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Knight-Shift Anisotropy in Cubic Crystals*†

A. Rubens B. deCastro‡ and R. T. Schumacher
Department of Physics, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213
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A general calculation of the Knight shift in metals with spin-orbit interaction is presented. For terms involving the electron-nuclear contact interaction the spin-orbit interaction was included to second order and is shown to result in anisotropy of the Knight shift even in cubic metals. Our formalism for electron-nuclear dipole interaction with spin-orbit coupling also yields anisotropy in cubic metals and reduces in the tight-binding limit to the result previously obtained by Boon. Nuclear-magnetic-resonance measurements on single crystals of the cubic metals lead and platinum have shown the anisotropy in our samples to be less than, respectively, 3.4 and 1.5×10^{-4} of the isotropic shifts. The upper limit for lead is half the anisotropy in lead reported by Schratter and Williams.

I. INTRODUCTION

The Knight shift is normally taken to be magnetic shielding of a nucleus in a metal by the surrounding electronic magnetic moments and their orbital currents. If $\Delta\vec{B}$ is the internal field seen by the nucleus, and the external field $\vec{B}_0$ is applied in the z direction, then the Knight shift K is

$$K=\Delta B_z/B_0 .$$

In a (hypothetical) noncrystalline, isotropic substance, the direction of the internal field $\Delta\vec{B}$ is the same as the direction of the applied field $\vec{B}_0$. In a real metal the nature of the electronic wave functions is determined by the periodic crystalline potential; the orbital currents and, if there is spin-orbit coupling, the spin direction are sensitive to the nature of the crystal potential, and consequently, in general, $\Delta\vec{B}$ is not parallel to $\vec{B}_0$. The consequences are familiar in noncubic metals, where the Knight shift has long been known to be anisotropic. It is less obvious that the Knight shift can be anisotropic in cubic metals as well. That it can was first (to our knowledge) pointed out by Boon,[1] who displayed a formula for the anisotropic part of the shift due to the combined effects of

spin-orbit coupling, which allows the spin to sense the lattice symmetry, and the nucleus-electron dipole-dipole interaction.

In this paper we investigate the problem theoretically in rather more general terms than Boon, including the contact as well as the dipole-dipole part of the nuclear-electron-spin interaction, and derive a general formula for the Knight shift in the presence of spin-orbit, dipole-dipole, and electron-nuclear contact interactions. We verify that our expression involving the dipole-dipole part of the electron-nuclear interaction reduces to Boon's in the tight-binding limit, and confirm the formula derived phenomenologically by Weinert and Schumacher[2] for the anisotropy of the Knight shift from the spin-orbit and contact interactions for noncubic metals. We have also conducted a careful search for Knight-shift anisotropy in single crystals of the heavy cubic nuclear-spin-$\frac{1}{2}$ metals lead and platinum. In both cases no anisotropy was observed, and an experimental upper limit of $K_{an} \leq (3.4\times10^{-4})K_{iso}$ for lead and $K_{an} \leq (1.5\times10^{-4})K_{iso}$ for platinum. The result for lead is in disagreement with the recent experiment of Schratter and Williams.[3]

For readers who wish to grasp the essential physical nature of the theoretical result without contemplating the details of the calculations, we conclude this introduction with a summary of the theoretical calculation, Sec. II, from which it is hoped the reader can perceive the origins of the possible anisotropy. The normal derivation of the Knight shift[4] passes fairly rapidly to the stage where one can write the electron-nuclear interaction between a nucleus and an electron in Bloch state $\psi_{n\vec{k}}$, where n is the band index and $\vec{k}$ the electron wave vector, in terms of the direction cosines λ_α ($\alpha = x, y, z$) of the internal field $\Delta\vec{B}$ produced by the electrons at the nucleus:

$$\Delta B_\gamma = \tfrac{8}{3}\pi\mu_N^2 |\vec{B}| \lambda_\gamma \left(\sum_{\alpha\beta} \lambda_\alpha\lambda_\beta G_{\alpha\beta}(n,\vec{k}) \right)^{1/2} |\psi_{n\vec{k}}(0)|^2 . \tag{1.1}$$

The only aspect of (1.1) that is unfamiliar from the completely elementary treatment is the radical, which is

$$g(n,\vec{k}) = \left(\sum_{\alpha\beta} \lambda_\alpha\lambda_\beta G_{\alpha\beta}(n,\vec{k}) \right)^{1/2} , \tag{1.2}$$

the g factor for the Bloch electronic state $\psi_{n\vec{k}}$. That G, a symmetric second-rank tensor, is important for our final results. It can be written

$$G_{\alpha\beta}(n,\vec{k}) = \delta_{\alpha\beta} + \Delta_{\alpha\beta}(n,\vec{k}) + \cdots , \tag{1.3}$$

where $\Delta_{\alpha\beta}(n,\vec{k})$ is a symmetric second-rank tensor which depends on the spin-orbit and orbit-field interactions, and is very similar in form to the unfamiliar expression for the g shift in paramagnetic ions. The γth component of the field produced by all the electrons is obtained from (1.1) by summing over the band index n and the wave vector $\vec{k}$, after introducing the thermal average via the Fermi function $f(\epsilon)$:

$$\Delta B_\gamma = \tfrac{8}{3}\pi |\vec{B}| \lambda_\gamma \mu_e^2 \sum_{n\vec{k}} \left(\frac{df}{d\epsilon}\right)_{E_n(\vec{k})} |\psi_{n\vec{k}}(0)|^2 \times \left(1 + \sum_{\alpha\beta} \lambda_\alpha\lambda_\beta \Delta_{\alpha\beta}(n,\vec{k})\right)^{1/2} . \tag{1.4}$$

The nuclear-spin Hamiltonian is

$$\mathcal{H}_N = -\mu_N \textstyle\sum_\gamma I_\gamma (B_\gamma + \Delta B_\gamma)$$
$$= -\mu_N |\vec{B}| \textstyle\sum_\gamma I_\gamma \lambda_\gamma [1 + K_{an}(\vec{\lambda})] , \tag{1.5}$$

where

$$K_{an}(\vec{\lambda}) = \tfrac{8}{3}\pi\mu_e^2 \sum_{n\vec{k}} \left(\frac{df}{d\epsilon}\right)_{E_n(\vec{k})} |\psi_{n\vec{k}}(0)|^2 \times \left(1 + \sum_{\alpha\beta} \lambda_\alpha\lambda_\beta G_{\alpha\beta}(n,\vec{k}) \right)^{1/2} \tag{1.6}$$

is the Knight shift. We have explicitly indicated its dependence on the direction of the applied field with direction cosines λ_x, λ_y, and λ_z with respect to the (arbitrary) coordinate system fixed in the laboratory.

It remains to be seen that $K_{an}(\vec{\lambda})$ leads, even in principle, to anisotropy in a cubic metal. To show that it does, expand the radical so that (1.6) may be written

$$K_{an}(\vec{\lambda}) = A + \sum_{\alpha\beta} B_{\alpha\beta}\lambda_\alpha\lambda_\beta + \sum_{\alpha\beta\gamma\eta} C_{\alpha\beta\gamma\eta}\lambda_\alpha\lambda_\beta\lambda_\gamma\lambda_\eta + \cdots , \tag{1.7}$$

where

$$A = \tfrac{8}{3}\pi\mu_e^2 \sum_{n\vec{k}} \left(\frac{df}{d\epsilon}\right)_{E_n(\vec{k})} |\psi_{n\vec{k}}(0)|^2 \tag{1.8}$$

is the ordinary isotropic Knight shift,

$$B_{\alpha\beta} = \tfrac{4}{3}\pi\mu_e^2 \sum_{n\vec{k}} \left(\frac{df}{d\epsilon}\right)_{E_n(\vec{k})} |\psi_{n\vec{k}}(0)|^2 \Delta_{\alpha\beta}(n,\vec{k}) \tag{1.9}$$

is a term which vanishes in cubic symmetry since $\beta_{\alpha\beta}$ is a second-rank tensor, and

$$C_{\alpha\beta\gamma\eta} = -\tfrac{1}{3}\pi\mu_e^2 \sum_{n\vec{k}} \left(\frac{df}{d\epsilon}\right)_{E_n(\vec{k})} |\psi_{n\vec{k}}(0)|^2 \Delta_{\alpha\beta}(n\vec{k})\Delta_{\gamma\eta}(n\vec{k}) \tag{1.10}$$

is a fourth-rank tensor whose components do not all vanish in cubic symmetry. In fact, three nonvanishing components of $C_{\alpha\beta\gamma\eta}$ are allowed, just as in elasticity theory (for the same reasons, of course): $C_{XXXX} = C_{11}$, $C_{XXYY} = C_{12}$, and $C_{XYXY} = C_{44}$, where the subscripts refer now to the cubic axes. In cubic symmetry, then, (1.7) reduces to

$$K_{\rm an}(\vec{\lambda}) = (A + C_{12} + 2C_{44}) + (\lambda_X^4 + \lambda_Y^4 + \lambda_Z^4) \times (C_{11} - C_{12} - 2C_{44}) \ . \quad (1.11)$$

The angular dependence in (1.11) is the expected dependence in cubic symmetry based on lowest-order Kubic harmonics. Higher-order terms in the expansion of the square root would give tensors of sixth, eighth, etc., rank, with angular dependence given by higher-order Kubic harmonics.

Expressions for all of the above quantities will be derived in Sec. II. However, to help the reader fix in his mind the magnitudes of the quantities involved, we note that the ordinary g shift δg, detected in conduction-electron spin resonance (CESR), is [from (1.2) and (1.3)],

$$\delta g_{zz} \cong \sum_{n\vec{k}} \left(\frac{df}{d\epsilon}\right)_{E_n(\vec{k})} \Delta_{zz}(n\vec{k}) \ ,$$

where the sum over n and $\vec{k}$ provides in effect an average of $\delta g(n,\vec{k})$ over the Fermi surface, the CESR-measured quantity. The sum in (1.10) is similar to the sum in (1.8), the expression for the isotropic shift, with the additional weighting proportional to $[\delta g(n,\vec{k})]^2$. If one makes the guess that the average over the Fermi surface of the product of $|\psi_{n\vec{k}}(0)|^2[\delta g(n,\vec{k})]^2$ is similar in magnitude to the product of the averages of $|\psi_{n\vec{k}}(0)|^2$ and $\delta g(n,\vec{k})$, then we crudely estimate the amplitude of the angular dependence, $K_{\rm an}$, to be

$$K_{\rm an} \approx \tfrac{1}{8} A(\delta g)^2 \ . \quad (1.12)$$

Hence the ratio of the anisotropic to the isotropic Knight shift might well be $(\delta g)^2$. The heaviest metals for which δg has been observed are Cu and Cs, for both of which $\delta g \approx 0.02$. Hence we expect the anisotropic shift to be about 10^{-4} times the isotropic shift. Although this number is somewhat smaller than the upper limit that we were able to place on $K_{\rm an}$, it does not seem *apriori* undetectable since we also used metals with larger spin-orbit coupling than Cu or Cs, namely, lead and platinum, and the estimate (1.12) is very crude.

In Appendix B we rederive Boon's result for the anisotropy from the spin-orbit dipole-dipole mechanism. A crude estimate in the same spirit as above of the size of the anisotropy leads to $K_{\rm an} \approx 10^{-3} K_{\rm iso}$ for a metal, such as lead and platinum, for which the conduction electrons at the Fermi surface have substantial p character. The reported result of Schratter and Williams[3] for lead falls within the order of magnitude of these estimates.

II. THEORY

A. Introduction

We intend to show that it is possible to write an effective nuclear Hamiltonian in the form

$$\mathcal{H}_N = \mu_N \sum_\alpha B_\alpha I_\alpha + \sum_{\alpha\beta} B_\alpha K_{\alpha\beta} I_\alpha + \sum_{\alpha\beta\gamma\eta} B_\alpha B_\beta B_\gamma K_{\alpha\beta\gamma\eta} I_\eta + \cdots \ , \quad (2.1)$$

where B_α are components of a static magnetic field, the K's are sets of quantities transforming as tensors under certain restricted circumstances to be discussed later, I_α are (nuclear) spin operators, and $\mu_N = \gamma_N \hbar$ is the nuclear magnetic moment. The coordinate system is arbitrary but fixed in the laboratory.

For $I = \frac{1}{2}$ (the only case of interest for us), $\mathcal{H}_N$ is a 2×2 matrix,

$$\mathcal{H}_N = \begin{pmatrix} a_z & a_x - ia_x \\ a_x + ia_y & -a_z \end{pmatrix} \ ,$$

and the eigenvalues are $\pm E$, with E^2 given by

$$E^2 = a_x^2 + a_y^2 + a_z^2 \quad (2.2)$$

and

$$a_j = \mu_N B_j + \sum_\alpha B_\alpha K_{\alpha j} + \sum_{\alpha\beta\gamma} B_\alpha B_\beta B_\gamma K_{\alpha\beta\gamma j} + \cdots \ . \quad (2.3)$$

The K's will be interpreted as contributions to the various NMR shifts, and experimentally they are found to be small, of order 10^{-2} or less. Neglecting all but the contributions linear in K, the energies can be written

$$E = \pm \mu_N |\vec{B}| \left[1 + \frac{1}{\mu_N} \left(\sum_{\alpha\beta} \lambda_\alpha \lambda_\beta K_{\alpha\beta} + \sum_{\alpha\beta\gamma\eta} \lambda_\alpha \lambda_\beta \lambda_\gamma \lambda_\eta K_{\alpha\beta\gamma\eta} + \cdots \right) \right] . \quad (2.4)$$

The terms in $K_{\alpha\beta}$, $K_{\alpha\beta\gamma\eta}$, ... in (2.1) have the significance of internal fields that add to the applied external field $\vec{B}$. The fractional shift $K_{\rm an}(\vec{\lambda})$ in the Zeeman energy is

$$K_{\rm an}(\vec{\lambda}) = \frac{1}{\mu_N} \left(\sum_{\alpha\beta} \lambda_\alpha \lambda_\beta K_{\alpha\beta} + \sum_{\alpha\beta\gamma\eta} \lambda_\alpha \lambda_\beta \lambda_\gamma \lambda_\eta |\vec{B}|^2 K_{\alpha\beta\gamma\eta} + \cdots \right) \quad (2.5)$$

and will in general be anisotropic. The quantities $K_{\alpha\beta}$, $K_{\alpha\beta\gamma\eta}$, ... do not transform as tensors under rotations of the crystalline frame with respect to the magnetic field $\vec{B}$, but it will be shown that $K_{\rm an}(\vec{\lambda})$ *is expressible, to zero order in* $|\vec{B}|$, in terms of the direction cosines λ_α of $\vec{B}$ and certain tensors of even rank:

$$K_{\rm an}(\vec{\lambda}) = A + \sum_{\alpha\beta} \lambda_\alpha \lambda_\beta B_{\alpha\beta} + \sum_{\alpha\beta\gamma\eta} \lambda_\alpha \lambda_\beta \lambda_\gamma \lambda_\eta C_{\alpha\beta\gamma\eta} + \cdots \ . \quad (2.6)$$

The symmetry properties of $B_{\alpha\beta}$ and $C_{\alpha\beta\gamma\eta}$ can

be studied by using the law for transformation of tensors under change of coordinate axes and the following formal relations,[5] valid for any operation R belonging to the symmetry group of the electronic Hamiltonian:

$$B_{\alpha\beta} = \sum_{\alpha'\beta'} R_{\alpha\alpha'} R_{\beta\beta'} B_{\alpha'\beta'} ,$$

$$C_{\alpha\beta\gamma\eta} = \sum_{\alpha'\beta'\gamma'\eta'} R_{\alpha\alpha'} R_{\beta\beta'} R_{\gamma\gamma'} R_{\eta\eta'} C_{\alpha'\beta'\gamma'\eta'} . \quad (2.7)$$

These relations show, for example, that in cubic symmetry $B_{\alpha\beta} = b\,\delta_{\alpha\beta}$, while there are only three independent coefficients $C_{\alpha\beta\gamma\eta}$.

B. Derivation of $\mathcal{H}_N$ in Independent-Electron Approximation

The Hamiltonian for a system of independent electrons interacting with just one nuclear spin can be written

$$\mathcal{H}_N = \sum_j \mathcal{H}_{\text{elec}}^{(j)} + \mu_N \sum_\alpha B_\alpha I_\alpha + \mu_N \sum_\alpha D_\alpha I_\alpha , \quad (2.8)$$

where j runs over the electrons, $\mathcal{H}_{\text{elec}}^{(j)}$ is the Hamiltonian for the jth electron (including spin-orbit coupling and interactions with an applied magnetic field $\vec{B}$), I_α are (nuclear) spin operators, μ_N is the nuclear magnetic moment, and D_α are the components of an "internal field" operator originating in the "contact" and dipolar interactions between nuclear and electronic spins. They are given by

$$D_\alpha = \sum_j \left(\mathcal{J}(\vec{r}^{(j)}) \sigma_\alpha + \tfrac{1}{2}\mu_e \sum_\beta \sigma_\beta \mathcal{R}_{\beta\alpha}^{(j)} \right) , \quad (2.9)$$

$$\mathcal{R}_{\beta\alpha}^{(j)} = [3 r_\alpha^{(j)} r_\beta^{(j)} - \delta_{\alpha\beta} (r^{(j)})^2] / (r^{(j)})^5 . \quad (2.10)$$

Here $\vec{r}^{(j)}$ is the vector joining the nucleus to the jth electron, and σ_α are the Pauli matrices.

The two last terms in (2.8) lead to a correction in the energy levels of the electronic system of order E_{hf}^2/E_F, where E_{hf} and E_F are the hyperfine and Fermi energies, respectively. It is an excellent approximation to consider the nuclear system as "driven" by the electronic motions. Thus we compute the expectation value of the hyperfine coupling terms in the eigenstates of $\mathcal{H}_{\text{elec}}$ and take the thermal average. For a system of fermions the result is given in terms of the Fermi function. The effective nuclear Hamiltonian resulting from the thermal averaging of the hyperfine coupling terms is

$$\mathcal{H}_N = \mu_N \sum_\alpha B_\alpha I_\alpha + \mu_N \sum_\alpha \left(\sum_{q\rho} \langle q\rho | D_\alpha | q\rho \rangle f(\epsilon_{q\rho}) \right) I_\alpha , \quad (2.11)$$

where $\mathcal{H}_{\text{elec}} |q\rho\rangle = \epsilon_{q\rho} |q\rho\rangle$, ρ is a spin index, and q stands for any other indices required to specify the state. $f(\epsilon) \equiv (e^{(\epsilon - E_F)/k_B T} + 1)^{-1}$ is the Fermi function.

The nature of the eigenstates $|q\rho\rangle$ and eigenvalues $\epsilon_{q\rho}$ for an electron subject to a uniform magnetic field $\vec{B}$ and a periodic electrostatic potential has been investigated by many researchers. The result emerging from the work of Kohn,[6] Blount,[7,8] and Roth[9] on Bloch electrons in a magnetic field is that both $|q\rho\rangle$ and $\epsilon_{q\rho}$ can be developed in power series of $|\vec{B}|$. It has been proved that those series are convergent in the limit $|\vec{B}| \to 0$; it is found that in practice even for moderately large values of $|\vec{B}|$ they are useful. In particular, the splitting of the Kramers degeneracy is described by a g-factor tensor $G_{\alpha\beta}(n, \vec{k})$ which has been reviewed by Yafet,[10] and more recently by de Graaf and Overhauser.[11] The electronic energies to first order in $|\vec{B}|$ are

$$\epsilon_{q\rho} = E_q \pm \mu_e |\vec{B}| \left(\sum_{\alpha\beta} \lambda_\alpha \lambda_\beta G_{\alpha\beta}(n, \vec{\mathfrak{k}}) \right)^{1/2} , \quad (2.12)$$

where E_q is complicated but does not depend on the spin index ρ; $\vec{\mathfrak{k}} = \vec{k} + (e/\hbar c)\vec{A}(\vec{R})$, $\vec{A}(\vec{R})$ is the vector potential, and $\vec{R}$ is a lattice vector.

We will need the expansion of $G_{\alpha\beta}(n, \vec{\mathfrak{k}})$ to first order in spin-orbit coupling; an expression has been given by Roth,[12] valid for Ge and Si. We show in Appendix A that it is possible to write for the *symmetric* part $G'_{\alpha\beta}$ of $G_{\alpha\beta}$,

$$G'_{\alpha\beta} = \delta_{\alpha\beta} + \Delta_{\alpha\beta}(n, \vec{k}) , \quad (2.13)$$

where $\Delta_{\alpha\beta}$ is first order in spin-orbit coupling.

Ignoring the delicate question of just where the power-series expansions in $|\vec{B}|$ for $|q\rho\rangle$ and $\epsilon_{q\rho}$ converge, it is seen that the large parentheses in (2.11) enclose a power series in $|\vec{B}|$. If this is to be invariant under spatial rotations (applied to *both* the magnetic field and the crystal), the form given in (2.1) is required. Furthermore, all K's with an odd number of indices will be missing, as (2.1) describes a reversible microscopic process, and must therefore be invariant under the operation of time reversal. This concludes our justification for the structure of (2.1).

We will now restrict ourselves to the calculation of the contributions to $K_{\text{an}}(\vec{\lambda})$ independent of $|\vec{B}|$, which require knowledge of the contributions linear in $|\vec{B}|$ to the thermal average of D_α.

The quantity needed is

$$\sum_{q\rho} \langle q\rho | D_\alpha | q\rho \rangle f(\epsilon_{q\rho}) . \quad (2.14)$$

From the definition (2.9), D_α is linear in the spin operators σ_α; thus

$$\sum_\rho \langle q\rho | D_\alpha | q\rho \rangle = 0 \quad (2.15)$$

as a consequence of the angular momentum operators being traceless, quite independently of the detailed nature of $|q\rho\rangle$.

Expanding $f(\epsilon_{q\rho})$ about $E_n(k)$ and using (2.15), we obtain, to first order in $|\vec{B}|$,

$$\sum_{q\rho}\langle q\rho\,|D_\alpha\,|q\rho\rangle f(\epsilon_{q\rho}) \cong |\vec{B}|\sum_{q\rho}\langle q\rho\,|D_\alpha\,|q\rho\rangle \times(\pm)\,\mu_e\Big(\sum_{\gamma\eta}\lambda_\gamma\lambda_\eta G_{\gamma\eta}(n\vec{l})\Big)^{1/2}\left(\frac{df}{d\epsilon}\right)_{E_n(\vec{l})} . \quad (2.16)$$

This is already first order in $|\vec{B}|$; so we can replace $\vec{l}$ with $\vec{k}$ and $|q\rho\rangle$ with $|n\vec{k}\rho\rangle$, where we understand that $|n\vec{k}\rho\rangle = \lim|q\rho\rangle$ as $B\to 0$.

The thermal average is now written in terms of zero-order quantities only:

$$\sum_{q\rho}\langle q\rho\,|D_\alpha\,|q\rho\rangle f(\epsilon_{q\rho}) \cong |B|\sum_{n\vec{k}\rho}\langle n\vec{k}\rho\,|D_\alpha\,|n\vec{k}\rho\rangle \times(\pm)\,\mu_e\Big(\sum_{\gamma\eta}\lambda_\gamma\lambda_\eta G_{\gamma\eta}(n\vec{k})\Big)^{1/2}\left(\frac{df}{d\epsilon}\right)_{E_n(\vec{k})} . \quad (2.17)$$

Inserting (2.17) in (2.11) and comparing with (2.1), we get

$$\sum_\beta \lambda_\beta K_{\beta\alpha} = \sum_{n\vec{k}\rho}(\pm)\mu_e\Big(\sum_{\gamma\eta}\lambda_\gamma\lambda_\eta G_{\gamma\eta}(n\vec{k})\Big)^{1/2}\left(\frac{df}{d\epsilon}\right)_{E_n(\vec{k})} \times\Big(\mu_N\langle n\vec{k}\rho\,|\mathcal{J}(\vec{r})\sigma_\alpha|n\vec{k}\rho\rangle + \tfrac{1}{2}\mu_e\mu_N\langle n\vec{k}\rho\,|\sum_\eta\sigma_\eta\mathfrak{R}_{\eta\alpha}\,|n\vec{k}\rho\rangle\Big) . \quad (2.18)$$

We calculate the contributions to (2.18) arising from the dipolar electron-nucleus interactions in Appendix B.

C. Calculation of Contribution of Contact Interaction to $K_{an}(\vec{\lambda})$

We take

$$\mathcal{J}(\vec{r}) = \mathcal{J}\,\delta(\vec{r}) = \tfrac{4}{3}\pi\,\mu_e\,\delta(\vec{r}) . \quad (2.19)$$

It is not possible to proceed without separating the spin and spatial degrees of freedom. Thus we write

$$\begin{aligned}
&\mathcal{H}_{\rm elec}\,|n\vec{k}\rho\rangle = E_n(\vec{k})\,|n\vec{k}\rho\rangle ,\\
&\mathcal{H}'_{\rm elec}\,|ps\rangle = \epsilon_p\,|ps\rangle ,\\
&\mathcal{H}_{\rm elec} = \mathcal{H}'_{\rm elec} + \tfrac{1}{2}\vec{\sigma}\cdot\vec{\mathrm{N}} ,\\
&\mathcal{H}'_{\rm elec} = p^2/2m + U(\vec{r}) ,\\
&\vec{\mathrm{N}} = (\hbar^2/2m^2c^2)\vec{\nabla}U(\vec{r})\times\vec{p} .
\end{aligned} \quad (2.20)$$

The index p specifies both n and $\vec{k}$, and, of course, $|ps\rangle = |p\rangle|s\rangle$, s being a spin index.

The state $|n\vec{k}\rho\rangle$ is given, to second order in spin-orbit coupling N, by

$$|n\vec{k}\rho\rangle = |p\rho\rangle + \sum_{\substack{p's'\\ p'\neq p}}|p's'\rangle\left(\frac{\langle p's'\,|\vec{\sigma}\cdot\vec{\mathrm{N}}\,|p\rho\rangle}{2\omega_{pp'}} - \frac{\langle p's'\,|\vec{\sigma}\cdot\vec{\mathrm{N}}\,|p\rho\rangle\langle p\rho\,|\vec{\sigma}\cdot\vec{\mathrm{N}}\,|p\rho\rangle}{4\omega_{pp'}^2}\right) + \sum_{\substack{p's'p''s''\\ p',p''\neq p}}|p's'\rangle\frac{\langle p's'\,|\vec{\sigma}\cdot\vec{\mathrm{N}}\,|p''s''\rangle\langle p's''\,|\vec{\sigma}\cdot\vec{\mathrm{N}}\,|p\rho\rangle}{4\omega_{pp'}\omega_{pp''}} , \quad (2.21)$$

with

$$\omega_{pp'} \equiv \epsilon_p - \epsilon_{p'} . \quad (2.22)$$

Examining the second-order wave function, Eq. (2.21), we see that there is one term involving $\langle p\rho\,|\vec{\sigma}\cdot\vec{\mathrm{N}}\,|p\rho\rangle$. This vanishes because N_β is Hermitian for Bloch states, and purely imaginary. Thus $N_{\beta_{pp'}} = 0$. Also, we observe that $N_{\beta_{pp'}}$ is diagonal in $\vec{k}$ owing to the translational invariance of $\vec{\mathrm{N}}$.[1]

The choice of spin states $|\rho\rangle$ is not completely arbitrary. We defined $|n\vec{k}\rho\rangle$ as $\lim|q\rho\rangle$ as $B\to 0$; if $\vec{B}\neq 0$, the spin is quantized along the field in the absence of spin-orbit coupling, and thus $\langle s\,|\sigma_\alpha\,|s\rangle = \pm\lambda_\alpha$ depending on whether $s = \uparrow$ or $\downarrow$. By using $\sigma_x\sigma_y = i\sigma_z$ plus cyclic permutations, we can express the matrix element $\langle n\vec{k}\rho\,|\delta(\vec{r})\sigma_\alpha\,|n\vec{k}\rho\rangle$ as

$$\pm\lambda_\alpha|\psi_{n\vec{k}}(0)|^2 \pm i\sum_{\gamma\beta}\epsilon_{\gamma\beta\alpha}\lambda_\gamma\sum_{p'}\frac{N_{\beta_{pp'}}\psi^*_{p'}(0)\psi_p(0) - \psi^*_p(0)\psi_{p'}(0)N_{\beta_{p'p}}}{2\omega_{pp'}} \pm \sum_{\gamma\gamma'\beta\beta'}\epsilon_{\gamma\alpha\beta}\epsilon_{\gamma\gamma'\beta'}\lambda_{\gamma'}\mathcal{K}_{\beta\beta'} . \quad (2.23)$$

The result for

$$K_{\rm an}(\vec{\lambda}) = \frac{1}{\mu_N}\sum_{\alpha\beta}\lambda_\alpha\lambda_\beta K_{\alpha\beta}$$

is

$$K_{\rm an}(\vec{\lambda}) = \tfrac{8}{3}\pi\,\mu_e^2\sum_p\left(\frac{df}{d\epsilon}\right)_{E_p}\Big(\sum_{\gamma\eta}\lambda_\gamma\lambda_\eta G_{\gamma\eta}(p)\Big)^{1/2} \times\Big(|\psi_p(0)|^2 + \sum_{\beta\beta'}(\delta_{\beta\beta'} - \lambda_\beta\lambda_{\beta'})\mathcal{K}_{\beta\beta'}\Big) , \quad (2.24)$$

where $\mathcal{K}_{\beta\beta'}$ is given by

$$\mathcal{K}_{\beta\beta'}(p) = \sum_{p'p''\neq p}(4\omega_{pp'}\omega_{pp''})^{-1}[\psi^*_p(0)\psi_{p'}(0)N_{\beta_{p'p''}}N_{\beta'_{p''p}} - N_{\beta_{pp'}}\psi^*_{p'}(0)\psi_{p''}(0)N_{\beta'_{p''p}}$$

$$+N_{\beta p p'}N_{\beta' p' p''}\psi^*_{p''}(0)\psi_p(0)] \,. \quad (2.25)$$

The G-factor tensor is shown in Appendix A to have the form

$$G_{\alpha\beta}(p)=\delta_{\alpha\beta}+\Delta_{\alpha\beta}(p)+\Xi_{\alpha\beta}(p)+\cdots \,, \quad (2.26)$$

where $\Delta_{\alpha\beta}$ is first order in spin-orbit coupling and $\Xi_{\alpha\beta}$ is second order. Expanding the parenthesis containing the g-factor tensor in 2.24 to second order in spin-orbit coupling, we obtain for $K_{\rm an}(\vec{\lambda})$ the following result:

$$K_{\rm an}(\vec{\lambda})=A+\sum_{\alpha\beta}\lambda_\alpha\lambda_\beta B_{\alpha\beta}+\sum_{\alpha\beta\gamma\eta}\lambda_\alpha\lambda_\beta\lambda_\gamma\lambda_\eta C_{\alpha\beta\gamma\eta} \,,$$

$$A=\tfrac{8}{3}\pi\mu_e^2\sum_p\left(\frac{df}{d\epsilon}\right)_{E_p}\left(|\psi_p(0)|^2+\sum_\beta \mathcal{K}_{\beta\beta}(p)\right) \,,$$

$$B_{\alpha\beta}=-\tfrac{8}{3}\pi\mu_e^2\sum_p\left(\frac{df}{d\epsilon}\right)_{E_p} \quad (2.27)$$

$$\times\{-\mathcal{K}_{\alpha\beta}(p)+\tfrac{1}{2}|\psi_p(0)|^2[\Delta_{\alpha\beta}(p)+\Xi_{\alpha\beta}(p)]\} \,,$$

$$C_{\alpha\beta\gamma\eta}=\tfrac{1}{3}\pi\mu_e^2\sum_p\left(\frac{df}{d\epsilon}\right)_{E_p}|\psi_p(0)|^2\Delta_{\alpha\beta}(p)\Delta_{\gamma\eta}(p) \,.$$

The discussion up to now has been for an arbitrary frame XYZ. Now we choose for XYZ the set of principal axes for the surfaces $U(\vec{r})=$ const. In cubic symmetry $B_{\alpha\beta}=b\delta_{\alpha\beta}$ and does not contribute an anisotropy. $C_{\alpha\beta\gamma\eta}$, on the other hand, has many vanishing elements, the ones that do not vanish being of form $C_{\alpha\alpha\alpha\alpha}$ or $C_{P(\alpha\alpha\beta\beta)}$, where by $P(\alpha\alpha\beta\beta)$ we mean any of the six permutations of the four indices $\alpha\alpha\beta\beta$. Since $\Delta_{\alpha\beta}$ is symmetric, $C_{44}=C_{\alpha\beta\alpha\beta}=C_{\alpha\beta\beta\alpha}=C_{\beta\alpha\alpha\beta}=C_{\beta\alpha\beta\alpha}$, and $C_{12}=C_{\alpha\alpha\beta\beta}=C_{\beta\beta\alpha\alpha}$. Thus the 81 terms in the sum $\sum_{\alpha\beta\gamma\eta}\lambda_\alpha\lambda_\beta\lambda_\gamma\lambda_\eta C_{\alpha\beta\gamma\eta}$ reduce to

$$C_{11}(\lambda_X^4+\lambda_Y^4+\lambda_Z^4)+2(C_{12}+2C_{44})(\lambda_X^2\lambda_Y^2+\lambda_Y^2\lambda_Z^2+\lambda_Z^2\lambda_X^2) \,,$$

where $C_{11}=C_{\alpha\alpha\alpha\alpha}$ and

$$K_{\rm an}(\vec{\lambda})=\mathcal{A}^{(0)}+\mathcal{C}^{(2)}(\lambda_X^4+\lambda_Y^4+\lambda_Z^4) \,, \quad (2.28)$$

with

$$\mathcal{A}^{(0)}=\tfrac{8}{3}\pi\mu_e^2\sum_p\left(\frac{df}{d\epsilon}\right)_{E_p}|\psi_p(0)|^2 \,,$$

$$\mathcal{C}^{(2)}=C_{11}-C_{12}-2C_{44} \,. \quad (2.29)$$

Again, the superscript indicates the order in spin-orbit coupling. The isotropic contribution to $K_{\rm an}(\vec{\lambda})$ is dominated by $\mathcal{A}^{(0)}$, which is zero order in $\vec{N}$, and thus we omit the isotropic terms of higher order. $\mathcal{A}^{(0)}$ is identical to the expression obtained by Townes, Herring, and Knight.[13]

If the symmetry is lower than cubic, there are anisotropic terms to first order in spin-orbit coupling. Then we have, to lowest order in spin-orbit coupling,

$$K_{\rm an}(\vec{\lambda})=\mathcal{A}^{(0)}+\sum_{\alpha\beta}\lambda_\alpha\lambda_\beta\mathcal{B}_{\alpha\beta} \,, \quad (2.30)$$

where

$$\mathcal{B}_{\alpha\beta}=\tfrac{4}{3}\pi\mu_e^2\sum_p\left(\frac{df}{d\epsilon}\right)_{E_p}|\psi_p(0)|^2\Delta_{\alpha\beta}(p) \,. \quad (2.31)$$

The simplest case is that of tetragonal symmetry; one can show using (2.7) that $\mathcal{B}_{XX}=\mathcal{B}_{YY}$, $\mathcal{B}_{\alpha\beta}=0$ for $\alpha\neq\beta$, if Z is chosen as the axis of maximum symmetry.

$K_{\rm an}(\vec{\lambda})$ can be written as

$$K_{\rm an}(\vec{\lambda})=\tfrac{8}{3}\pi\mu_e^2\sum_n\langle g_Z(n\vec{\rm k})|\psi_{n\vec{k}}(0)|^2\rangle_{\rm Fermi\ Surface}\rho(E_F) \,, \quad (2.32)$$

where $g_Z(n,\vec{\rm k})$ is given by

$$g_Z(n\vec{\rm k})=1+\tfrac{1}{2}[(\lambda_X^2+\lambda_Y^2)\Delta_{XX}(n\vec{\rm k})+\lambda_Z^2\Delta_{ZZ}(n\vec{\rm k})] \,. \quad (2.33)$$

Expression (2.32) was first given by Weinert and Schumacher,[2] who pointed out, in connection with their work on the anisotropic Knight shift in Hg, that the contact interaction should contribute an anisotropy via the anisotropic g-factor tensor. The effect in noncubic metals is first order in spin-orbit coupling because the g factor is isotropic regardless of crystal symmetry if the spatial and spin degrees of freedom for the electrons are separable.

III. EXPERIMENT

A. Samples

a. Lead. All lead samples were spark cut from an approximately cylindrical single crystal obtained from Research Crystals, Richmond, Va. The quoted purity was 99.999%. All samples were cut to cylindrical shape, $\frac{3}{4}$ in. long, $\frac{1}{4}$ in. in diameter, with the cylindrical axis along the crystalline [100] direction. Orientation was accomplished by etching and observing flash planes. Three samples were used. The first was cut and wound with sample coil wire several years ago for preliminary investigations. Knight-shift and linewidth data were taken on it. Sample 2 was prepared in order to study the effect on linewidth of working with a freshly cleaned and etched surface. Since the angular anisotropy of the linewidth seemed not to be quite identical to sample 1, a third sample was prepared by "peeling off" the outer shell of sample 1 with a hollow cylindrical tool in the spark cutter. The new surface was chemically polished and lacquered with two thin layers of GE 7031 low-temperature varnish before the sample coil was wound on it.

b. Platinum. The platinum data were taken on two samples, both approximately cylindrical in

shape, $\frac{3}{4}$ in. long, $\frac{1}{4}$ in. in diameter. Sample 1 was oriented with the cylindrical axis along the [110] direction. It had a resistivity ratio of about 200. The second sample was similar in shape and size, but was not oriented. Its resistivity ratio was 1000, and de Haas–van Alphen signals had been observed in this sample. All Knight-shift data were obtained with sample 1; sample 2 was investigated in the hopes of clarifying the cause of the anomalously large linewidth observed in sample 1.

B. Measurements

All samples were tightly wound with approximately 150 turns of No. 38 enameled copper wire which formed the inductance of the tank circuit of a Robinson oscillator. The magnetic field at the sample was measured by monitoring the NMR frequency of Al^{27} in a reference sample consisting of Epoxy mixed with aluminum powder machined to the form of a hollow cylinder, and mounted coaxially with the lead or platinum sample. The reference-sample tank coil was wound coaxially around the outside of the reference sample and connected to a second Robinson oscillator. Because their frequencies were different by several megahertz, the reference and sample Robinson oscillators were unaffected by each other as long as their oscillation levels were comparable.

All data were taken at 1.2 °K in fields up to 18 kG provided by a Varian 3900 magnet. Field modulation and lock-in detection was used in the standard fashion, and signals were recorded either on a strip chart or in a Fabritek 1072 signal averager if extensive line-shape analysis was desired.

The initial value of the magnetic field just before initiating the field sweep of the magnetic field was measured with the reference Al^{27} NMR to ±20 mG; the frequency of the sample oscillator at the center of the lead or platinum resonances was measured with a precision of ±10 Hz and was reproducible to ±40 Hz from one field sweep to the next. The linearity and reproducibility of the field sweep was checked in separate experiments. A typical field sweep took 5 min. A reasonable estimate of our nonsystematic errors in determining the sample line center is ±50 mG.

C. Data Analysis

The principal object of the experiment may be described to be a measurement of the first moment of the NMR line as a function of the angle between the magnetic field and the crystal axis. If the line shape and the second moment are independent of that angle, it is sufficient to record the magnetic field at which some characteristic feature of the line occurs. Such was the case for platinum for which the line shape was observed always to be of the form

$$\frac{d}{dB}\ (a\chi' + b\chi'')\,, \tag{3.1}$$

where χ' and χ'' are Lorentzian functions independent of angle, as was the admixture fraction a/b which is caused by the sample being large compared to the skin depth.

In general, however, the linewidth and line shape will not be independent of the crystal–magnetic-field relative orientation; nor can one expect in a high-purity sample at low temperatures that a/b will be angularly independent, since that ratio depends in real metals on the surface impedance, which is not in general isotropic in high magnetic fields. The problem, then, is to determine for every field orientation the center of the line, i.e., the field for which $\chi'(\omega) = 0$ and $\chi''(\omega)$ is maximum, for unknown absorption line shape χ'' and unknown ratio a/b. To do this the data in derivative form were first integrated using the Fabritek internal, "hard-wired" integration routine; they are then in the form

$$\mathfrak{D}(\omega) = a\chi'(\omega) + b\chi''(\omega)\,. \tag{3.2}$$

Next we evaluate the integral

$$\mathcal{T}(\omega) = \frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{\infty}\frac{\mathfrak{D}(\omega')\,d\omega'}{\omega' - \omega}\,. \tag{3.3}$$

Since χ' and χ'' are the real and imaginary parts of a complex susceptibility function χ, they obey the Kramers–Kronig dispersion relations. Consequently,

$$\mathcal{T}(\omega) = b\chi'(\omega) - a\chi''(\omega)\,. \tag{3.4}$$

Since χ'' is symmetric and χ' antisymmetric about the resonance frequency, we can integrate (3.2) and (3.4) to find

$$-\frac{a}{b} = \frac{\int \mathfrak{D}(\omega)\,d\omega}{\int \mathcal{T}(\omega)\,d\omega}\,.$$

In our experiments the Kramers–Kronig transform of the integrated experimental data was done by a Digital Equipment Corp. PDP-8I computer attached to the signal averager. Figure 1 shows (1) the integrated NMR signal for Pt, (2) the Kramers–Kronig transform of (1), and (3) the symmetric and antisymmetric parts of (1). Figure 2 shows the same quantities for lead. Both figures represent a single sweep recorded in 512 channels of the signal averager. The line center, as determined by the maximum of χ'' and/or the zero crossing of χ', could reproducibly be determined to ±1 channel (±50 mG) by this procedure.

IV. RESULTS AND DISCUSSION

A. Knight Shifts

a. Lead. The isotropic Knight shift for lead was measured to be $K_{iso} = (1.1994 \pm 0.0003)\%$ at

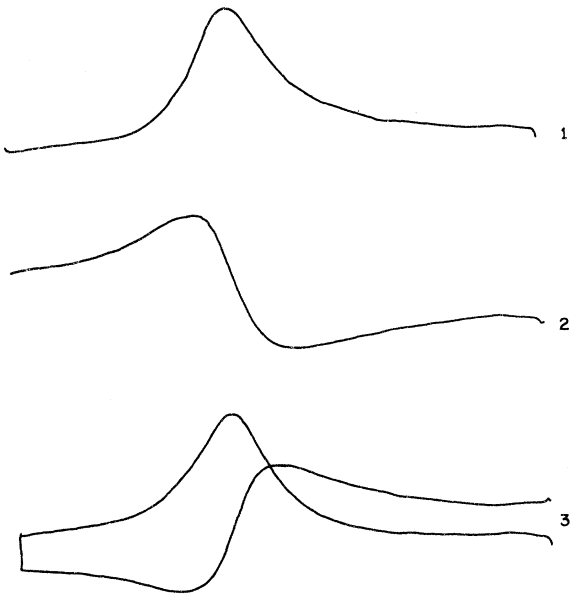

FIG. 1. (1) Integrated NMR signal for Pt. (2) Kramers–Kronig transform of (1). (3) Symmetric and antisymmetric parts of (1). Total sweep 35 G.

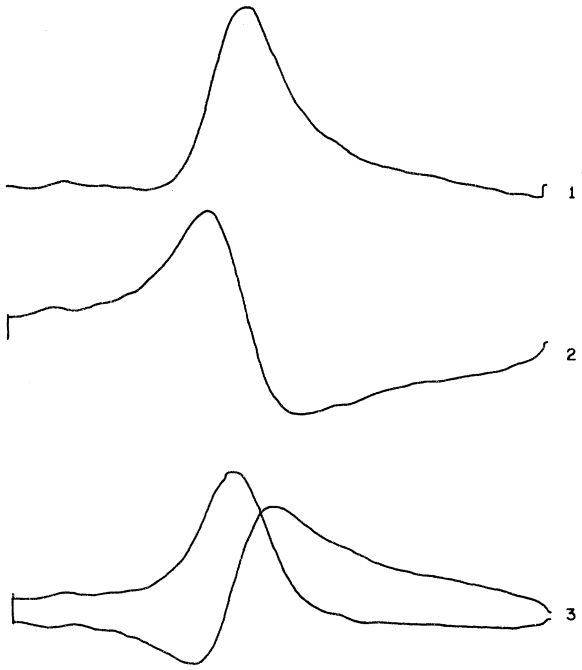

FIG. 2. (1) Integrated NMR signal for Pb. (2) Kramers–Kronig transform of (1). (3) Symmetric and antisymmetric parts of (1). Total sweep 25 G.

18 kG and 1.2°K. The implied accuracy of the measurement is relative, not absolute, and the numbers were obtained using the following constants:

$$(\gamma/2\pi)_{Pb} = 0.8899 \text{ kHz/G},$$

$$(\gamma/2\pi)_{Al} = 1.1094 \times (1 + 0.0016) \text{ kHz/G}.$$

The effective moment of Al^{27} was corrected assuming a 0.16% Knight shift in Al metal. Figure 3 shows the measured Knight shift as a function of magnetic field orientation for 19 angles in the (100) plane. The rms deviation of the 19 points

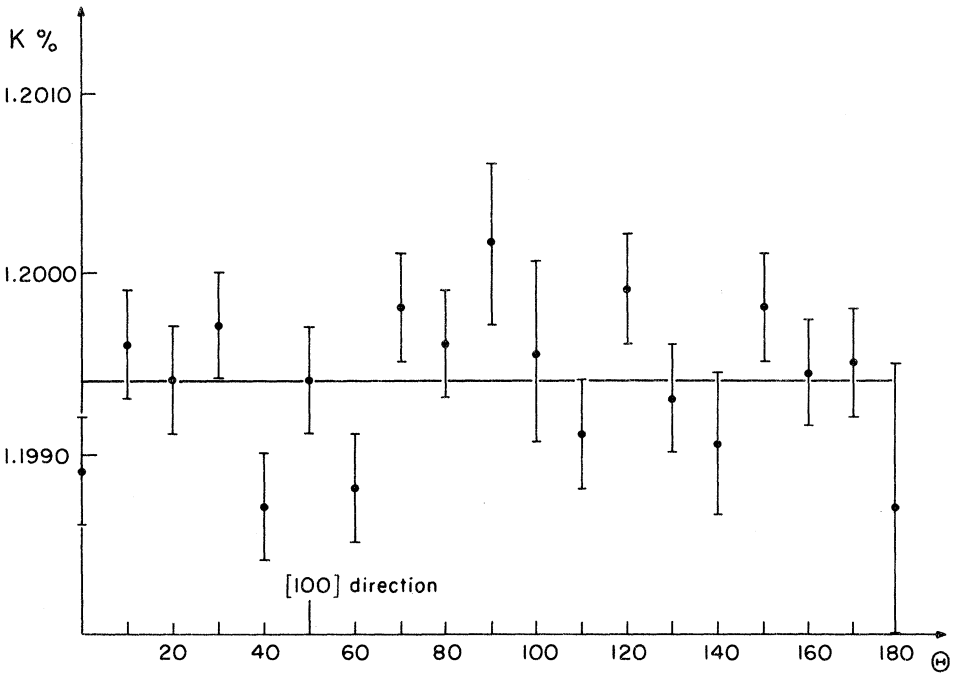

FIG. 3. Measured Knight shift in lead as a function of magnetic field orientation in the (100) plane.

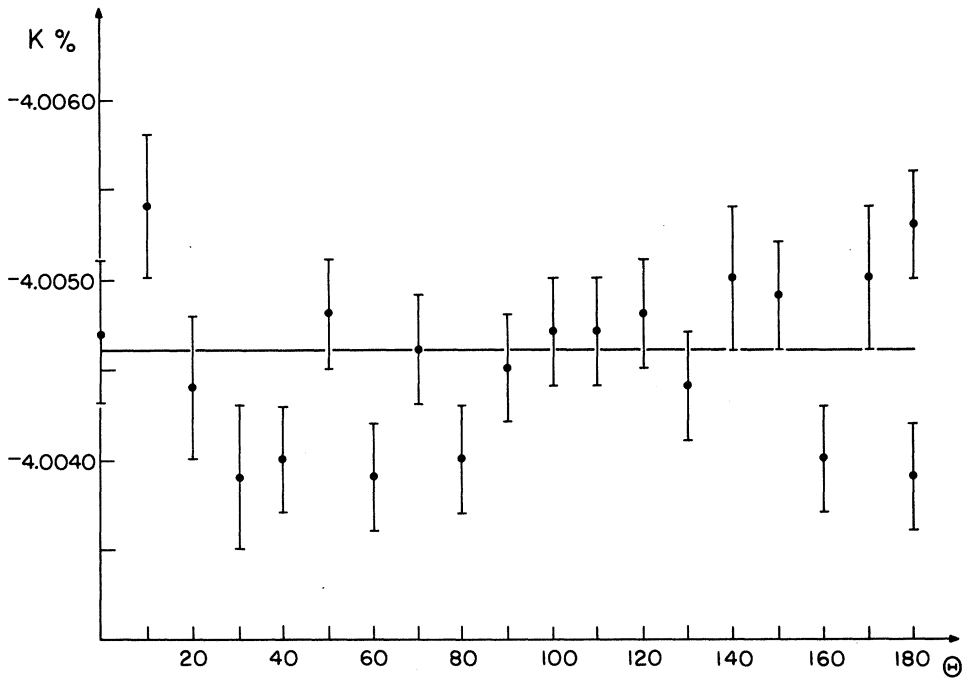

FIG. 4. Measured Knight shift in platinum as a function of magnetic field orientation in the (110) plane.

from their mean is $(4\times10^{-4})\%$, or $(3.4\times10^{-4})K_{\rm iso}$, which we quote as our result for an upper bound on the anisotropic Knight shift:

$$K_{\rm an} \leq (3.4\times10^{-4})K_{\rm iso} .$$

In addition, we computed the rms deviation of the data from an angular function of the form expected from (1.11) for cubic symmetry in the (100) plane:

$$K_{\rm an}\sin(4\theta+\phi) ,$$

where θ is the angle between the field and a cubic axis, and ϕ an angle which was varied to allow for the possibility that our identification of the [100] axis from flash planes and linewidth variation was somehow in error. The minimum rms deviation occurred for $\phi=0$, $K_{\rm an}=0$ and was, of course, $(3.4\times10^{-4})K_{\rm iso}$, as above. Thus the data, which to the eye might seem barely to reveal an anisotropy, do not in fact conceal an anisotropy with the correct angular dependence. If one takes $K_{\rm an}=(7\times10^{-4})\%$, the value measured by Schratter and Williams in the (100) plane, one finds a minimum rms deviation of $(5.4\times10^{-4})\%$ occurring when $\phi=0$.

b. Platinum. The isotropic Knight shift was measured to be $K_{\rm iso}=(4.0046\pm0.0003)\%$ by the same method as described above for lead. The magnetic resonance frequency for platinum was assumed to be 0.9155 kHz/G. The rms deviation of the Knight shift from isotropy in the (110) plane, for 22 data points (Fig. 4), was 6×10^{-6}, which we use to determine the following upper bound: $K_{\rm an}\leq(1.4\times10^{-4})K_{\rm iso}$.

We note that our experimental determination of the upper limit of the coefficient $K_{\rm an}=C_{11}-C_{12}-2C_{44}$ in Eq. (1.11) is comparable in magnitude to our very crude guess about the possible size of the effect in the Introduction. It is clear that a further search requires the initial promise of at least an order of magnitude greater stability of field and electronics than is presently available in our laboratory. The search should also check with a variety of samples in case there is a sample-dependent effect. Unstrained and undamaged surfaces of lead are difficult to obtain, and in both the lead and platinum linewidth data (see below) there are anomalies and evidence of sample dependences. If we accept the present level of precision, our results, if nothing else, rule out the anisotropic Knight shift as a measurable contribution to the measured width of powdered samples in lead.

B. Linewidths and Line Shapes

In both metals the lines were Lorentzian, at least near the center. Signal-to-noise limitations precluded effective investigation of the tails. The lead results for full width at half-maximum as a function of field orientation are shown in Fig. 5, where the solid line is given by $\Delta B(\theta)=3.10(1-0.103\cos4\theta)$ G, where θ is the angle between the field and a [100] axis in the (100) plane. The rms deviation of the data from the above expression is 0.15 G. The observed anisotropy is anomalously small. If one assumes, as the Lorentz lines shape leads one to assume, that the nuclei interact via a very large isotropic exchange interaction, then

the Anderson–Weiss model of exchange narrowing yields

$$\Delta B(\theta) = (\hbar/\mathcal{J}) M_2(\theta) ,$$

where M_2 is the Van Vleck second moment and $\mathcal{J}$ the isotropic exchange. If the angular dependence were caused by pure dipole-dipole interactions, in the (100) plane of an fcc crystal one would expect

$$\Delta B(\theta) = \Delta B_0 (1 - 0.176 \cos 4\theta) .$$

However, ΔB_0 would be about 200 mG, less than a tenth of the observed width. If the principal anisotropic internuclear interaction is pseudo-dipolar between nearest neighbors, $\Delta B(\theta) = \Delta B_0 \times (1 - 0.273 \cos 4\theta)$. Both of these results show considerably more anisotropy than we observe. It should be noted that Schratter and Williams[3] have also observed a linewidth anisotropy of 0.17 in lead (to be compared to our 0.103), a discrepancy which lends support to speculation that our results for the Knight-shift anisotropy might be sample dependent. However, we did not take the care to correct for possible modulation broadening that Schratter and Williams took; so the differences in the linewidth and its anisotropy may reflect smaller sample dependences than the data seem to show.

The width of the Lorentz line that we measured in platinum was anomalous in several respects: It was angularly independent, 3.4 ± 0.3 G broad (full width at half-maximum) at 18.5 kG. These results were sample independent. Walstedt *et al.*[14] and Butterworth[15] measured T_2 by pulse techniques, and from their results we expect a full width at half-maximum of 0.30 ± 0.05 G. Other workers [Walstedt (private communication)] have found anomalously broad platinum lines, but at least in one case the extra width has been field dependent, and extrapolates to the Walstedt–Butterworth value as B_0 approaches zero. Our measured width was not only field independent, as mentioned above, but also independent of the magnitude of the modulation field (although modulation large enough to broaden the line could be used), its frequency (18–920 Hz), and the rf voltage (5–70 mV peak to peak) at the input of the Robinson oscillator. We have no explanation of this phenomenon, but we do note that if a Pt single crystal could be found with a high-field linewidth of 0.3 G, an order of magnitude improvement in the upper limit of the anisotropic Knight shift would immediately result.

V. CONCLUSIONS

We have investigated the angular dependence of the Knight shift in cubic metals theoretically and experimentally for lead and platinum. The theoretical investigation has shown that the Knight shift is not isotropic in cubic metals if the calculation involves the contact interaction and is second order in the spin-orbit interaction, or if it is first order in spin-orbit and involves the electron-nuclear dipole interaction. In the latter case we have demonstrated a formula (Appendix B) which reduces to one previously found by Boon[1] in the tight-binding limit. The magnitude of the anisotropy is in any event not expected to be large. A very crude estimate is 10^{-3}–10^{-4} times the isotropic Knight shift, but no numerical calculation using our formulas has been undertaken.

We have investigated the nuclear magnetic resonance in single crystals of the spin-$\frac{1}{2}$ heavy metals

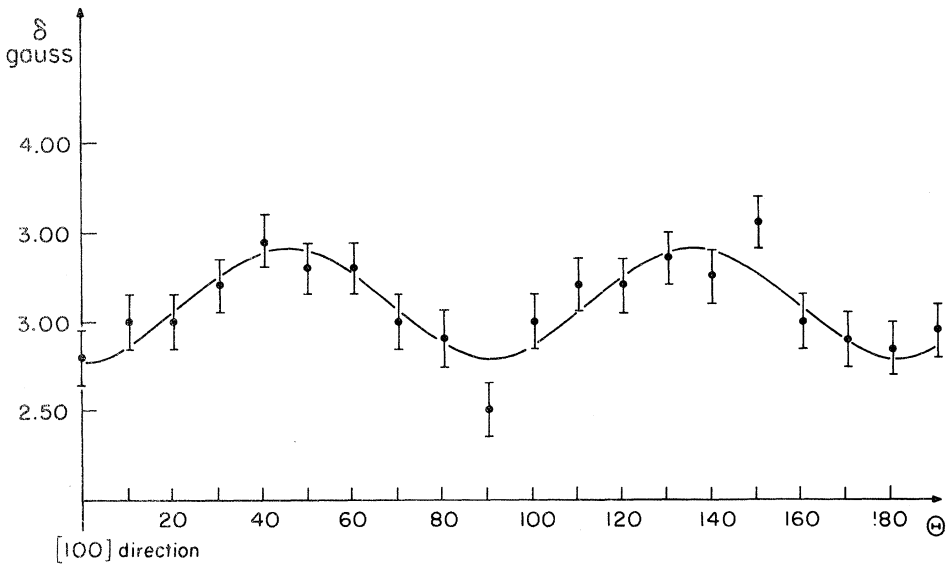

FIG. 5. Full width at half-maximum for Pb as a function of magnetic field orientation in the (100) plane.

lead and platinum, and found the position of the NMR line to be independent of angle to $(3.4 \times 10^{-4})K_{iso}$ for lead and $(1.5 \times 10^{-4})K_{iso}$ for platinum. Some anomalies in the linewidths in both metals lead us to fear that existing anisotropy could be obscured by crystal imperfections. In lead, particularly, the crystal surface is easily damaged. If the local cubic symmetry for nuclei near the surface were lifted by small, randomly oriented distortions, the normal first-order dipolar interaction could produce small local anisotropy fields that would not have to be large to obscure an effect as small as 0.05% of the isotropic Knight shift. Randomly oriented axial Knight shifts as small as, say, 0.2% of the isotropic shift would not show up as a troublesome, or even measurable, contribution to the total linewidth (about 400 mG at 18 kG), the origins of which are not well understood in any event.[3] Axial shifts as large as 10% of the isotropic shift are not uncommon in noncubic metals. It is certainly possible that sample dependence is responsible for the difference between our experimental results on lead and those of Schratter and Williams.

Finally, we wish to emphasize that we have been investigating anisotropies in the term of the Hamiltonian (2.1) which is linear in $\vec{B}$. It is perhaps worth pointing out that anisotropies originating in terms of the third and higher order in $\vec{B}$ have already been implicitly, if not explicitly, observed in the cubic metal aluminum. Khan *et al.*[16] have observed an oscillation in the magnitude of the Knight shift which is periodic in $1/B$, and which originates in the fluctuations of the density of states at the Fermi surface when the electron mean free path is longer than the circumference of the cyclotron orbit. Since the amplitude, phase, and frequency (in $1/B$) of these oscillations depend on the orientation of the field, it is clear that a reorientation of the field produces a different shift. This anisotropy is strongly dependent on field magnitude and sample purity and is quite distinct from the anisotropy that we have been investigating. Its undeniable existence should help comfort any who, in common with one of the authors at one time, find anisotropy of the nuclear shielding in cubic metals a difficult concept to accept.

ACKNOWLEDGMENTS

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APPENDIX A: ELECTRONIC G-FACTOR TENSOR

Our starting point will be the spin-dependent part of the effective Hamiltonian obtained by Blount[7] and Roth[9]; following Yafet,[10] we define an effective magnetic moment $\vec{\mu}_{nn\rho\rho'}(\vec{k})$ given by

$$\frac{1}{\beta}\vec{\mu}_{nn\rho\rho'}(\vec{k}) = \sigma_{nn\rho\rho'}(k) + \frac{m}{\hbar}\sum_{\rho''n''\neq n}\vec{V}_{nn''\rho\rho''}\times\vec{\mathfrak{x}}_{n''n\rho''\rho'} + \frac{m}{\hbar}\vec{V}_{nn}\times\vec{\mathfrak{x}}_{nn\rho\rho'} . \quad \text{(A1)}$$

The matrix elements of $\vec{\sigma}$ and the velocity operator $\vec{V} = [\vec{r}; \mathcal{H}_{elec}]$ are calculated between two-component Bloch states $|n\vec{k}\rho\rangle$, and $\vec{\mathfrak{x}}_{nn'\rho\rho'}(\vec{k})$ is defined as $\int d\tau\, u^{+}_{n\vec{k}\rho} i\nabla_k u_{n'\vec{k}\rho'}$, the volume integral extending over a unit cell.

Then, the electronic effective Hamiltonian describing the splitting of the Kramers degeneracy is simply

$$\mathcal{H}_{elec} = -\vec{B}\cdot\mu_{nn\rho\rho'}(\vec{k}) \quad \text{(A2)}$$

and its eigenvalues are

$$\epsilon_{\pm} = \pm\beta\,|\,\vec{B}\,|\left(\sum_{\alpha\beta}\lambda_\alpha\lambda_\beta G_{\alpha\beta}(n,\vec{k})\right)^{1/2} , \quad \text{(A3)}$$

where

$$G_{\alpha\beta}(n,\vec{k}) = \mu_{\alpha nn\uparrow\uparrow}(\vec{k})\mu_{\beta nn\uparrow\uparrow}(\vec{k}) + \mu_{\alpha nn\uparrow\downarrow}(\vec{k})\mu_{\beta nn\downarrow\uparrow}(\vec{k}) . \quad \text{(A4)}$$

Use was made of the relation $\mu_{\alpha\uparrow\uparrow} = -\mu_{\alpha\downarrow\downarrow}$.[10] It is obvious that only the symmetric part of $G_{\alpha\beta}(n,\vec{k})$ contributes to $\sum_{\alpha\beta}\lambda_\alpha\lambda_\beta G_{\alpha\beta}(n,\vec{k})$. It can be written conveniently as

$$\tfrac{1}{2}(G_{\alpha\beta}+G_{\beta\alpha}) \equiv G_{\alpha\beta} = \tfrac{1}{2}\sum_{\rho\rho'}\mu_{\alpha nn\rho\rho'}\mu_{\beta nn\rho'\rho} . \quad \text{(A5)}$$

Now we use the first-order part of (2.19) to evaluate $G'_{\alpha\beta}(n\vec{k})$ to first order in spin-orbit coupling. We obtain

$$G'_{\alpha\xi}(n,\vec{k}) = \delta_{\alpha\xi} + \sum_{n''\neq n}\frac{\mathfrak{L}_{\alpha nn''}N_{\xi n''n} + \mathfrak{L}_{\xi nn''}N_{\alpha n''n}}{\omega_{nn''}} + \left(\frac{m}{\hbar}\right)\sum_{\eta\gamma}\epsilon_{\alpha\eta\gamma}$$

$$\times\sum_{n''\neq n}V_{\eta nn''}\frac{\partial}{\partial k_\gamma}\frac{N_{\xi n''n}}{2\omega_{nn''}} + \left(\frac{m}{\hbar^2}\right)\sum_{\eta\gamma}\epsilon_{\alpha\eta\gamma}\sum_{n''\neq n}\frac{\mathrm{Re}(\mathfrak{x}_{\gamma nn''}N_{\xi n''n})}{2\omega_{nn''}}\frac{\partial}{\partial k_\eta}E_n(\vec{k})$$

$$+ [\text{terms obtained from last two by interchange of indices } \alpha \text{ and } \xi] , \quad \text{(A6)}$$

where

$$\mathfrak{L}_{nn'} = \left(\frac{m}{\hbar}\right) \sum_{n'} \vec{\nabla}_{nn'} \times \vec{\mathfrak{x}}_{n'n'} ,$$

and $\vec{\mathfrak{L}}_{nn} = 0$ owing to quenching.[10]

It was assumed in the foregoing that $\vec{\mathfrak{x}}_{nn} = 0$. de Graaf and Overhauser[11] point out that the eigenvalues (A3) are phase dependent (although their average over a cyclotron oribit is not) owing to the transformation properties of $\vec{\mathfrak{x}}_{nn\rho\rho'}(\vec{k})$. If, as in the present calculation, use is made of perturbation theory to separate the spin and spatial degrees of freedom of the Bloch states $|n\vec{k}\rho\rangle$, it is $\vec{\mathfrak{x}}_{nn}(\vec{k})$ rather than $\vec{\mathfrak{x}}_{nn\rho\rho'}(\vec{k})$ that appears in the results. There is a choice of phases for the Bloch states $\psi_{n\vec{k}}(\vec{r})$ which corresponds to minimum spread of the localized Wannier states, which is equivalent to the requirement $\vec{\nabla} \cdot \vec{\mathfrak{x}}_{nn}(\vec{k}) = 0$. If there is inversion symmetry, then $\vec{\nabla} \vec{\mathfrak{x}}_{nn}(\vec{k}) = 0$ is also satisfied. Thus, it is possible to set $\mathfrak{x}_{nn}(\vec{k}) = 0$ everywhere, provided that there are no degeneracies.[8] We assume for simplicity that this is the case.

Taking for $|n\vec{k}\rangle$ a tight-binding function, it has been shown[17] that $\mathfrak{L}_{\alpha nn'}(\vec{k}) = L_{\alpha nn'}(\vec{k}) +$ (surface integrals), where now $\hbar\vec{L} = \vec{p} \times \vec{r}$. Thus, if one takes the limit of large distance between atoms, then

$$G'_{\alpha\rho}(a) = \delta_{\alpha\beta} + \sum_{a' \neq a} \frac{L_{\alpha_{aa'}} N_{\beta_{a'a}} + L_{\beta_{aa'}} N_{\alpha_{a'a}}}{\omega_{aa'}} , \tag{A7}$$

where a and a' denote bound-state orbitals. All other terms of (A6) vanish, since it can be easily seen that both $E_n(\vec{k})$ and $N_{\beta_{nn'}}(\vec{k})/\omega_{nn'}$ become independent of $\vec{k}$ if overlap integrals are negligible.

The result (A7) is the well-known ionic g-factor tensor.

APPENDIX B: CALCULATION OF CONTRIBUTION OF DIPOLAR INTERACTION TO $K_{an}(\vec{\lambda})$ TO FIRST ORDER IN SPIN-ORBIT COUPLING

This is the problem that Boon[1] solved. It is shown here that (2.1) leads to the same results as Boon's and, in addition, the explicit angular dependence of K_{an} is obtained, as well as expressions for all the coefficients which do not vanish in cubic symmetry.

The contribution of the dipolar coupling to the internal field $\sum_\beta \lambda_\beta K_{\beta\alpha}$ is, according to (2.18),

$$2\sum_\beta \lambda_\beta K_{\beta\alpha} = \sum_{n\vec{k}\rho} (\pm)\mu_e^2 \mu_N \left(\sum_{\alpha'\beta'} \lambda_{\alpha'} \lambda_{\beta'} G_{\alpha'\beta'}(n\vec{k}) \right)^{1/2} \times \left(\frac{df}{d\epsilon}\right)_{E_n(k)} \langle n\vec{k}\rho \,|\, \sum_\eta \sigma_\eta \mathfrak{R}_{\eta\alpha} \,|\, n\vec{k}\rho \rangle , \tag{B1}$$

$$\mathfrak{R}_{\eta\alpha} = (3r_\eta r_\alpha - \delta_{\eta\alpha} r^2)/r^5 . \tag{B2}$$

The matrix element gives, using the first-order part of $\psi_{n\vec{k}\rho}(\vec{r})$ defined in (2.21),

$$\begin{aligned} &\langle n\vec{k}\rho \,|\, \sum_\eta \sigma_\eta \mathfrak{R}_{\eta\alpha} \,|\, n\vec{k}\rho \rangle \\ &= \langle p\rho \,|\, \sum_\eta \sigma_\eta \mathfrak{R}_{\eta\alpha} \,|\, p\rho \rangle + \sum_{\substack{p's' \neq ps}} (2\omega_{pp'})^{-1} \\ &\times \langle p\rho \,|\, \sum_\beta \sigma_\beta N_\beta \,|\, p's' \rangle \langle p'A' \,|\, \sum_\eta \sigma_\eta \mathfrak{R}_{\eta\alpha} \,|\, p\rho \rangle \\ &+ \langle p\rho \,|\, \sum_\eta \sigma_\eta \mathfrak{R}_{\eta\alpha} \,|\, p's' \rangle \langle p's' \,|\, \sum_\beta \sigma_\beta N_\beta \,|\, p\rho \rangle \end{aligned} \tag{B3}$$

or

$$\begin{aligned} &\langle n\vec{k}\rho \,|\, \sum_\eta \sigma_\eta \mathfrak{R}_{\eta\alpha} \,|\, n\vec{k}\rho \rangle \\ &= \pm \sum_\eta \lambda_\eta \mathfrak{R}_{\eta\alpha_{pp}} \pm i \sum_{\beta\gamma\eta} \epsilon_{\gamma\beta\eta} \lambda_\gamma \\ &\times \sum_{p' \neq p} \frac{N_{\beta_{pp'}} \mathfrak{R}_{\eta\alpha_{p'p}} - \mathfrak{R}_{\eta\alpha_{pp'}} N_{\beta_{p'p}}}{2\omega_{pp'}} . \end{aligned} \tag{B4}$$

The plus sign goes with $\rho = 1$, the minus sign with $\rho = 2$.

Inserting (B4) in (B1) and expanding the square root to first order in N using (A6), we get

$$\begin{aligned} \sum_\beta \lambda_\beta K_{\beta\alpha} = \mu_N \mu_e^2 \sum_p \left(\frac{df}{d\epsilon}\right)_{E_p} &\left(1 + \frac{1}{2}\sum_{\xi\rho} \lambda_\xi \lambda_\rho \Delta_{\xi\rho}(p)\right) \\ &\times \left(\sum_\eta \lambda_\eta \mathfrak{R}_{\eta\alpha_{pp}} + i \sum_{\beta\gamma\eta} \epsilon_{\gamma\beta\eta} \lambda_\gamma \right. \\ &\left. \times \sum_{p' \neq p} \frac{N_{\beta_{pp'}} \mathfrak{R}_{\eta\alpha_{p'p}} + \mathfrak{R}_{\eta\alpha_{pp'}} N_{\beta_{p'p}}}{2\omega_{pp'}} \right) , \end{aligned} \tag{B5}$$

giving, for

$$K_{an}(\vec{\lambda}) = \frac{1}{\mu_N} \sum_{\alpha\beta} \lambda_\alpha \lambda_\beta K_{\alpha\beta} ,$$

$$K_{an}(\vec{\lambda}) = \sum_{\alpha\eta} \lambda_\alpha \lambda_\eta (Q^{(0)}_{\eta\alpha} + W^{(0)}_{\eta\alpha}) + \sum_{\alpha\beta\gamma\eta} \lambda_\alpha \lambda_\beta \lambda_\gamma \lambda_\eta T^{(1)}_{\alpha\beta\gamma\eta} ,$$

$$Q^{(0)}_{\alpha\eta} = \mu_e^2 \sum_p \left(\frac{df}{d\epsilon}\right)_{E_p} \mathfrak{R}_{\alpha\eta_{pp}} ,$$

$$W^{(1)}_{\alpha\eta} = \mu_e^2 \sum_{pp'} \left(\frac{df}{d\epsilon}\right)_{E_p} i \sum_{\beta\gamma} \epsilon_{\gamma\beta\eta} \times \frac{N_{\beta_{pp'}} \mathfrak{R}_{\eta\alpha_{p'p}} - \mathfrak{R}_{\eta\alpha_{pp'}} N_{\beta_{p'p}}}{2\omega_{pp'}} ,$$

$$T^{(1)}_{\alpha\beta\gamma\eta} = \frac{1}{2}\mu_0^2 \sum_p \left(\frac{df}{d\epsilon}\right)_{E_p} \mathfrak{R}_{\alpha\beta_{pp}} \Delta_{\gamma\eta}(p) . \tag{B6}$$

$\Delta_{\alpha\beta}(p)$ is defined in (A6).

We now discuss the tensors $Q^{(0)}_{\alpha\beta}$, $W^{(1)}_{\alpha\beta}$, and $T^{(1)}_{\alpha\beta\gamma\eta}$. Boon defines a function

$$F(\vec{r}) = \mu_e^2 \sum_p \left(\frac{df}{d\epsilon}\right)_{E_p} |\psi_p(\vec{r})|^2 , \tag{B7}$$

in terms of which the tensor $Q^{(0)}_{\alpha\beta}$ takes the form

$$Q_{\alpha\alpha} = \int \frac{d^3r}{r^3} F(r)(3\cos^2\theta_\alpha - 1) ,$$

$$Q_{yx}=Q_{xy}=\int\frac{d^3r}{r^3}\,F(r)3\sin^2\theta\cos\phi\sin\phi\,,$$

$$Q_{zy}=Q_{yz}=\int\frac{d^3r}{r^3}\,F(r)3\sin\theta\cos\theta\sin\phi\,, \qquad \text{(B8)}$$

$$Q_{zx}=Q_{xz}=\int\frac{d^3r}{r^3}\,F(r)3\sin\theta\cos\theta\cos\phi\,.$$

Here θ_α is the angle between $\vec{r}$ and the αth axis; θ and ϕ are just the polar angles of $\vec{r}$. Equations (B8) can be rewritten in terms of Legendre polynomials; the λ's can be written in terms of the polar angles Θ and Φ of $\vec{B}$. Considering that, owing to the relation $\sum_\alpha\cos^2\theta_\alpha=1$, $\mathrm{Tr}Q=0$, one finds, to zeroth order in N,

$$\begin{aligned}K_{\rm an}(\vec{\lambda})&=\sum_{\alpha\beta}\lambda_\alpha\lambda_\beta Q_{\alpha\beta}^{(0)}\\&=A\,P_z^0(\cos\Theta)+B_1P_2^1(\cos\Theta)\sin\Phi\\&\quad+B_2P_2^2(\cos\Theta)\sin2\Phi+C_1P_2^1(\cos\Theta)\cos\Phi\\&\quad+C_2P_2^2(\cos\Theta)\cos2\Phi+D,\end{aligned} \qquad \text{(B9)}$$

where

$$D=\mathrm{Tr}Q=0\,,$$

$$A=Q_{zz}=2\int\frac{d^3r}{r^3}\,F(r)\,P_2^0(\cos\Theta)\,,$$

$$B_1=-\tfrac{1}{3}(Q_{yz}+Q_{zy})=-\frac{2}{3}\int\frac{d^3r}{r^3}\,F(r)\,P_2^1(\cos\theta)\sin\phi\,, \qquad \text{(B10)}$$

$$C_1=-\tfrac{1}{3}(Q_{xz}+Q_{zx})=-\frac{2}{3}\int\frac{d^3r}{r^3}\,F(r)\,P_2^1(\cos\theta)\cos\phi\,,$$

$$B_2=\tfrac{1}{6}(Q_{xy}+Q_{yx})=\frac{1}{6}\int\frac{d^3r}{r^3}\,F(r)\,P_2^2(\cos\theta)\sin2\phi\,,$$

$$C_2=\tfrac{1}{6}(Q_{xx}-Q_{yy})=\frac{1}{6}\int\frac{d^3r}{r^3}\,F(r)\,P_2^2(\cos\theta)\cos2\phi\,.$$

Expressions (B9) and (B10) agree with Boon's equations (11a) and (11b) if his equations are rewritten in terms of *normalized* Legendre polynomials.

This discussion was independent of the choice of a particular coordinate frame and crystal symmetry. We now specialize by considering only cubic symmetry and choosing as coordinate axes the set of principal axes of the equipotential surfaces $U(\vec{r})=\mathrm{const}$. Going back to expressions (B6), we have $Q_{\alpha\beta}=0$ for $\alpha\neq\beta$ and $Q_{XX}=Q_{YY}=Q_{ZZ}$, which, combined with the traceless property of $Q_{\alpha\beta}$, gives $Q_{\alpha\beta}=0$ for all α, β. Also

$$T_{XXXX}=T_{YYYY}=T_{ZZZZ}\equiv T\,,$$

$$T_{P(XXYY)}=T_{P(YYZZ)}=T_{P(ZZXX)}\,, \qquad \text{(B11)}$$

and

$$\sum_{\alpha\beta\gamma\eta}\lambda_\alpha\lambda_\beta\lambda_\gamma\lambda_\eta T_{\alpha\beta\gamma\eta}=(T-\tilde{T})(\lambda_X^4+\lambda_Y^4+\lambda_Z^4)+\tilde{T}\,,$$

where

$$\tilde{T}=\sum_P T_{P(XXYY)}\,.$$

Although it is not immediately apparent, $W_{\alpha\beta}$ can also be shown to vanish in cubic symmetry. Thus the only contribution to (B6) comes from the terms involving T, and is in general anisotropic, with an angular dependence identical to (2.28).

By choosing $\vec{B}$ along Z, (B6) gives for arbitrary symmetry

$$\begin{aligned}K_{\rm an}=Q_{ZZ}+W_{ZZ}+T_{ZZZZ}&=\int\frac{d^3r}{r^3}\left[\mu_e^2\sum_p\left(\frac{df}{d\epsilon}\right)_{E_p}|\,\psi_p(\vec{r})\,|^2\right](3\cos^2\theta-1)\\&+\int\frac{d^3r}{r^3}\left[\mu_e^2\sum_{pp'}\left(\frac{df}{d\epsilon}\right)_{E_p}|\,\psi_p(\vec{r})\,|^2\,\frac{N_{Zpp'}\mathfrak{L}_{Zp'p}+\mathfrak{L}_{Zpp'}N_{Zp'p}}{\epsilon_p-\epsilon_{p'}}\right](3\cos^2\theta-1)\\&+\int\frac{d^3r}{r^3}\left[\mu_e^2\sum_{pp'}\left(\frac{df}{d\epsilon}\right)_{E_p}\frac{(iN_{Xpp'})(3yz)-(iN_{Ypp'})(3xz)}{\epsilon_p-\epsilon_{p'}}\,\psi_{p'}^*(\vec{r})\psi_p(\vec{r})\right]\\&+(\text{terms which vanish in limit of large distance between atoms})\,,\end{aligned} \qquad \text{(B12)}$$

which can also be written

$$K_{\rm an}=\int\frac{d^3r}{r^3}\left[F_{ZZ}(r)\,P_2^0(\cos\theta)+\mathcal{O}_X(r)\times P_2^1(\cos\theta)\sin\phi-\mathcal{O}_Y(r)\,P_2^1(\cos\theta)\cos\phi\right], \qquad \text{(B13)}$$

with

$$F_{ZZ}(\vec{r})=\mu_e^2\sum_p\left(\frac{df}{d\epsilon}\right)_{E_p}\times\left(2+\sum_{p'\neq p}\frac{N_{Zpp'}\mathfrak{L}_{Zp'p}+\mathfrak{L}_{Zpp'}N_{Zp'p}}{\epsilon_p-\epsilon_{p'}}\right)|\,\psi_p(\vec{r})\,|^2\,,$$

$$\Theta_\alpha(\vec{r}) = \frac{\mu_e^2}{2} \sum_{p \neq p'} \left(\frac{df}{d\epsilon}\right)_{E_p} \frac{iN\alpha_{pp'}}{\epsilon_p - \epsilon_{p'}} \psi^*_{p'}(\vec{r})\psi_p(\vec{r}) . \quad \text{(B14)}$$

Equations (B13) and (B14) reduce to Boon's equations (A4)–(A6) in the tight-binding limit when $\mathcal{L}_{\alpha pp'} \to L_{\alpha pp'}$.[17]

To estimate the magnitude of the dipolar effect in cubic symmetry from typical experimental magnitudes in metals, we proceed in the spirit of the Introduction to replace the average of products by the product of averages. Thus the expression for T in (B6) is in effect the average of the dipolar interaction weighted by the g shift for an electron with wave vector p. In noncubic metals, where the dipolar term does not vanish because of symmetry, anisotropic shifts as large as 10% of the isotropic shift have been observed. Thus in the spirit of the estimate in the Introduction, $|T| \leq (K_{an})(\delta g) \approx 0.1 K_{iso}(\delta g) \approx 10^{-3} K_{iso}$. This result, in common with the estimate is Sec. I, must be regarded as an upper limit. The anisotropy vanishes, for example, if $\Delta_{\alpha\beta}(p)$ is independent of p.

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‡Present address: Instituto de Fisica, UEC, CP1170, Campinas, Brazil.

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