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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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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 stud-

ies.[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

erroneous. Sapoval studied the Knight shift in single crystals of P-type PbTe at helium temperatures by using helicon waves to excite the nuclei in the bulk of single crystals.[9,14] He measured the variation of the resonance field of the Pb[207] nuclei as a function of the carrier concentration. This was the first experimental result which could be interpreted unambiguously as a Knight shift. He gave a simplified theoretical expression for the contact Knight shift, ignoring the spinor character of the electronic wave function. Senturia and co-workers made a careful study of the Knight shift in P-type PbTe as a function of both temperature and concentration[10]; they gave a more comprehensive expression of the contact Knight shift by taking into account the spinor character of the wave function. Following this work, Hewes[15] gave a new expression for the contact Knight shift due to s-like electrons as well as an expression for the orbital shift created by p-like electrons. Some of his results are incorrect because he overlooked the nontensorial character of the g factor and did not take into account the dipolar shift.[16,17]

It then appears that after the earlier misinterpretation of experimental data, the origin of the Knight shift of Pb[207] in P-type PbTe is understood, albeit qualitatively. In contrast, no explanation has been given so far for the observed large shifts in N-type material.

We show that the theory presented in the preceding paper[17] on the Knight shift in multivalley semiconductors gives the first quantitative explanation of the shift in P-type lead salts (where the wave function is s-like around the lead nuclei). We also show that a p-like level can produce a Knight shift of the same magnitude as that produced by s-like electrons. This is due first to the relativistic behavior of the wave function near the nuclei and second to the existence of a dipolar field, *even in cubic crystals*, in presence of spin-orbit interaction.

In Sec. II we give a description of the experimental results in P-type and N-type PbSe and PbTe.

In Secs. III and V we apply the theory of the preceding paper to the valence and conduction bands of the lead salts. For this we use the double-group wave functions adapted to the lead salts band symmetry and the numerical results of augmented-plane-wave (APW) calculations.[3,11,18]

In Sec. IV, we compare the hyperfine structure in the crystal valence band with the hyperfine structure in the lead atom. Other possible contributions to the Knight shift, namely, core polarization, diamagnetic shift, and effects of mixing with neighboring bands, are discussed in Sec. VI.

In Sec. VII we discuss the shift of Te[125] and give an explanation for its smallness[9,10,15] as compared to the large shift of Pb[207].

II. EXPERIMENTAL RESULTS

We have performed nuclear magnetic resonance experiments on Pb[207] nuclei at helium temperature in bulk single crystals of lead selenide and lead telluride, using helicon waves.[9,19-21] Our experimental results are shown in Fig. 1, together with previous results of Sapoval[14] and Hewes.[15] Figure 1 represents the variation of the resonance field of the lead nuclei as a function of $N_c^{1/3}$, N_c being the carrier concentration. This concentration is measured from the helicon dimensional resonances.[9] The coordinate $N_c^{1/3}$ has been chosen because in the case of parabolic bands, one expects a linear dependence of the resonance field as a function of $N_c^{1/3}$.[14]

For a given compound, the Knight shift curves of N- and P-type material can be extrapolated to zero carrier concentration. They extrapolate to a single field, which is the resonance field of the Pb nuclei in an insulating crystal. This field constitutes the *internal* reference, from which the Knight shift is measured. Such an extrapolation is not possible in the case of metals, where an *exter-*
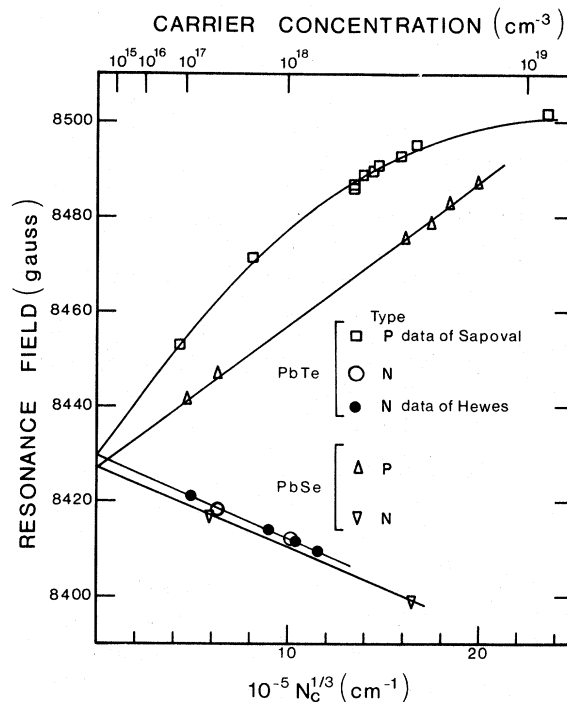
FIG. 1. Resonance field of Pb[207] as a function of the carrier concentration in N- and P-type PbSe and PbTe. All data are scaled to a resonance frequency of 7.5056 MHz. The experiments are performed at 1.3 °K. The resonance field is temperature independent between 1.3 and 4.2 °K. The data of Sapoval are from Ref. 14 and the data of Hewes are from Ref. 15. In a parabolic band the shift should be a linear function of $N_c^{1/3}$.

nal reference has to be chosen. The similarity of the shifts of both compounds can be seen in Fig. 1: The reference field is approximately the same. This shows that the chemical shift is nearly the same in both compounds.[22] The measured Knight shift has the same order of magnitude in PbSe and PbTe, and its sign is the same; negative in P-type material and positive in N-type material.

A difference of behavior between the two compounds appears at high carrier concentration ($N_c \gtrsim 10^{18}$ cm^{-3}). For P-type PbTe, the concentration dependence of the Knight shift differs from $N_c^{1/3}$. This is due to the strong nonparabolic behavior of the valence band of PbTe.[14,15,23] The Knight shift of P-type PbSe presents an apparent parabolic behavior though it is well known that the valence band is also strongly nonparabolic in this material.[1] This point and the difficulties introduced by the nonparabolicity are briefly discussed in Sec. VI.

III. KNIGHT SHIFT OF P-TYPE LEAD SALTS

The Knight shift due to the carriers in one valley j is given by[17]

$$\Delta \vec{H}_j = - \mu_B \rho(E_F) [\lambda_{jx}^2 g_{x1} \langle \alpha_{n\vec{k}} | H_{hf,x} | \beta_{n\vec{k}} \rangle$$
$$+ i\lambda_{jy}^2 g_{y2} \langle \alpha_{n\vec{k}} | H_{hf,y} | \beta_{n\vec{k}} \rangle$$
$$+ \lambda_{jz}^2 g_{z3} \langle \alpha_{n\vec{k}} | H_{hf,z} | \alpha_{n\vec{k}} \rangle] \vec{H}_0 , \quad (1)$$

where μ_B is the Bohr magneton; $\rho(E_F)$ is the density of states at the Fermi level for one ellipsoid and for one spin orientation; λ_{jx}, λ_{jy}, and λ_{jz} are the direction cosines of the external magnetic field $\vec{H}_0$ with respect to the principal axes of the ellipsoid; $|\alpha_{n\vec{k}}\rangle$ and $|\beta_{n\vec{k}}\rangle$ are conjugate states for band n and wave vector $\vec{k}$ and constitute a standard basis[16]; g_{x1}, g_{y2}, and g_{z3} are the three principal g factors defined in this standard basis; $\vec{H}_{hf}$ is the hyperfine field operator. This hyperfine-field operator is the sum of a "contact," "orbital," and "dipolar" field[17]:

$$\vec{H}_{hf} = \vec{H}_{cont} + \vec{H}_{orb} + \vec{H}_{dip} , \quad (2)$$

where

$$\vec{H}_{cont} = - \mu_B \Delta(r) [\vec{\sigma} - \vec{r}(\vec{\sigma} \cdot \vec{r})/r^2] ,$$

which reduces to

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

for a s-like wave function with

$$\Delta(r) = \frac{Z r_0}{2 r^2 (r + \tfrac{1}{2} Z r_0)^2} , \quad (3)$$

$$\vec{H}_{orb} = - \frac{2 \mu_B \vec{l}}{r^3} , \quad (4)$$

$$\vec{H}_{dip} = \mu_B \left(\frac{\vec{\sigma}}{r^3} - \frac{3\vec{r}(\vec{\sigma} \cdot \vec{r})}{r^5} \right) . \quad (5)$$

In these equations, $\vec{\sigma}$ is twice the true spin $\vec{S}$ of the electron, Z is the atomic number of the nucleus under consideration, r_0 is the classical radius of the electron, $\vec{l}$ is the orbital momentum of the electron around the nucleus.

In the lead salts, the constant energy surfaces of the conduction and valence bands are made of four prolate ellipsoids centered at the L points of the Brillouin zone, that is, in the [111] and equivalent directions. The symmetry of the Hamiltonian for a particular L point is D_{3d}. For the valley around L_1 (in the [111] direction) we choose coordinate axes x, y, and z along the [$\bar{1}\bar{1}2$], [$1\bar{1}0$], and [111] directions. Because of the axial symmetry of the D_{3d} group, it is always possible to take $g_{x1} = g_{y2} = g_\perp$, where $g_\perp$ is the transverse g factor. Inspection of the coupling coefficients of the D_{3d} group proves that the components of any axial vector $\vec{\Sigma}$ obey the relation[24]

$$\langle \alpha_{n\vec{k}} | \Sigma_x - i\Sigma_y | \beta_{n\vec{k}} \rangle = 0 .$$

This is true in particular for the hyperfine field $\vec{H}_{hf}$:

$$\langle \alpha_{n\vec{k}} | H_{hf,x} | \beta_{n\vec{k}} \rangle = i\langle \alpha_{n\vec{k}} | H_{hf,y} | \beta_{n\vec{k}} \rangle .$$

Then Eq. (1) becomes

$$\Delta \vec{H}_j = - \mu_B \rho(E_F) [(\lambda_{jx}^2 + \lambda_{jy}^2) g_\perp \langle \alpha_{n\vec{k}} | H_{hf,x} | \beta_{n\vec{k}} \rangle$$
$$+ \lambda_{jz}^2 g_\parallel \langle \alpha_{n\vec{k}} | H_{hf,z} | \alpha_{n\vec{k}} \rangle] \vec{H}_0 ,$$

where $g_\parallel = g_{z3}$ is the longitudinal g factor. This is now summed over the four valleys, that is, the λ_{jx}^2, λ_{jy}^2, and λ_{jz}^2 are replaced by their sum over the four valleys. The total shift $\Delta \vec{H}$ is

$$\Delta \vec{H} = - \tfrac{4}{3} \mu_B \rho(E_F) [2 g_\perp \langle \alpha_{n\vec{k}} | H_{hf,x} | \beta_{n\vec{k}} \rangle$$
$$+ g_\parallel \langle \alpha_{n\vec{k}} | H_{hf,z} | \alpha_{n\vec{k}} \rangle] \vec{H}_0 . \quad (6)$$

This shift is isotropic. It is proportional to the external field $\vec{H}_0$ and to the density of states at the Fermi level. In a parabolic band, the density of states is given by

$$\rho(E_F) = \frac{1}{\sqrt{2}\, \pi^2 \hbar^3} (m_L m_T^2)^{1/2} m^{3/2} E_F^{1/2} ,$$

where m_L and m_T are the longitudinal and transverse effective masses, in units of the free-electron mass m. In the parabolic model, the Fermi energy is proportional to $N_c^{2/3}$; the density of states $\rho(E_F)$ is thus proportional to $N_c^{1/3}$. This explains our choice of the coordinate $N_c^{1/3}$ in Fig. 1.

In order to make a numerical estimate of the matrix elements that appear in Eq. (6), it is necessary to know the electronic wave function $|\alpha_{n\vec{k}}\rangle$. We use the functions derived by Mitchell and Wallis[25] using a parametrized $\vec{k} \cdot \vec{p}$ treatment of the band structure of the lead salts in a six-band model. The expression of the valence-band wave function

TABLE I. Integrated charge densities in the APW sphere around lead in PbSe and PbTe. The integrated densities of the s, p, d, and f components of the wave functions are given for the single-group states at point L: $X_\pm$; Z; R and $\Sigma_\pm$. The dots indicate that the corresponding quantities are not given in the literature.

Single-group representation	Basis function	Integrated charge densities			
		s	p	d	f
Γ_2^-	Z	0	0.337	0	$\cdots$
Γ_1^+	R	0.379	0	$\cdots$	0
PbTe					
Γ_3^-	$X_\pm$	0	0.555	0	0.006
Γ_2^-	Z	0	0.309	0	0.018
Γ_1^+	R	0.365	0	0.025	0
Γ_3^+	$\Sigma_\pm$	0	0	0.060	0

around the lead nuclei is given by these authors in terms of the basis functions R and $\Sigma_\pm = 2^{-1/2}$ $\times(\Sigma_x \pm i\Sigma_y)$ of the single-group representations Γ_1^+ and Γ_3^+, respectively.[24] These functions are even. The function R is invariant under the transformations of the group. The functions Σ_x and Σ_y transform like x and y except that they do not change sign under the inversion. Around a lead nucleus, the function R is a superposition of s, d, and higher orbitals and the functions $\Sigma_\pm$ are superposition of d and higher orbitals. The contribution of each of these orbitals has been calculated for PbTe by Conklin et al.[3] and for PbSe by Rabii[18] by an APW method. They give the value of integrated charge density for each orbital in an APW sphere surrounding a lead nucleus. Their results are summarized in Table I.

The function R appears to be mainly s-like around lead (the remaining part of R, besides a plane wave region between the nuclei, is p- and f- like around the anion). The functions Σ_+ or Σ_- are mainly located around the anion (Se or Te) where their character is p like, while they are d like around lead but with a weak density. Theory and experiment[3,26] have shown that around the lead nuclei, the valence-band wave function is at the band edge a Γ_4^+ state, which we denote Γ_4^+ (Γ_1^+) because it reduces to Γ_1^+ in the absence of spin-orbit interaction.[27] According to our phase conventions,[16] the expressions for the states $|\alpha_{n\vec{k}}\rangle$ and $|\beta_{n\vec{k}}\rangle$ are[25]

$$|\alpha_{n\vec{k}}\rangle = \cos\theta^+ R|+\rangle - i\sin\theta^+\Sigma_+|-\rangle ,$$

$$|\beta_{n\vec{k}}\rangle = \cos\theta^+ R|-\rangle - i\sin\theta^+\Sigma_-|+\rangle .$$

In these expressions the states $|+\rangle$ and $|-\rangle$ are standard eigenstates of the spin component S_z in the z direction, and $\cos\theta^+$ is a mixing parameter,

describing the admixture of the Γ_4^+ (Γ_3^+) level in the Γ_4^+ (Γ_1^+) level due to the spin-orbit interaction. The values of $\cos\theta^+$ and $\sin\theta^+$ have been evaluated by Bernick and Kleinman[5] using a pseudopotential calculation and are given in Table II. The valence-band wave function has a dominant s character around the lead nuclei because the d character of R and $\Sigma_\pm$ is small (Table I) and because the value of $\cos\theta^+$ is close to unity (Table II).

The Knight shift is thus mainly due to the contact interaction of the lead nuclei with the s holes. From Eqs. (2), (3), and (6), the value of the relative shift $K_{cont}^v = \Delta H/H_0$ due to the valence band is

$$K_{cont}^v = \tfrac{4}{3}g_s \mu_B^2\rho_v(E_F)(\cos^2\theta^+)\langle R|\Delta(r)|R\rangle\tfrac{1}{3}(g_\parallel^v + 2g_\perp^v).$$

(7)

Equation (7) contains a valence equivalent g factor $g_{eq}^v = \tfrac{1}{3}(g_\parallel^v + 2g_\perp^v)$. The Knight shift due to s-like carriers provides the sign of g_{eq}^v. Expression (7) also enables us to obtain the "density of probability" of the carriers near the Pb nuclei: $(\cos^2\theta^+)$ $\times\langle R|\Delta(r)|R\rangle/4\pi$. This density of probability is the relativistic equivalent of the electronic probability of presence at the nuclear site $|\psi(0)|^2$ which is found in the classical expression for the Knight shift.[28] In order to obtain from our measurements the value of this density of probability, values for the effective masses and the g factors have to be chosen from the published experimental data.[29-35] These values are listed in Table III. Owing to the dispersion of the results obtained through various methods some values of the g factors might be submitted to corrections of the order of 20%. Using these values, one can deduce from the measurements reported in Fig. 1 the value of the density of probability. The interesting quantity, which can be compared with an atomic system, is in fact the value of this density of probability, renormalized in the volume Ω of a primitive cell[36]

$$d_\Omega = (\cos^2\theta^+)\langle R|\Delta(r)|R\rangle/4\pi\Omega .$$

The value of this volume is 5.84×10^{-23} cm^3 for PbSe and 6.81×10^{-23} cm^3 for PbTe. The value of d_Ω that we deduce from the Knight-shift measurements is

$$d_\Omega \text{ (PbSe)} = 2.79\times10^{26} \text{ cm}^{-3} ,$$

$$d_\Omega \text{ (PbTe)} = 2.82\times10^{26} \text{ cm}^{-3} .$$

TABLE II. Spin-orbit mixing coefficients for PbSe and PbTe. These values are theoretical values from Ref. 5.

PbSe	PbTe
$\cos\theta^+ = 0.978$	$\cos\theta^+ = 0.990$
$\sin\theta^+ = -0.204$	$\sin\theta^+ = -0.138$

TABLE III. The effective masses and g factors for PbSe and PbTe. The signs of the g factors are not known from the experiments. They are determined by a $\vec{k} \cdot \vec{p}$ calculation similar to that given in Ref. 15, and using the phase convention (Ref. 16) between the conjugate states $|\alpha_{n\vec{k}}\rangle$ and $|\beta_{n\vec{k}}\rangle$. These experimental data, unless noted otherwise, are from Ref. 23.

	PbSe	PbTe
m_L^v	0.068 ± 0.015	0.31 ± 0.05
m_T^v	0.034 ± 0.007	0.022 ± 0.003
$g_\parallel^v$	-32 ± 7	-48 ± 5 [a]
$g_\perp^v$	-16.1 ± 1.7 [b]	-19.6 [a]
m_L^c	0.07 ± 0.015	0.24 ± 0.05
m_T^c	0.040 ± 0.008	0.024 ± 0.003
$g_\parallel^c$	27 ± 7	57.5 ± 2 [c]
$g_\perp^c$	-16.6 ± 1.1 [b]	-15 ± 1 [c]

[a]Reference 35.   [b]Reference 34.   [c]Reference 32.

For comparison, we give in Table IV the value of the density of probability of a $6s_{1/2}$ electron in atomic lead $d\,(\text{Pb}) = \langle 6s_{1/2}|\Delta(r)|6s_{1/2}\rangle$. The values of Desclaux[37] are theoretical values. Note that the density of probability varies very little between Pb, Pb^+, and Pb^{2+}. The value from Ref. 39 is obtained from the hyperfine splitting of the ESR line of Pb^{3+} in ThO_2. All these results are close together. Taking the value 4.15×10^{26} cm^{-3} corresponding to a lead atom, we have

$$\frac{d_\Omega(\text{PbSe})}{d(\text{Pb})} \approx \frac{d_\Omega(\text{PbTe})}{d(\text{Pb})} = 0.67 \ .$$

These experimental results show that the electron density near the lead nuclei looks very much the same in the valence bands of PbSe and PbTe.

IV. DENSITY OF PROBABILITY AROUND LEAD

We now compare our results to the theories of the valence band. For PbTe, Bailey gives the results of an APW calculation of the band-edge wave function around lead.[11] He finds that, inside the APW sphere, the wave function is a $6s$ lead atomic wave function, apart from a renormalization factor. If this is true, the ratio $d_\Omega(\text{PbTe})/d(\text{Pb})$ is exactly equal to this renormalization factor. Bailey's value for this is 0.64, which is to be compared with our measured value $d_\Omega(\text{PbTe})/\cos^2\theta^+ d(\text{Pb}) = 0.70$. The agreement is very good. However the integrated charge density obtained from Bailey's data (0.64) differs by a factor of about 2 from the value 0.365 calculated by Conklin *et al.* This discrepancy, which is of fundamental importance here, is not discussed in Bailey's paper.

For PbSe there is no work comparable to

Bailey's. Following Bailey's APW calculation for PbTe, we assume that the wave function is similar around lead to a $6s$ lead atomic wave function with a renormalization factor. The $6s$ state is almost entirely contained in the APW sphere so that the ratio $d_\Omega(\text{PbSe})/d(\text{Pb})$ is equal to the integrated charge density of the s component of the wave function. For this charge density, Rabii[18] gives the value 0.379. We measure 0.67.

The above development shows that the values of the hyperfine-coupling constants predicted from APW calculations are in agreement with the value we determine from experiment. This agreement is very good for PbTe and within a factor of 2 for PbSe.

V. KNIGHT SHIFT IN N-TYPE LEAD SALTS

Around the lead nuclei, the single-group basis states of the conduction band are Z and $X_\pm = 2^{-1/2} (X \pm iY)$. These functions are odd and constitute a basis, respectively, for the Γ_2^- and Γ_3^- representations.[24] The results of the APW calculations show that they are mainly p like around lead.[1-3] For atoms, it is well known that the hyperfine-coupling constant of a $p_{1/2}$ state is appreciably greater than the hyperfine-coupling constant of a $p_{3/2}$ state. For instance, the ratio of the $p_{1/2}$ constant to the $p_{3/2}$ constant is equal to 3 for Bi^{4+} and 200 for Tl,[40] these species being the two neighbors of lead in the periodic chart. The large Knight shift exhibited by the N-type lead salts leads us to assume that the conduction-band wave function has a dominant $p_{1/2}$ behavior around lead. This assertion must be considered here as a working hypothesis; it will be confirmed by the fact that a $p_{3/2}$ behavior is not consistent with the magnitude of the measured shift.

The double-group basis states at the edge of the conduction band belong to the Γ_4^- representation; they are,[25] with our phase conventions,

TABLE IV. Density of probability $d(\text{Pb})$ of $6s_{1/2}$ electrons in Pb, Pb^+, Pb^{2+}, Pb^{3+}, and mean value of r^{-3}, $\langle f(r)|r^{-3}|f(r)\rangle$, computed with the radial part $f(r)$ of the $6p_{1/2}$ wave function of Pb and Pb^+. All these values are given in units of 10^{26} cm^{-3}. The data of Ref. 37 are theoretical values and those of Refs. 38 and 39 are experimental values.

	$d(\text{Pb})$	$\langle r^{-3}\rangle$
Pb	4.15 [a]	2.17 [a]
Pb^+	4.50 [a]	2.73 [a]
Pb^{2+}	$\begin{cases} 4.92\ [a] \\ 5.44\ [b] \end{cases}$	
Pb^{3+}	2.64 [c]	

[a]Reference 37.   [b]Reference 38.   [c]Reference 39.

$$|\alpha_c\rangle = i(\cos\theta^- Z|+\rangle - \sin\theta^- X_+|-\rangle) ,$$

$$|\beta_c\rangle = i(\cos\theta^- Z|-\rangle + \sin\theta^- X_-|+\rangle) ,$$

where $\cos\theta^-$ is a mixing parameter that characterizes the mixing of the Γ_3^- and Γ_2^- states due to the spin-orbit interaction. The above states are in fact the basis states of the Γ_4^- (Γ_2^-) representation when $|\cos\theta^-| > |\sin\theta^-|$. In the opposite situation ($|\sin\theta^-| > |\cos\theta^-|$), they would be the basis states of the Γ_4^- (Γ_3^-) representation, but a rephasing would then be necessary to be consistent with our phase convention. The important point is that these states, whether Γ_4^- (Γ_2^-) or Γ_4^- (Γ_3^-), are assumed to possess a strong $p_{1/2}$ character around the lead nuclei. They must then exhibit the same angular dependence as the $p_{1/2}$ central field spinors:

$$\psi_{1/2}^{1/2} = -\sqrt{\tfrac{1}{3}}\, y_1^0|+\rangle + \sqrt{\tfrac{2}{3}}\, y_1^1|-\rangle ,$$

$$\psi_{1/2}^{-1/2} = \sqrt{\tfrac{1}{3}}\, y_1^0|-\rangle - \sqrt{\tfrac{2}{3}}\, y_1^{-1}|+\rangle ,$$

where y_1^0 and $y_1^{\pm 1}$ are the usual spherical harmonics.[41] This implies that the value of $|\sin\theta^-|$ is not close to 0 or 1 and that the product $\sin\theta^-\cos\theta^-$ is negative. This sign is opposite to the sign given by Bernick and Kleinman in the case of PbSe.[5] However a negative sign of the product $\sin\theta^-\cos\theta^-$ is essential to explain the large experimental shift.

The expression of the Knight shift can now be determined using the $p_{1/2}$ component of $|\alpha_c\rangle$ and $|\beta_c\rangle$. These functions can be written

$$|\alpha_c\rangle = -i|\psi_{1/2}^{1/2} f(r)\rangle + |N_{hfs}\rangle ,$$
$$|\beta_c\rangle = i|\psi_{1/2}^{-1/2} f(r)\rangle + JK|N_{hfs}\rangle . \qquad (8)$$

The function $f(r)$ is given by the angular integral

$$f(r) = -\sqrt{\tfrac{1}{3}}\cos\theta^- \int d\omega Z(\vec{r}) y_1^0 - \sqrt{\tfrac{2}{3}}\sin\theta^- \int d\omega X_+(\vec{r}) y_1^1$$

and represents the radial $p_{1/2}$ component of the doublet; the function $|N_{hfs}\rangle$ is a state (orthogonal to $p_{1/2}$) which give a negligible contribution to the hyperfine structure; J is the inversion operator and K is the time reversal operator.[16,42] The hyperfine coupling of the $p_{1/2}$ electrons is characterized by an important property: These electrons are coupled to the nuclei not only through the orbital interaction, as is the case in a standard calculation, but also through the dipole and contact interactions. The dipole interaction is indeed zero in cubic geometry if the spin-orbit coupling is neglected, but it is *not* when the spin orbit is taken into account.[43,44] The relative Knight shift is the sum of three different contributions K_{orb}^c, K_{dip}^c, and K_{cont}^c, where K_{orb}^c and K_{dip}^c are the orbital and dipolar terms, and are given, from Eqs. (4)-(6) and (8), by

$$K_{orb}^c = K_{dip}^c = \tfrac{8}{3} g_s \mu_B^2 \rho_c(E_F)$$

$$\times \tfrac{1}{3}(g_\parallel^c - 2g_\perp^c)(f(r)|r^{-3}|f(r)) . \qquad (9)$$

The contact term K_{cont}^c is given, from Eqs. (2), (3), (6), and (8), by

$$K_{cont}^c = -\tfrac{4}{3} g_s \mu_B^2 \rho_c(E_F)$$

$$\times \tfrac{1}{3}(g_\parallel^c - 2g_\perp^c)(f(r)|\Delta(r)|f(r)) , \qquad (10)$$

where

$$(f(r)|P(r)|f(r)) = \int_0^\infty f^*(r)\, P(r) f(r)\, r^2 dr .$$

Equations (9) and (10) involve an equivalent g factor $g_{eq}^c = \tfrac{1}{3}(g_\parallel^c - 2g_\perp^c)$ that must not be confused with the equivalent valence-band g factor $g_{eq}^v = \tfrac{1}{3}(g_\parallel^v + 2g_\perp^v)$. Two important aspects must be emphasized about these results:

(i) The contact Knight shift K_{cont}^c is smaller than the orbital and the dipolar Knight shift. It is reasonable to think that the ratio

$$\xi = \left| \frac{K_{cont}^c}{K_{orb}^c + K_{dip}^c} \right| = \frac{(f(r)|\Delta(r)|f(r))}{4(f(r)|r^{-3}|f(r))}$$

is approximately the same in PbSe and in PbTe. An order of magnitude of this ratio can be evaluated using for $f(r)$ the large component of the $6p_{1/2}$ relativistic wave function computed by Desclaux[37] for atomic lead (see Table IV):

$$\xi_{at} = \frac{(6p_{1/2}|\Delta(r)|6p_{1/2})}{4(6p_{1/2}|r^{-3}|6p_{1/2})} = 6.8\times 10^{-2} .$$

This comparison shows that the large Knight shift created by $p_{1/2}$ electrons does not arise from the contact interaction. The contact term [Eq. (10)] is neglected in the following.

(ii) A straightforward calculation shows that if the conduction band were mainly $p_{3/2}$ instead of $p_{1/2}$, the factor $\tfrac{1}{3}(g_\parallel^c - 2g_\perp^c)$ in Eq. (9) should be replaced by $\tfrac{1}{15}(g_\parallel^c + 4g_\perp^c)$. The values of the conduction-band g factors given in Table III enable one to compare these two cases. Using these values, we have $\tfrac{1}{3}(g_\parallel^c - 2g_\perp^c) = 20$ for PbSe and 29 for PbTe, whereas $\tfrac{1}{15}(g_\parallel^c + 4g_\perp^c)$ is much smaller for both PbSe and PbTe. Thus, the Knight shift created by $p_{3/2}$ electrons is much smaller than that created by $p_{1/2}$ electrons, simply because of a numerical effect of the g factors. Since the hyperfine interaction, i.e., the expectation value of r^{-3}, is also smaller in the $p_{3/2}$ state than in the $p_{1/2}$ state, the possiblity that the conduction-band wave function is mainly $p_{3/2}$ must be ruled out. To summarize: The contact Knight shift is negligible and the conduction-band Knight shift K^c reduces to

$$K^c = K_{orb}^c + K_{dip}^c$$

$$= \tfrac{16}{3} g_s \mu_B^2 \rho_c(E_F)\tfrac{1}{3}(g_\parallel^c - 2g_\perp^c)(f(r)|r^{-3}|f(r)) . \qquad (11)$$

Using this expression and the experimental data of Fig. 1, we can deduce the expectation value of r^{-3}

in the $p_{1/2}$ radial crystal wave function. With the values of band parameters of Table III this expectation value, renormalized in the primitive cell, is equal to 5.3×10^{26} cm^{-3} for PbSe and to 2.9×10^{26} cm^{-3} for PbTe. The ratio η of the expectation value of r^{-3} measured in the crystal to that calculated in the Pb atomic wave function (see Table IV) is

$$\eta = 2.4 \quad (\text{PbSe})$$

$$= 1.3 \quad (\text{PbTe}) .$$

For the Pb$^+$ atomic wave function, this ratio is

$$\eta = 1.9 \quad (\text{PbSe})$$

$$= 1.1 \quad (\text{PbTe}) .$$

In the case of the lead salts the ratio of orbital and dipolar Knight shift in the conduction band to the contact Knight shift in the valence band can be put in a very simple form: As the band parameters (effective masses and g factors) have approximately the same absolute value in the valence band and in the conduction band, one can write for a given Fermi energy

$$\rho_c(E_F) \approx \rho_v(E_F) ,$$

$$|g_{\|v} + 2g_{\perp v}| \approx |g_{\|c} - 2g_{\perp c}| .$$

Using Eqs. (7) and (11), we find that the ratio of the orbital and dipolar Knight shift to the contact Knight shift is (taking $\cos^2\theta^+ = 1$)

$$(K_{\text{orb}}^c + K_{\text{dip}}^c)/K_{\text{cont}}^c \approx 4(f(r)|r^{-3}|f(r))/\langle R|\Delta(r)|R\rangle .$$

This expression is formally analogous to the ratio of the hyperfine-coupling constants for $p_{1/2}$ and s-like electrons in atoms[45]: It only involves the ratio of the hyperfine parameters $(f(r)|r^{-3}|f(r))$ and $\langle R|\Delta(r)|R\rangle$.

VI. OTHER POSSIBLE CONTRIBUTIONS TO KNIGHT SHIFT

Besides the hyperfine interaction studied in the preceding sections, several other possible mechanisms should be examined, namely, (i) the exchange core polarization, (ii) the electron diamagnetism, and (iii) the mixing of neighboring levels due to the $\vec{k} \cdot \vec{p}$ interaction.

(i) The core polarization is due to the exchange coupling between the spin of the carriers and the spin of inner core electrons. This coupling results in a modification of the hyperfine interaction between carriers and nuclei. There is no calculation of this effect in the lead salts and there is a priori no reason to neglect the contribution of the exchange core polarization to the hyperfine structure.

However, the work of Tterlikkis, Mahanti, and Das indicates that this effect is weak in metallic lead.[46] The core polarization is an intra-atomic phenomenon and we think that its effect should also be small for lead in PbSe and PbTe. We can ob-

tain another indication on the magnitude of this effect from the work of Desclaux on the hyperfine structure of heavy alkali atoms.[47] Desclaux has compared the hyperfine structure calculated with restricted and unrestricted Dirac–Hartree–Fock wave functions. For cesium and francium he found that the core polarization effect enhances the hyperfine structure of ^2S states by about 20%. In our case, the core polarization effects could be of similar magnitude.

(ii) The electron diamagnetism, which is a consequence of the orbital motion of the carriers in the magnetic field, gives rise to a diamagnetic Knight shift.[48] The ratio of this shift to the contact shift studied in Sec. III is approximately given, in the case of the valence band,[49] by

$$\frac{1}{3} \frac{(m/m^*)^2}{\frac{1}{3}(g_\| + 2g_\perp)} \frac{4\pi}{(\cos^2\theta^+)\langle R|\Delta(r)|R\rangle\Omega} .$$

This quantity is equal to 10^{-3} for PbSe and PbTe and leads to a negligible diamagnetic shift.

(iii) Our calculation of the Knight shift involved band-edge wave functions. In fact, the carriers responsible for the shift have finite wave vectors $\vec{k}$ (with $\vec{k}$ referred to an L point). In particular, because of the $\vec{k} \cdot \vec{p}$ interaction, the conduction-band states are no longer pure odd (p, f) states, but admix a small s component from the valence band.[50] This s character which appears in the conduction band corresponds to a nonzero density of probability around the lead nuclei, and gives rise to a contact Knight shift. The $\vec{k} \cdot \vec{p}$ perturbation theory shows that the value of this density of probability is smaller than the valence-band-edge value by a factor E_F/E_G, where E_G is the energy gap. Since E_F goes like $N_c^{2/3}$, the related Knight shift is proportional to the total number N_c of carriers, and not to $N_c^{1/3}$. As appears on Fig. 1, the Knight shift in the N-type lead salts exhibits a linear dependence as a function of $N_c^{1/3}$. Also the ratio E_F/E_G is too small to account for the magnitude of the shift in samples with low carrier concentration. This result can be transposed to the case of the Knight shift in the valence band. In this band, the $\vec{k} \cdot \vec{p}$ interaction admixes the p-like conduction states with the s-like valence states. This p-like character gives rise to orbital and dipolar Knight shifts which are also much smaller than the contact Knight shift. The effect on the Knight shift of the admixture of neighboring bands is thus negligible, as long as we limit ourselves to a low carrier concentration ($N_c \approx 10^{18}$ cm^{-3}). For higher concentrations this effect should be taken into account. The resulting modification of the hyperfine structure is one of the causes of a nonparabolic behavior of the Knight shift (deviation from the $N_c^{1/3}$ dependence). In fact, at high concentration the problem is much more involved. First, the hyperfine-

coupling constant is actually a function of a wave vector $\vec{k}$. Second, one should sum the contribution to the Knight shift of the different points of the actual Fermi surface which is nonellipsoidal.

For these three reasons we believe that the previous attempts to interpret the nonparabolic behavior of the Knight shift in P-type PbTe are oversimplified.[9,15] The apparent parabolic behavior of the Knight shift in PbSe must be due to a compensation of various nonparabolic effects.

VII. KNIGHT SHIFT OF TELLURIUM IN PbTe

We have shown in Sec. V that p-like electrons can give rise to a large Knight shift, comparable to the shift created by s-like electrons. The example of the shift of Te^{125} in N-type PbTe,[9,10,15] which is about 20 times smaller than that of Pb^{207}, shows clearly that consideration of the symmetry of the wave function around the nucleus is quite insufficient to foresee even an order of magnitude of the Knight shift. The atomic hyperfine-coupling constants of Pb and Te are of the same order of magnitude[51] and only a detailed analysis of the combinations of the g factors arising in our theory can explain this apparent anomaly.

Since the conduction band is s-like around the tellurium site, the contact shift is the dominant term; it contains the term $(g_{\parallel}^c + 2g_{\perp}^c)$, the value of which is 27.5 ± 4, whereas for lead, the orbital and dipolar shift contains the term $(g_{\parallel}^c - 2g_{\perp}^c)$ with a value of 87.5 ± 4 (see Table III). Furthermore, the conduction-band wave function is mainly located around the lead site and in the plane-wave region between atoms (in an APW model) so that a conduction electron spends only 12.4% of its time in the tellurium APW sphere.[3] These two reasons explain the smallness of the observed shift of Te^{125} in N-type PbTe.

In P-type PbTe, the influence of the g factors is even larger: In the valence band the value of the quantity $(g_{\parallel}^v - 2g_{\perp}^v)$ is 8 ± 5, whereas the value of the correct combination for lead $(g_{\parallel}^v + 2g_{\perp}^v)$ is 88 ± 5.

These qualitative arguments do not pretend to explain the exact values of the Knight shift of Te^{125} in N- or P-type PbTe but they justify its smallness and illustrate the necessity of the theory developed

in the present paper to understand this apparent contradiction.

VIII. CONCLUSION

We have presented a detailed account of the very large Knight shifts of Pb^{207} observed in the lead salts. In the present knowledge of the band structure, our theory and experimental results are in quantitative agreement for the valence band and in semiquantitative agreement for the conduction band (within a factor of 2). To obtain a better agreement, we would need a more precise knowledge of the values of the band parameters such as effective masses and g factors, and a direct computation of the conduction band wave function near the lead nuclei.

The study of the lead salts shows that in materials with large atomic number, the relativistic effects play an important role for the hyperfine structure. This is also the case of the dipolar field, which is large, even in cubic crystals, because of the spin-orbit interaction. As exemplified by the study of the shift of Pb^{207} and Te^{125} in both N- and P-type PbTe, depending on the various contributions to the hyperfine interaction, the Knight shifts involve different linear combination of the g factors. This has a profound effect on the magnitude of the shifts.

Finally, we have explained why p-like levels can create very large Knight shifts. Consequently a large shift must not be taken as experimental evidence of the s-like character of the wave function.

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