PHYSICAL REVIEW B VOLUME 7, NUMBER 12 15 JUNE 1973

Knight Shift in Multivalley Semiconductors. I. Theory of Contact, Orbital, and Dipolar Shift and Relativistic Effects

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(Received 27 June 1972)

A theory of the Knight shift in degenerate multivalley semiconductors is presented which takes into account the spin-orbit interaction and the relativistic effects on the hyperfine coupling. This theory treats rigorously the spinor character of the wave function and the nontensorial nature of the g matrix. We give a formula for the shift created by an arbitrary ellipsoidal valley. This formula involves a simple linear combination of g factors and matrix elements of the hyperfine field. In most cases (except that of a spherical valley) the Knight shift is not proportional to the Pauli paramagnetic susceptibility.

I. INTRODUCTION

This paper presents a theory of the Knight shift in multivalley semiconductors. In such materials, the spin-orbit interaction has a profound effect on the energy eigenstates. These states are mixed spin and orbital states, i.e., the Bloch wave functions are spinors. The previous theories of the Knight shift in semiconductors have not correctly taken into account this spinor character of the wave function. The first theory, given by Sapoval in the case of PbTe, ignored this property[1,2]; the expression given by Sapoval in the case of the contact interaction was essentially correct but its derivation was oversimplified. Bailey gave an expression of the contact Knight shift in PbTe, but he ignored Yafet's treatment of the hyperfine coupling showing that the hyperfine Hamiltonian does not involve the effective g factors.[3,4] He then obtained a Knight-shift expression proportional to the electronic paramagnetic susceptibility. This is incorrect. Senturia and co-workers were the first to use spinor wave functions and derived a more comprehensive expression for the contact Knight shift in PbTe.[5] However, they overlooked the difference between the fictitious spin and the real electron spin, which leads to an ambiguity on the final sign of the contact Knight shift. A similar shortcoming is found in the work of Hewes, who gave another expression for the contact Knight shift due to s-like electrons and an expression for the orbital shift created by p-like electrons.[6] There exists no theory of the dipolar shift in cubic crystals.

It thus appears that there exists no rigorous theory of the Knight shift in semiconductors. The purpose of this paper is to give a rigorous derivation of the Knight shift when the spin-orbit interaction cannot be considered as a small perturbation. This is the case in many semiconductors.

In many cases of multivalley semiconductors or semimetals, the nuclei have a high atomic number Z and the relativistic effects on the hyperfine coupling are of major importance. The relativistic corrections to the hyperfine interaction will be described in Sec. II. In Sec. III we derive general expressions for the Knight shift due to the carriers in one valley, in the case of parabolic bands.

II. HYPERFINE INTERACTION

The Knight shift is the value of the magnetic field created at the nuclear site by electrons partially polarized in an external magnetic field. The electronic field depends first on crystalline factors which are the density of states and the effective g factors. The value of these quantitites is usually evaluated in a two-component spinor formalism which includes relativistic corrections to the Pauli Hamiltonian.[7-9] The other physical quantity entering the Knight shift is the hyperfine-coupling constant in the solids,[10] whose value is strongly affected by relativistic effects as shown below.

The hyperfine-coupling constant in the solid depends on the behavior of the electronic wave function very near to the nucleus, in a region where the electrostatic energy of the electron in the nuclear potential becomes comparable to the rest mass energy mc^2. To calculate the hyperfine-coupling constant the full relativistic Dirac Hamiltonian and four-component wave functions should be used. However, a four-component band theory does not generally exist for semiconductors, because a two-component approximation which includes relativistic corrections is sufficient to describe the crystalline parameters (energy levels, effective masses, and effective g factors). The situation is similar to that of a heavy atom[11]: The energy eigenvalues can be calculated reasonably well using a Pauli Hamiltonian but the evaluation of the hyperfine-coupling constant requires the use of a four-component Dirac Hamiltonian. To compare the hyperfine-coupling constant in the solid with the experimental hyperfine-coupling constant in atoms, it is necessary to match the two-component theory with the four-component theory. This is done by using an equivalent Hamiltonian $\mathcal{H}_{\text{hf}}$ which has the same expectation value over the large component of the Dirac wave function as the Dirac hyperfine Hamiltonian over the four-component Dirac wave function.[11,12] This procedure is excellent, as long as the total energy remains of the order of the rest energy.[13] The large component of the Dirac wave function is then identified with the nonrelativistic Bloch-function solution of the two-component Hamiltonian which is used to evaluate the crystalline parameters. This approximation consists in neglecting the influence of the small component far from the nuclei; this is a good approximation. Whenever crystal wave functions are used to calculate matrix elements of the hyperfine Hamiltonian, these wave functions are considered to be the large components of the Dirac wave function.

The equivalent hyperfine Hamiltonian $\mathcal{H}_{\text{hf}}$ can be written

$$\mathcal{H}_{\text{hf}}=\mathcal{H}_{\text{hf}1}+\mathcal{H}_{\text{hf}2}\,.$$

The operator $\mathcal{H}_{\text{hf}1}$ is the equivalent of the nonrelativistic Fermi contact interaction[11]:

$$\mathcal{H}_{\text{hf}1}=\left(\frac{2mc^2}{mc^2+E+e\varphi}\right)^2 \times\left[\frac{e\hbar}{4m^2c^3}\,(\vec{\sigma}\times\vec{\nabla})(-e\varphi)\cdot\left(\frac{\vec{\mu}\times\vec{\mathrm{r}}}{r^3}\right)\right],$$

where E is the total energy of the electron including the rest energy mc^2, $\vec{\mu}$ is the magnetic momentum of the nucleus, φ is the electrostatic potential, $\frac{1}{2}\vec{\sigma}$ is the spin of the electron, and $\vec{\mathrm{r}}$ is the electron coordinate relative to the nucleus. The second term $\mathcal{H}_{\text{hf}2}$ represents the orbital and dipolar interactions[11]:

$$\mathcal{H}_{\text{hf}2}=\frac{2mc^2\mu_B}{mc^2+E+e\varphi}\left[(\vec{\sigma}\cdot\vec{\nabla})(\vec{\mu}\cdot\vec{\nabla})\left(\frac{1}{r}\right)+2\,\frac{\vec{\mu}\cdot\vec{\mathrm{l}}}{r^3}\right],$$

where μ_B is the Bohr magneton and $\vec{\mathrm{l}}$ is the orbital angular momentum of the electron. In the case where the electrostatic potential φ is the Coulomb potential of a nucleus of charge Ze, the first Hamiltonian $\mathcal{H}_{\text{hf}1}$ can be rewritten, neglecting $E-mc^2$ with respect to mc^2:

$$\mathcal{H}_{\text{hf}1}=\mu_B\,\frac{Zr_0}{2}\,\frac{1}{r^2}\,\frac{1}{(r+\frac{1}{2}Zr_0)^2} \times\left(\vec{\sigma}\cdot\vec{\mu}-\frac{(\vec{\sigma}\cdot\vec{\mathrm{r}})(\vec{\mu}\cdot\vec{\mathrm{r}})}{r^2}\right),\qquad(1)$$

where $r_0=e^2/mc^2$ is the classical radius of the electron. The distance Zr_0 defines a "relativistic region" around the nucleus. In the case of lead, for instance, the value Zr_0 is 2.3×10^{-11} cm. Inside this region, the electrostatic energy of the electron is larger than mc^2 and the crystal potential is negligible. Furthermore, the distance Zr_0 is smaller than the mean radius of the orbit of the 1s electrons so that the use of a pure Coulomb potential, due only to the charge Ze of the nucleus, is well justified.

The Hamiltonian $\mathcal{H}_{\text{hf}1}$ corresponds to the classical Fermi contact Hamiltonian and we name it the contact hyperfine Hamiltonian. It contributes to the shift mainly for an s-like wave function and, to a lesser extent, for non-s-like wave functions. In the case of a pure s-like wave function, a straightforward calculation shows that it reduces to

$$\mathcal{H}_{\text{hf}1}=-\vec{\mu}\cdot\vec{\mathrm{H}}_{\text{cont}}\,,\qquad(2)$$

where

$$\vec{\mathrm{H}}_{\text{cont}}=-\tfrac{2}{3}\,\mu_B\,\Delta(r)\,\vec{\sigma},$$

with

$$\Delta(r)=\frac{Zr_0}{2r^2(r+\frac{1}{2}Zr_0)^2}\,.$$

The operator $\vec{\mathrm{H}}_{\text{cont}}$ represents the correct expression of the contact field created at the nucleus by an s-like electron. The function $\Delta(r)$ replaces the usual function $4\pi\delta(\vec{\mathrm{r}})$,[14] where $\delta(\vec{\mathrm{r}})$ is the Dirac function. In the nonrelativistic limit when $c\to\infty$, that is, when $\frac{1}{2}Zr_0\to 0$, both functions $\Delta(\vec{\mathrm{r}})$ and $4\pi\delta(\vec{\mathrm{r}})$ yield the same hyperfine interaction for s electrons. Note that the contact interaction involves not only the value of the electron wave function at the nuclear site but also its value over a distance Zr_0. This leads to significant differences for heavy nuclei. Within the same approximations, the Hamiltonian $\mathcal{H}_{\text{hf}2}$ can be written

$$\mathcal{H}_{\text{hf}2}=-\vec{\mu}\cdot(\vec{\mathrm{H}}_{\text{orb}}+\vec{\mathrm{H}}_{\text{dip}}),$$

where

$$\vec{\mathrm{H}}_{\text{orb}}=-\frac{r}{r+\frac{1}{2}Zr_0}\,\mu_B\left(2\,\frac{\vec{\mathrm{l}}}{r^3}\right),$$

$$\vec{\mathrm{H}}_{\text{dip}}=-\frac{r}{r+\frac{1}{2}Zr_0}\,\mu_B\left(-\frac{\vec{\sigma}}{r^3}+\frac{3\vec{\mathrm{r}}(\vec{\sigma}\cdot\vec{\mathrm{r}})}{r^5}\right).$$

The operators $\vec{\mathrm{H}}_{\text{orb}}$ and $\vec{\mathrm{H}}_{\text{dip}}$ represent, respectively, the orbital and dipolar fields at the nuclear site, and contribute to the hyperfine interaction only for non-s electrons. It must be noted that the hyperfine Hamiltonians $\mathcal{H}_{\text{hf}1}$ and $\mathcal{H}_{\text{hf}2}$ involve the free-electron g factor $g_s=2$ and not the g factors modified by the spin-orbit interaction and the crystalline potential. This is due to the very short range of the electron-nucleus interaction.[4] The above expressions differ from the usual expressions for orbital and dipolar hyperfine fields by the factor $r/(r+\frac{1}{2}Zr_0)$. In practice this factor is very close to unity in the effective range of r^{-3} and we can keep the classical expressions

$$\vec{\mathrm{H}}_{\mathrm{orb}} = -2\vec{\mu}_B \cdot \vec{\mathrm{l}}/r^3 \ , \tag{3a}$$

$$\vec{\mathrm{H}}_{\mathrm{dip}} = -\vec{\mu}_B \cdot [3\vec{\mathrm{r}} \cdot (\vec{\sigma} \cdot \vec{\mathrm{r}})/r^5 - \sigma/r^3]. \tag{3b}$$

The expectation value of these quantities must be evaluated with the large component of the Dirac wave function.

It is interesting to compare the value of the hyperfine-coupling constant, in this approximate two-component reduction, to the classical value and to the fully relativistic value. In the case of atomic lead, for instance, the calculated classical probability of presence at the nuclear site of the $6s$ electrons is[15]

$$|\psi_{6s}(0)|^2 = 1.39 \times 10^{26}\ \mathrm{cm}^{-3}.$$

The calculated classical expectation value of r^{-3} in the $6p$ atomic-lead wave function is[15]

$$\langle r^{-3}\rangle_{6p} = 7.54 \times 10^{25}\ \mathrm{cm}^{-3}.$$

The corresponding "two-component" and "four-component" relativistic values can be deduced from the fully relativistic values of the atomic-lead wave functions computed by Desclaux.[16] Desclaux performed a restricted Hartree–Fock computation of the Dirac wave functions and of the corresponding hyperfine-coupling constants for Pb, Pb^{+}, and Pb^{++}, taking into account the finite size of the nucleus. For the $6s_{1/2}$ states of Pb, the value of the relativistic equivalent of $|\psi_{6s}(0)|^2$ is $3.95\times10^{26}\ \mathrm{cm}^{-3}$ using the two-component reduction and $4.15\times10^{26}\ \mathrm{cm}^{-3}$ using the four-component formalisms. For the $6p_{1/2}$ states of Pb, the value of the relativistic equivalent of $\langle r^{-3}\rangle_{6p}$ is, respectively, 2.10×10^{26} and $2.17\times10^{26}\ \mathrm{cm}^{-3}$, using the two-component and the four-component formalisms. It is clear that the "two-component" reduction of the hyperfine-structure Hamiltonian is a good approximation provided the hyperfine-coupling constants are calculated with the large component of the Dirac wave function. One also notes that, in the case of lead, the relativistic effects enhance the hyperfine-coupling constant by a factor of about 3.

In conclusion, the electron nucleus interaction gives rise to a one-electron additional field $H_{\mathrm{hf}} = H_{\mathrm{cont}} + H_{\mathrm{orb}} + H_{\mathrm{dip}}$ given by Eqs. (2), (3a), and (3b). This field, summed over all the electrons in the crystal, gives rise to the Knight shift.

III. KNIGHT SHIFT ARISING FROM AN ELLIPSOIDAL VALLEY

We now proceed to the calculation of the Knight shift in the simple case where the symmetry at the band edge is not lower than D_{2h}, with inversion.[17,18] The magnetic Hamiltonian of the electron in the external field $\vec{\mathrm{H}}_0$ can be written

$$\mathcal{H}_M = \mu_B \vec{\mathrm{S}}' \otimes \overleftrightarrow{\mathrm{g}} \otimes \vec{\mathrm{H}}_0, \tag{4}$$

where $\vec{\mathrm{S}}'$ is the fictitious spin and $\overleftrightarrow{\mathrm{g}}$ is the g matrix[17]

$$\overleftrightarrow{\mathrm{g}} = \begin{bmatrix} g_{x1} & 0 & 0 \\ 0 & g_{y2} & 0 \\ 0 & 0 & g_{z3} \end{bmatrix}.$$

To obtain a single diagonal g matrix, the g factors are calculated in states $|\alpha_{n\vec{k}}\rangle$ and $|\beta_{n\vec{k}}\rangle = JK|\alpha_{n\vec{k}}\rangle$, which are conjugates by space and time inversion J and K, and which belong to the same complex representation of the double group[19]; these states satisfy the relations[17]

$$\begin{aligned} &\langle \alpha_{n\vec{k}}|\sigma_z|\beta_{n\vec{k}}\rangle = \langle \alpha_{n\vec{k}}|\sigma_x|\alpha_{n\vec{k}}\rangle = \langle \alpha_{n\vec{k}}|\sigma_y|\alpha_{n\vec{k}}\rangle = 0, \\ &\mathrm{Re}\,\langle \alpha_{n\vec{k}}|\sigma_y|\beta_{n\vec{k}}\rangle = \mathrm{Im}\,\langle \alpha_{n\vec{k}}|\sigma_x|\beta_{n\vec{k}}\rangle = 0, \\ &\mathrm{sgn}\,\langle \alpha_{n\vec{k}}|\sigma_z|\alpha_{n\vec{k}}\rangle = \mathrm{sgn}(\mathrm{Re}\langle \alpha_{n\vec{k}}|\sigma_x|\beta_{n\vec{k}}\rangle) \\ &\qquad = \mathrm{sgn}(-\mathrm{Im}\langle \alpha_{n\vec{k}}|\sigma_y|\beta_{n\vec{k}}\rangle), \end{aligned} \tag{5}$$

where σ_x, σ_y, and σ_z represent twice the components of the spin operator.

Let $|\Phi_{n\vec{k}}\epsilon\rangle$ $(\epsilon = \pm 1)$ be two conjugate eigenstates of the magnetic Hamiltonian (4). Their magnetic energies are $\frac{1}{2}\epsilon g\,\mu_B H_0$, where $g = (\lambda_x^2 g_{x1}^2 + \lambda_y^2 g_{y2}^2 + \lambda_z^2 g_{z3}^2)^{1/2}$, λ_x, λ_y, and λ_z being the direction cosines of the magnetic field.[17] The states $|\Phi_{n\vec{k}}\epsilon\rangle$ are linear combinations of the states $|\alpha_{n\vec{k}}\rangle$ and $|\beta_{n\vec{k}}\rangle$. The diagonalization of the Hamiltonian $\mathcal{H}_M$ is straightforward and it is easily shown that

$$\langle \Phi_{n\vec{k}}\epsilon|S'_a|\Phi_{n\vec{k}}\epsilon\rangle = \sum_q \epsilon\lambda_q g_{qa}/2g, \tag{6}$$

where S'_a is the a component of the fictitious spin operator. The expectation value of the hyperfine field is given by the matrix elements within the states $|\Phi_{n\vec{k}}\epsilon\rangle$ of the axial vector operator $\vec{\mathrm{H}}_{\mathrm{hf}}$ defined in Sec. II. In the cases of symmetry considered above, there are always irreducible representations Γ_i whose basis functions are the components $\sum_x, \sum_y$, and $\sum_z$ of such an axial vector.[19] It can be verified that, if $\Gamma_{\alpha,\beta}$ is the irreducible representation to which the states $|\alpha_{n\vec{k}}\rangle$ and $|\beta_{n\vec{k}}\rangle$ belong, the tensorial product $\Gamma^*_{\alpha,\beta}\otimes\Gamma_i\otimes\Gamma_{\alpha,\beta}$ contains once the unit representation Γ_1.[19] The Wigner–Eckart theorem shows then that the matrix elements of the qth component of $\vec{\mathrm{H}}_{\mathrm{hf}}$ and of the vector operator representing the magnetic moment $\vec{\mu}_e = (-\mu_B g_{x1}S'_1; -\mu_B g_{y2}S'_2; -\mu_B g_{z3}S'_3)$ are proportional in the $\Phi_{n\vec{k}\epsilon}$ manifold:

$$\langle \Phi_{n\vec{k}\epsilon}|H_{\mathrm{hf},q}|\Phi_{n\vec{k}\epsilon'}\rangle = -\gamma_q\,\mu_B g_{qa}\langle \Phi_{n\vec{k}\epsilon}|S'_a|\Phi_{n\vec{k}\epsilon'}\rangle \tag{7}$$

for all ϵ and ϵ'. The proportionality constant γ_q is obtained by application of Eq. (7) to particular states in the $\Phi_{n\vec{k}\epsilon}$ manifold; it is found that

$$\begin{aligned} \gamma_x &= -(2/\mu_B g_{x1})\langle \alpha_{n\vec{k}}|H_{\mathrm{hf},x}|\beta_{n\vec{k}}\rangle, \\ \gamma_y &= -(2i/\mu_B g_{y2})\langle \alpha_{n\vec{k}}|H_{\mathrm{hf},y}|\beta_{n\vec{k}}\rangle, \\ \gamma_z &= -(2/\mu_B g_{z3})\langle \alpha_{n\vec{k}}|H_{\mathrm{hf},z}|\alpha_{n\vec{k}}\rangle. \end{aligned} \tag{8}$$

Thus, from Eqs. (6)–(8), the expectation value of the field $\vec{H}_{hf}$ is

$$\langle \Phi_{n\vec{k}\epsilon} | \vec{H}_{hf} | \Phi_{n\vec{k}\epsilon} \rangle = (\epsilon/g)(\lambda_x g_{x1} \langle \alpha_{n\vec{k}} | H_{hf,x} | \beta_{n\vec{k}} \rangle \vec{I} + i\lambda_y g_{y2} \langle \alpha_{n\vec{k}} | H_{hf,y} | \beta_{n\vec{k}} \rangle \vec{J} + \lambda_z g_{z3} \langle \alpha_{n\vec{k}} | H_{hf,z} | \alpha_{n\vec{k}} \rangle \vec{K}),$$

$\vec{I}$, $\vec{J}$, and $\vec{K}$ being unit vectors along the $0x$, $0y$, and $0z$ directions. This one-electron contribution is next summed over all the occupied electron states to obtain the field $\vec{H}$ created at the nuclei by the carriers in the valley. This is a standard calculation[5,12,14] which gives, in degenerate statistics and for an electronic Zeeman energy small as compared to the Fermi energy E_F,

$$\vec{H} = -\mu_B \rho(E_F)(\lambda_x g_{x1} \langle \alpha_{n\vec{k}} | H_{hf,x} | \beta_{n\vec{k}} \rangle \vec{I} + i\lambda_y g_{y2} \langle \alpha_{n\vec{k}} | H_{hf,y} | \beta_{n\vec{k}} \rangle \vec{J} + \lambda_z g_{z3} \langle \alpha_{n\vec{k}} | H_{hf,z} | \beta_{n\vec{k}} \rangle \vec{K}) H_0,$$

where $\rho(E_F)$ is the density of states at the Fermi level for one-spin orientation, in the valley under consideration. This expression is valid as long as nonparabolic effects are negligible, that is, under the assumption that the hyperfine-coupling parameters γ_q and the g factors are $\vec{k}$ independent. This is the case for low carrier concentration: The values at the band edge and at the Fermi level of all the above quantities are then approximately equal.

The Knight shift of the valley $\Delta\vec{H}$ is the part of this supplementary field which is parallel to $\vec{H}_0$:

$$\Delta\vec{H} = -\mu_B \rho(E_F)(\lambda_x^2 g_{x1} \langle \alpha_{n\vec{k}} | H_{hf,x} | \beta_{n\vec{k}} \rangle + i\lambda_y^2 g_{y2} \langle \alpha_{n\vec{k}} | H_{hf,y} | \beta_{n\vec{k}} \rangle + \lambda_z^2 g_{z3} \langle \alpha_{n\vec{k}} | H_{hf,z} | \alpha_{n\vec{k}} \rangle)\vec{H}_0 . \quad (9)$$

The second term in Eq. (9) is real since the matrix element $\langle \alpha_{n\vec{k}} | H_{hf,y} | \beta_{n\vec{k}} \rangle$ is purely imaginary. This can be seen in the following way: The real part of this matrix element is written

$$2\,\mathrm{Re}\,\langle \alpha_{n\vec{k}} | H_{hf,y} | \beta_{n\vec{k}} \rangle = \langle \alpha_{n\vec{k}} | H_{hf,y} | \beta_{n\vec{k}} \rangle + \langle \beta_{n\vec{k}} | H_{hf,y} | \alpha_{n\vec{k}} \rangle .$$

From the Wigner–Eckart theorem, the following relations hold:

$$\langle \alpha_{n\vec{k}} | H_{hf,y} | \beta_{n\vec{k}} \rangle = C \langle \alpha_{n\vec{k}} | \sigma_y | \beta_{n\vec{k}} \rangle ,$$

$$\langle \beta_{n\vec{k}} | H_{hf,y} | \alpha_{n\vec{k}} \rangle = C \langle \beta_{n\vec{k}} | \sigma_y | \alpha_{n\vec{k}} \rangle ,$$

where C is a constant. It follows that

$$\mathrm{Re}\,\langle \alpha_{n\vec{k}} | H_{hf,y} | \beta_{n\vec{k}} \rangle = C\,\mathrm{Re}\,\langle \alpha_{n\vec{k}} | \sigma_y | \beta_{n\vec{k}} \rangle .$$

This last term is zero from Eq. (5).

In the case where the g matrix is scalar and the wave functions are not spinors, Eq. (9) gives the usual expression of the Knight shift.[12,14] The usual Knight shift is proportional to the paramagnetic susceptibility. Although this is true in the case of a scalar g matrix, it is wrong in general, since expression (9) is proportional to a linear combination of the g factors whereas the paramagnetic susceptibility is proportional to a quadratic combination of the g factors.

To obtain the Knight shift in a specific case, one has to sum the effects of the different valleys so that the result depends on the specific band structure under consideration. This calculation is done in the following paper in the particular case of the lead salts.[20] In the general case the three parts of the hyperfine field (contact, orbital, and dipolar) contribute to the shift. The dipolar shift is generally considered to be zero in cubic crystals. This is correct in the absence of spin-orbit coupling.[21] It must be emphasized that in the presence of spin-orbit coupling the dipolar shift is nonzero in cubic crystals. It can even be very large: For example, in the N-type lead salts,[20] the dipolar field is responsible for as much as half of the large observed shift.

ACKNOWLEDGMENTS

The authors wish to thank Dr. J. P. Desclaux of the Commissariat à l'Energie Atomique, Centre de Limeil Brévannes, who adapted his programs to the computation of the hyperfine structure of lead. We acknowledge valuable correspondence and discussion with Professor S. D. Senturia and Dr. B. Hewes.

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Knight Shift in Multivalley Semiconductors. II. Determination of the Hyperfine Coupling Constants in *N*- and *P*-Type PbSe and PbTe

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(Received 27 June 1972)

We report a detailed experimental and theoretical investigation of the large Knight shifts of Pb^{207} in *N*- and *P*-type PbSe and PbTe at low temperature. The nuclear-resonance experiments are performed on bulk single crystals using the technique of helicon-spin interaction. We give the first quantitative account of the Knight shift of Pb^{207} due to s-like holes, and we determine a value of the hyperfine coupling constant that confirms the validity of augmented-plane-wave calculations for the lead salts. The large shift created by the p-like conduction electrons is shown to be due to the large orbital and dipolar hyperfine fields arising from $p_{1/2}$ states. In presence of spin-orbit interaction, the dipolar field (which previous studies, invoking cubic symmetry, ignored) cannot be neglected: It is in fact responsible for half of the shift. This study shows that a large Knight shift must not be interpreted as an experimental evidence of an s-like symmetry of the wave function.

I. INTRODUCTION

This paper presents a detailed study of the Knight shift of the Pb^{207} nuclei resonance in the semiconducting IV-VI compounds PbSe and PbTe at low temperature. Both PbSe and PbTe exhibit very large Knight shifts of Pb^{207} in *N*- and *P*-type materials (1% for 10^{19} carriers) while the shift of Te^{125} remains very small. The shifts of Pb^{207} are among the largest shifts per electron known in nontransition materials. The magnitude of this shift in *N*-type material is surprisingly large since the conduction-band wave function in these materials is of p-like symmetry around lead[1-3] and it is generally believed that only s-like electrons give rise to a large Knight shift. The observation of such large shifts in *N*-type PbSe and PbTe raises the following question: Should a large Knight shift still be considered as experimental evidence of the s-like symmetry of the wave function, or, is it possible to obtain large Knight shifts with p-like states? The answer to this question is of practical importance because the former argument is commonly put forward to clarify the nature of the electronic levels in band-structure theoretical studies.[4-6]

Various theoretical attempts have been made to explain the large Knight shift in PbTe. In fact, the origin of these shifts has not been quantitatively understood, even in the case of the s-like valence band.

The earlier nuclear-magnetic-resonance (NMR) measurements in the lead salts are those of Weinberg and Callaway[7] and Weinberg.[8] These authors studied the temperature dependence of the Pb^{207} NMR in powdered *P*-type PbTe between 260 and 450 °K. They interpreted as a temperature dependence of the Knight shift what was in fact a temperature dependence of the chemical shift.[9,10] A theoretical interpretation of the Weinberg-Callaway measurements, mistaken for a Knight shift, was given by Bailey in terms of relativistic augmented plane waves.[11] His theoretical expression of Knight shift is incorrect because he ignored Yafet's treatment[12] of the hyperfine coupling showing that the contact interaction is not modified by the crystal potential. Lee and co-workers[13] have made NMR measurements on Pb^{207} in PbSe. Their results are discussed in Ref. 10, where it is shown that their theoretical interpretation is