifts in other systems. The good agreement based on our calculations between theory and experiment is quite remarkable.

PbTe is the most extensively studied member of the semiconductor family known as lead salts, which also includes PbS and PbSe. These are multivalley semiconductors with large spin-orbit interaction. While the electronic properties of these semiconductors are fairly well understood,[1,2] interest in the magnetic[3,4] and hyperfine[5-7] properties is of more recent origin. This is due mainly to the complications involved in computing the various competing mechanisms which contribute to the magnetic susceptibility (χ) and the Knight shift (K). Furthermore, only recently a systematic theory for the Knight shift was derived which could be applied to a many-band semiconductor like PbTe with large spin-orbit interaction.[5] Unlike the Knight shift in p-type PbTe where the usual contact hyperfine interaction forms the major mechanism,[4,6] what we show in this Brief Report is that the orbital hyperfine interaction plays the dominant role in explaining the Knight shift of ^{207}Pb in n-type PbTe. This is one of the few examples where orbital hyperfine interaction gives a shift comparable to the contact Knight shift in most other systems including metals and semiconductors. This report is an extension of our work reported earlier.

The general expression for the Knight shift (K) at the jth site is given by the formula[5]

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

where K_{js}, K_{jo}, and $K_{js.o.}$ are the spin, orbital, and spin-orbit contributions to the Knight shift and these are expressed in terms of the matrix elements of momentum, spin, and hyperfine interaction operators.[5] The νth component of the hyperfine vertex, X_j^ν, is defined as

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

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

$$X_j^{1\nu} = 2\epsilon_{\nu\mu\eta}\frac{r_j^\mu(\pi + \hbar\mathbf{K})^\eta}{\hbar r_j^2} . \tag{4}$$

Equation (3) is a sum of contact and dipolar hyperfine vertices and Eq. (4) represents the orbital hyperfine vertex. $\epsilon_{\nu\mu\eta}$ is an antisymmetric tensor of third rank and we follow the Einstein summation convention for repeated indices. The matrix elements are taken between the periodic parts of the Bloch functions for different bands.

K_{js} differs from the conventional K_s (Ref. 8) in the sense that it is expressed as a function of the effective g factor, $g_{nn}(\mathbf{k})$, rather than as a function of χ_s, the effective Pauli spin susceptibility. Moreover, it contains the effects of all the hyperfine interactions through X_j^ν. The orbital contribution K_{jo} is expressed as a sum of a diamagnetic term and a paramagnetic term which are very similar to Langevin and Van Vleck susceptibilities.[9] $K_{js.o.}$ is due to the effect of spin-orbit interaction on the orbital motion of Bloch electrons, while the effect of the spin-orbit interaction on the spin of Bloch electrons is incorporated via the effective g factor. While K_{jo} is termed as the orbital contribution, the orbital effect also contributes through both K_{js} and $K_{js.o.}$ via the hyperfine operator $X_j^{1\nu}$ (Ref. 5).

The minimum energy gap E_g in PbTe occurs at the L point of the Brillouin zone. In addition to the band-edge levels, there are two more conduction and valence bands which contribute significantly to the $\mathbf{k}\cdot\boldsymbol{\pi}$ model. The double group Luttinger-Kohn amplitudes[10] for the six energy levels are taken from Mitchell and Wallis[11] (MW) and we follow the Bernick-Kleinman[12] band ordering. In order to know the nature of atomic orbitals involved, we quote only the MW band edge states:

$$|L_{62}^-\alpha\rangle = \sin\theta^-|Z\uparrow\rangle + \cos\theta^-|X_+\downarrow\rangle , \tag{5}$$

$$|L_{62}^-\beta\rangle = \sin\theta^-|Z\downarrow\rangle - \cos\theta^-|X_-\uparrow\rangle , \tag{6}$$

$$|L_{61}^+\alpha\rangle = -i\cos\theta^+|R\uparrow\rangle - \sin\theta^+|S_+\downarrow\rangle , \tag{7}$$

and

$$|L_{61}^+\beta\rangle = i\cos\theta^+|R\downarrow\rangle + \sin\theta^+|S_-\uparrow\rangle . \tag{8}$$

The minus and plus signs stand for conduction and valence bands, respectively. The transformation properties of the spatial parts of the wave functions around the Pb nucleus are as follows: R transforms like an atomic s orbital, X_+ and Z transform like atomic p functions with $m_z = \pm 1$ and 0, respectively, and S_+ transform like atomic d functions with $m_z = \pm 1$. The spin states $\uparrow$ and $\downarrow$ are the eigenstates of σ_z for z along [1,1,1] with eigenvalues 1

and -1, $\sin\theta^{\pm}$ and $\cos\theta^{\pm}$ are the spin-orbit mixing parameters.

In order to calculate the various contributions to the Knight shift, the conduction-band and the valence-band edge states are treated exactly and the interaction of far bands are considered up to second order within the framework of a $\mathbf{k}\cdot\boldsymbol{\pi}$ model. The matrix elements of $\boldsymbol{\pi}$, $\boldsymbol{\sigma}$, and $\mathbf{X}$ are evaluated as a function of $\mathbf{k}$ by using the renormalized wave functions, ψ_1, ψ_2, ψ_3, and ψ_4, obtained by the above method (Ref. 4). As the details of the evaluation of the first two types of matrix elements are discussed in our earlier papers,[3,6] we now write down the matrix elements of the hyperfine interaction terms taken between the renormalized band-edge states. These are

$$\langle \psi_1 | X^z | \psi_1 \rangle = \left[\frac{1+W_{\mathbf{k}}}{2W_{\mathbf{k}}} \right] A_{orb}^l$$
$$- \frac{\hbar^2}{m^2} \frac{A_c^l}{E_G^2 W_{\mathbf{k}}(1+W_{\mathbf{k}})} (s^2 k_\rho^2 - t^2 k_z^2) , \tag{9}$$

$$\langle \psi_1 | X^z | \psi_2 \rangle = \left[\frac{1+W_{\mathbf{k}}}{2W_{\mathbf{k}}} \right] (1-i) B_{dip}^l , \tag{10}$$

$$\langle \psi_1 | X^x | \psi_1 \rangle = \left[\frac{1+W_{\mathbf{k}}}{2W_{\mathbf{k}}} \right] A_{dip}^t - \frac{2\sqrt{2}\frac{\hbar^2}{m} t s k_x k_z}{E_G^2 W_{\mathbf{k}}(1+W_{\mathbf{k}})} A_c^t , \tag{11}$$

$$\langle \psi_1 | X^x | \psi_2 \rangle = \left[\frac{1+W_{\mathbf{k}}}{2W_{\mathbf{k}}} \right] (B_{orb}^t - i B_{dip}^t)$$
$$+ 2 \frac{\hbar^2}{m^2} \frac{A_c^t}{E_G^2 W_{\mathbf{k}}(1+W_{\mathbf{k}})} (s^2 k_-^2 - t^2 k_z^2) , \tag{12}$$

$$\langle \psi_1 | X^z | \psi_3 \rangle = = \frac{\hbar}{m} \frac{e k_z}{E_G W_{\mathbf{k}}} (A_{orb}^l - A_c^l)$$
$$- \frac{\hbar}{m} \frac{s k_+}{E_G W_{\mathbf{k}}} (1-i) B_{dip}^l , \tag{13}$$

$$\langle \psi_1 | X^z | \psi_4 \rangle = - \frac{\hbar}{m} \frac{s k_-}{E_G W_{\mathbf{k}}} (A_{orb}^l + A_c^l)$$
$$- \frac{\hbar}{m} \frac{t k_z}{E_G W_{\mathbf{k}}} (1-i) B_{dip}^l , \tag{14}$$

$$\langle \psi_1 | X^x | \psi_3 \rangle = \frac{\hbar}{m} \frac{t k_z}{E_G W_{\mathbf{k}}} A_{dip}^t - \frac{\hbar}{m} \frac{s k_+}{E_G W_{\mathbf{k}}} (B_{orb}^t - i B_{dip}^t)$$
$$+ \frac{\hbar}{m} \frac{s k_-}{E_G W_{\mathbf{k}}} A_c^t , \tag{15}$$

and

$$\langle \psi_1 | X^x | \psi_4 \rangle = - \frac{\hbar}{m} \frac{s k_-}{E_G W_{\mathbf{k}}} A_{dip}^t$$
$$- \frac{\hbar}{m} \frac{e k_z}{E_G W_{\mathbf{k}}} (B_{orb}^t - i B_{dip}^t - A_c^t) . \tag{16}$$

Here

$$W_{\mathbf{k}} = \left[1 + 2\frac{\hbar^2 s^2 k_\rho^2}{m^2 E_G^2} + 4\frac{\hbar^2 t^2 k_z^2}{m^2 E_G^2} \right]^{1/2} , \tag{17}$$

$$k_\rho^2 = k_x^2 + k_y^2 , \tag{18}$$

$$k_\pm = \frac{1}{\sqrt{2}}(k_x \pm i k_y) , \tag{19}$$

and s and t are single group momentum matrix elements (Ref. 4). In Eqs. (9)–(16), the L-point hyperfine matrix elements are

$$A_c^l = \frac{8\pi}{3}\cos^2\theta^+ \langle R_{60} | \delta(r) | R_{60} \rangle \Omega , \tag{20}$$

$$A_{orb}^l = 2\cos^2\theta^- \langle R_{61} | r^{-3} | R_{61} \rangle \Omega , \tag{21}$$

$$B_{dip}^l = \sin^2\theta^- \langle R_{61} | r^{-3} | R_{61} \rangle \Omega , \tag{22}$$

$$A_c^t = - A_c^l ,$$

$$B_{orb}^t = -2\sqrt{2}\sin\theta^- \cos\theta^- \langle R_{61} | r^{-3} | R_{61} \rangle \Omega , \tag{23}$$

$$A_{dip}^t = (\sin^2\theta^- - \cos^2\theta^-) \langle R_{61} | r^{-3} | R_{61} \rangle \Omega , \tag{24}$$

and

$$B_{dip}^t = \sin^2\theta^- \langle R_{61} | r^{-3} | R_{61} \rangle \Omega . \tag{25}$$

The radial functions R_{60} and R_{61} are the lead $6s$ and $6p$ orbitals and Ω is the unit cell volume of PbTe. While evaluating the hyperfine matrix elements, we have neglected the orbital contribution of d-like states. The neglect of this orbital part is justified in the sense that only 5% of the L_6^+ wave function is non-S-like.[11] Since there are four inequivalent L points, we calculate

TABLE I. Longitudinal and transverse contributions to the Knight shift.

n (cm^{-3})	Chemical potential (2 Ry)	K_s^l	K_s^t	K_{dia}	K_{para}^l	K_{para}^t	$K_{s.o.}^l$	$K_{s.o.}^t$
10^{17}	0.194×10^{-3}	0.371×10^{-3}	0.113×10^{-3}	-0.115×10^{-10}	0.241×10^{-7}	0.393×10^{-7}	0.221×10^{-4}	0.662×10^{-5}
1.5×10^{18}	0.106×10^{-2}	0.637×10^{-3}	0.236×10^{-3}	-0.175×10^{-9}	0.199×10^{-7}	0.361×10^{-6}	0.245×10^{-3}	0.784×10^{-4}

TABLE II. Spin, orbital, and spin-orbit contributions to K.

n (cm^{-3})	K_s (two band)	K_s (far band)	K_s	K_o	$K_{s.o.}$	K_{tot} ($T=0$ K)	K_{exp} ($T=5$ K) Ref. 13
10^{17}	0.916×10^{-3}	-0.117×10^{-3}	0.798×10^{-3}	0.1371×10^{-6}	0.4721×10^{-4}	0.105×10^{-2}	
1.5×10^{18}	0.174×10^{-2}	-0.026×10^{-2}	0.148×10^{-2}	0.9905×10^{-6}	0.5367×10^{-3}	0.201×10^{-2}	0.2×10^{-2}

the Knight shift from the formula[4]

$$K =4(\tfrac{1}{3}K^{l}+\tfrac{2}{3}K^{t}) ,\tag{26}$$

where the longitudinal and transverse contributions are

$$K^{l}=K_s^{l}+K_o^{l}+K_{s.o.}^{l}\tag{27}$$

and

$$K^{t}=K_s^{t}+K_o^{t}+K_{s.o.}^{t} .\tag{28}$$

We have calculated the Knight shift of ^{207}Pb in n-type PbTe for two typical values of carrier densities and present our results in Tables I and II.

Our results are given for carrier densities $10^{17}/$ cm^3 and 1.5×10^{18}/cm^3. The energy levels and spin-orbit mixing parameters are taken from Bernick and Kleinman.[12] The matrix elements $\langle R_{60}|\delta(r)|R_{60}\rangle$ and $\langle R_{61}|r^{-3}|R_{61}\rangle$ are taken from experiment.[13] It is seen that all the constituent contributions to K increase with increase in carrier concentration. Since K_{dia} is isotropic, there are no longitudinal and transverse contributions for it. It is seen that K_s is the dominant term, K_o is 4 orders less, and the strength of $K_{s.o.}$ is of the same order as K_s for higher carrier densities. The ratio of $K_{s.o.}/K_s$ increases from 0.059 at 10^{17}/cm^3 to 0.362 at 1.5×10^{18}/cm^3. In the case of K_s, we have separated the two-band (band-edge) and far-band contributions. The far-band contribution is opposite to that of the dominant two-band contribution. However, the ratio of far-band to two-band contributions increases from 12% at 10^{17}/cm^3 to 15% at 1.5×10^{18}/cm^3. Our calculated values of the total Knight shift for a carrier density of 1.5×10^{18}/cm^3 is 0.201 at 0 K which compares well with the experimental value of 0.2×10^{-2} at 5 K (Ref. 13). Since there is no appreciable change between the values at 0 and 5 K in p-type PbTe (Ref. 13) we expect the same trend here. Thus, there is excellent agreement between theory and experiment. The value given in Table II is obtained by considering all the hyperfine interactions. However, when we neglect the contact and dipolar hyperfine interactions we found K to be equal to 0.24×10^{-2}. Thus, the major contribution to the Knight shift comes from the orbital hyperfine interaction. The distinction between the orbital contribution K_{jo} and the contribution due to the orbital hyperfine in-

teraction can be understood as follows. Consider, for example, the spin contribution K_{js}. It has two parts—the hyperfine part and the crystalline part. The hyperfine part consists of contact, orbital, and dipolar interactions. Thus K_{js} is essentially a sum of three contributions, namely, contact, orbital, and dipolar contributions. Each contribution has the same crystalline part—product of the effective g factor and the energy derivative of the Fermi function.[5] This is also the case with some of the terms of $K_{js.o.}$ (Ref. 5). Thus, while K_{jo} is normally small, the orbital hyperfine contribution through K_{js} is significant, since it is associated with the effective g factor which is large in these systems. Inclusion of contact and dipolar interactions, however, improves our theoretical results. Furthermore, when we make only the contact hyperfine interaction zero, then our value for K equals 0.21×10^{-2} for an electron density of 1.5×10^{18}/cm^3. Thus, contact hyperfine interaction does not play any important role up to this carrier density. This is justified in the sense that the spatial parts of the conduction-band wave functions transform like p-type orbitals around the lead nucleus, which do not contribute to the contact hyperfine interaction. However, it is expected that the contact interaction might be important at higher electron densities because of the significant mixing of bands.

In conclusion, we note that we have made a careful analysis of the Knight shift of ^{207}Pb in n-type PbTe and show the various mechanisms as distinct physical contributions. The remarkable feature of the present work is that we have shown that the orbital hyperfine interaction gives a shift in n-type PbTe which is comparable to the contact Knight shift in most other systems including metals[14,15] and semiconductors.[4,6] The mechanisms we have not considered are core polarization, electron-electron interactions, and electron-phonon interactions. However, the latter two mechanisms are shown to be small in Refs. 4 and 16, respectively. As regards the core polarization, it has been shown to be small in metallic lead.[17] This mechanism, being an intra-atomic phenomenon, is expected to be small in this case.

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