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# Interpretation of Knight Shifts and Susceptibilities of Transition Metals: Platinum

A. M. Clogston, V. Jaccarino, and Y. Yafet
*Bell Telephone Laboratories, Murray Hill, New Jersey*

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Measurements of the magnitude, sign, and temperature dependence of the Knight shift and susceptibility in platinum are used to determine the contributions to each arising from the spin paramagnetism of the *s* and *d* bands, the orbital paramagnetism and the core diamagnetism. A complete expression for the orbital contribution to the Knight shift in a transition metal is derived, including spin-orbit coupling. We show that in the tight-binding limit, as in the free ion, a simple relation exists between the orbital susceptibility and the orbital hyperfine field. The relation of the enhancement of the *d*-spin susceptibility over its specific heat value to the possible occurrence of superconductivity is discussed.

## INTRODUCTION

In previous work[1] an interpretation of the Knight shift ($K$), susceptibility ($\chi$), and electronic specific heat of various transition metal compounds was given. It was seen that orbital paramagnetism made major contributions to $K$ and $\chi$ and that the temperature-dependent part of $K$ was associated with that of $\chi$ through core polarization. The present work (a) extends this to an analysis of platinum metal, thereby giving estimates of the various contributions to $K$ and $\chi$; (b) gives a more detailed treatment of the relation between orbital Knight shifts and orbital paramagnetism, including spin-orbit coupling; and (c) establishes a relation between the occurrence of superconductivity and the ratio of the observed spin susceptibility to that deduced from the measured specific heat.

## I. NUCLEAR MAGNETIC RESONANCE IN PLATINUM

Platinum, like nickel and palladium, represents the case of a nearly filled *d*-band transition metal. The electronic properties of these metals have been the subject of extensive experimental and theoretical study. The earliest interests[2] centered on the seeming simplicity with which one could understand the results of alloying (e.g., Ni-Cu, Pd-Au, etc.) and the fact that the degeneracy temperature of the positive holes was sufficiently low (~1500°K) as to be accessible to experimental study. The importance to the magnetic behavior of these metals of *d*-*d* exchange, *s*-*d* exchange, and of electron transfer between the two bands has been investigated.[3–7]

The utility of the Knight shift in further understanding the electronic properties of the *d*-band metals and alloys has only recently been exploited.[1,8] Certain procedures have been advanced for separating the various contributions to the Knight shift and susceptibility, particularly in those cases where $K$ and $\chi$ are dependent on temperature. A similar graphical analysis is now offered for platinum.

Rowland[9] studied the $Pt^{195}$ nuclear magnetic resonance (NMR) in platinum metal between 78 and 350°K. He found the NMR to be strongly temperature-dependent, and when compared with the Pt NMR in a nominally nonmagnetic chloroplatinic acid solution in the same field, the metal resonance was displaced towards a *lower* frequency by some 3.5%. This was opposite in sign, and a factor of two or more larger than had been expected. Rowland conjectured that the magnitude and sign of the shift of the metal NMR could result from a large chemical shift in the reference solution. Subsequent to Rowland's work a study of several intermetallic compounds[10] (e.g., $PtAl_2$, $PtGa_2$, $PtIn_2$) revealed that the Pt Knight shift in these metals was of the expected magnitude and sign (i.e., positive) when compared with the same chloroplatinic acid reference. Clearly, then some particular mechanism must be responsible for the unusual NMR properties of platinum metal. As will be shown below, the large negative Knight shift and its temperature dependence is a consequence of the core polarization of inner *s* electrons by the *d*-band electrons.

### 1. Contributions to the Susceptibility and Knight Shift in Platinum

### (a) *Susceptibility*

The delineation of the various contributions to the observed paramagnetism of a metal has been given by Blount[11] and Roth[12] in a detailed treatment of Bloch electrons in a magnetic field. We shall use a simplified

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two-band ($d$ and $s$) model in which the $d$ electrons are treated in the tight binding approximation. In this limit two contributions to the susceptibility are of prime importance. The spin paramagnetism $\chi_P{}^d$, and the orbital paramagnetism[13] to be expected in partially filled degenerate bands, $\chi_{VV}$ which is the analog in metals of the Van Vleck temperature-independent paramagnetism.

We shall treat the $s$ electrons as "free" with an effective mass $m^*$ and a $g$ factor of 2 (exchange and correlation effects nearly cancel).[14] At $T=0$ the Pauli paramagnetism $\chi_P$ and the Landau diamagnetism $\chi_L$ are given by

$$\begin{aligned}\chi_P&=2\beta^2N(\zeta),\\ \chi_L&=2\beta^2N(\zeta)[-\tfrac{1}{3}(m/m^*)^2],\end{aligned}\qquad\text{(I.1)}$$

where $\beta$ is the Bohr magneton, $m$ the electron mass, and $N(\zeta)$ is the density of states for one direction of the spin at the Fermi energy $\zeta$. For the $s$ electrons we take $m^*=m$ so that $\chi_L=-\frac{1}{3}\chi_P$ whereas for the $d$ holes one expects $m^*\gg m$ so that one may safely neglect $\chi_L$.

The total susceptibility of platinum includes the diamagnetism of the core $\chi_{\text{dia}}$; we include in $\chi_{\text{dia}}$ the diamagnetism of the filled portion of the outer $d$ shell, essentially because it is temperature-independent and it has a negligible effect on the Knight shift. The total susceptibility at temperature $T$, $\chi(T)$ is given by

$$\chi(T)=\tfrac{2}{3}\chi_P{}^s+\chi_P{}^d(T)+\chi_{VV}+\chi_{\text{dia}},\qquad\text{(I.2)}$$

where we allow for the fact that $\chi_P{}^d$ may be temperature-dependent in the temperature range of interest, primarily because of the relatively small degeneracy temperature of the holes. The dependence on temperature is further accentuated if exchange between the $d$ electrons is present. Neglect of the $s$-$d$ exchange interaction has but a small effect on $\chi(T)$.

To separate the various contributions to $\chi(T)$ we must now estimate the relatively small contributions $\chi_{\text{dia}}$ and $\chi_P{}^s$. The remaining quantities will be obtained from our graphical procedure.

$\chi_{\text{dia}}$: estimated values of $\chi_{\text{dia}}$ for platinum have been given in the literature based on earlier measurements of the susceptibilities of platinum compounds. The estimate used by Hoare and Matthews[15] and by Wohlfarth[3] is $\chi_{\text{dia}}\simeq-28\times10^{-6}$ emu/mole. That this is not an unreasonable choice, say $\pm15\%$, may be seen by taking the measured value of $\chi$ for gold, $\chi=-28\times10^{-6}$ emu/mole where the $d$ band is fully occupied, and subtracting a free-electron estimate for the $s$-electron susceptibility from which one obtains $\chi_{\text{dia}}=-36.6\times10^{-6}$ emu/mole. Both these values are to be contrasted with the large value of $\chi_{\text{dia}}=-75\times10^{-6}$ emu/mole computed from the Slater functions[16] which is twice as large as the "measured" value for Au. Since

$$\chi_{\text{dia}}=-\frac{Ne^2}{6mc^2}\sum_i\langle r_i{}^2\rangle,\qquad\text{(I.3)}$$

and the major part of $\chi_{\text{dia}}$ comes from the $5d$ shell, it appears that the Slater functions overestimate $\langle r^2\rangle_{5d}$.

$\chi_P{}^s$: the molar spin susceptibility of the $s$ electrons is given by

$$\chi_P{}^s=1.86\times10^{-6}(M/\rho)^{2/3}n_s{}^{1/3}\text{ emu/mole},\qquad\text{(I.4)}$$

where for platinum $M=195.09$, $\rho=21.37$ g/cm$^3$ and $n_s$ is the number of $s$ electrons per atom. We obtain $\chi_P{}^s=4.8\times10^{-6}$ if we choose $n_s=n_d=0.2$. This value follows from an interpretation of the temperature dependence of the susceptibility in terms of a parabolic $d$ band. A similar analysis[7] without the benefit of knowledge of the Knight shift gives values of $n_s=n_d=0.3$.

$\chi_{VV}$: if $f(E_{n\mathbf{k}})$ and $f(E_{n'\mathbf{k}})$ are the Fermi functions for electrons in state $n\mathbf{k}$ and $n'\mathbf{k}$ with energies $E_{n\mathbf{k}}$ and $E_{n'\mathbf{k}}$, respectively, the tensor susceptibility $\chi_{VV}$ may be written[13] in the tight-binding approximation, as

$$\chi_{VV}=\int\frac{d\mathbf{k}}{(2\pi)^3}\sum_{nn'}\frac{f(E_{n\mathbf{k}})-f(E_{n'\mathbf{k}})}{E_{n'\mathbf{k}}-E_{n\mathbf{k}}}\times\beta^2(n\mathbf{k}|\mathbf{L}|n'\mathbf{k})(n'\mathbf{k}|\mathbf{L}|n\mathbf{k}),\qquad\text{(I.5)}$$

where $\mathbf{L}$ is the orbital angular momentum operator (the symmetrical Wigner-Seitz cell is used for the integration). A great deal of information about the band structure would be required to calculate $\chi_{VV}$. However this quantity is related to the orbital contribution to the Knight shift as seen in detail in part II. Using this relation we are able to deduce $\chi_{VV}$ by an analysis of the Knight shift versus the susceptibility [see ($c$) below].

### ($b$) *Knight Shift*

The original interpretation given to the observed shifts of the NMR in the non-$d$ group metals assumes that only the $s$-electron hyperfine interaction contributes to the field at the nucleus.[17] As such, the Knight shift apart from any diamagnetic terms, could be expressed as

$$K_s\equiv\Delta H/H=(8\pi/3)\chi_s\Omega\langle|\psi_s(0)|^2\rangle_\zeta,\qquad\text{(I.6)}$$

where $\Omega$ is the atomic volume and $\langle|\psi_s(0)|^2\rangle_\zeta$ is the average at the Fermi surface of the $s$ conduction-electron probability density *at the nucleus*. The shift is measured with respect to a nonmagnetic, nonmetallic reference. More recently, it was recognized that additional contributions to the Knight shift must be con-

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sidered. Cohen, Goodings, and Heine[18] have shown that core polarization of the inner $s$-shell electrons by the conduction electrons modifies the Knight shift of the alkali metals. Core polarization has also been used to explain the negative Knight shifts observed in certain intermetallic compounds.[8] The existence of core polarization can be seen in the hfs spectra of $d$-group ions in crystals and was first described in terms of atomic configuration interaction[19] and more recently calculated by means of the unrestricted Hartree-Fock method.[20] For other than $s$ electrons, if one neglects spin-orbit coupling, the spin dipolar hyperfine field vanishes in cubic symmetry so that the spin magnetization of $p$- and $d$-band electrons is manifest only through core polarization. Because of the translational motion of the electrons through the crystal the angular momentum is quenched, $\langle l_z\rangle=0$ and the orbital hyperfine field, and therefore the orbital Knight shift is of second order in $l_z$ as is the orbital paramagnetism.

We may express $K(T)$ for platinum as

$$K(T)=K_s+K_d(T)+K_{VV}+\delta K_{\text{dia}}\,, \tag{I.7}$$

$$K(T)=\alpha_s\chi_P{}^s+\alpha_d\chi_P{}^d(T)+\beta'\bar{F}_j\chi_{VV}+\delta K_{\text{dia}}\,, \tag{I.8}$$

where

$$\alpha_s=0.895\times10^{-4}A\Omega H_{\text{hf}}(s),\ \alpha_d=0.895\times10^{-4}A\Omega H_{\text{hf}}(d),$$

and $H_{\text{hf}}(s)$ and $H_{\text{hf}}(d)$ are the hyperfine fields per spin in the metal arising from the contact and core polarization interactions, respectively, and $A$ is Avogadro's number (all susceptibilities expressed per unit volume). For platinum, $A\Omega=9.10$ cm$^3$. In the case of a free ion, $\beta'$ is rigorously given as

$$\beta'=2\langle 1/r^3\rangle\Omega\,, \tag{I.9}$$

where $\langle 1/r^3\rangle$ is the expectation value of $r^{-3}$ for the free-ion wave functions concerned; $\bar{F}_j$ is a relativistic correction factor discussed below. In the metal, corresponding to (I.5), the orbital field at the nucleus is [see Eqs. (II.5) and (II.9)]

$$H_{\text{orb}}=\frac{1}{N}\int\frac{d\mathbf{k}}{(2\pi)^3}\sum_{nn'}\frac{f(E_{n\mathbf{k}})-f(E_{n'\mathbf{k}})}{E_{n'\mathbf{k}}-E_{n\mathbf{k}}}\beta^2\left(n\mathbf{k}\left|\frac{2\mathbf{L}}{r^3}\right|n'\mathbf{k}\right)\times(n'\mathbf{k}|\mathbf{H}\cdot\mathbf{L}|n\mathbf{k})\,, \tag{I.10}$$

so that Eq. (9) may be used in the solid with a value of $\langle 1/r^3\rangle$ close to that of the free ion ($N$, number of atoms/unit volume).

Next an estimate of $\alpha_s$ and $\beta'$ is made and we show that $\delta K_D$, the *differential* diamagnetic contribution to the Knight shift is, for all practical purposes, unimportant.

$\alpha_s$ and $\beta'$: the neutral platinum atom has the configuration $\cdots 5d^96s^1;\,{}^3D$. The hfs of the Pt$^{195}$ isotope has been determined[21] in the fine structure levels $J=1$ and $J=3$ of the $^3D$ state. Expressing the hfs interaction as $\mathcal{H}=A_J\mathbf{I}\cdot\mathbf{J}$ we have

$$\begin{aligned}A_1&=(5/4)a_{3/2}-\tfrac{1}{4}a(s)=-168\times10^{-3}\ \text{cm}^{-1}\,,\\ A_3&=\tfrac{5}{6}a_{5/2}+\tfrac{1}{6}a(s)=199\times10^{-3}\ \text{cm}^{-1}\,,\end{aligned} \tag{I.11}$$

where $a_{3/2}$ and $a_{5/2}$ are the hfs interaction parameters for the single $5d$ ($l=2$) hole in the states $j=l\pm\frac{1}{2}$, and $a(s)$ is the hfs interaction parameter for the $6s$ electron.[22] The parameters $a_j$ are related to $\langle 1/r^3\rangle$;

$$a_j=\gamma\frac{2l(l+1)}{J(J+1)}F_j\times1.59\times10^{-3}\times\left\langle\frac{1}{r^3}\right\rangle'\ \text{cm}^{-1}, \tag{I.12}$$

where $F_j$ is a relativistic correction factor given by Casimir,[22] the prime on $\langle 1/r^3\rangle'$ indicates the use of atomic units, and $\gamma$ is the nuclear gyromagnetic ratio in units of $\mu_n$, the nuclear magneton.

For $Z=78$, the values of $F_j$ are $F_{3/2}=1.14$ and $F_{5/2}=1.05$. Using $\gamma^{195}=1.21$ and Eqs. (I.11) and (I.12) we find for platinum that $a_{3/2}=74.8$, $a_{5/2}=29.6$, and $a(s)=1046$ (all times $10^{-3}$ cm$^{-1}$). Values of $H_{\text{hf}}(s)$ and $\langle 1/r^3\rangle'$ are given in Table I where $H_{\text{hf}}(s)$ is obtained from the relation $H_{\text{hf}}(s)=a(s)/\gamma\mu_n$.

To calculate $\alpha$ and $\beta'$ we need to know how the hyperfine fields in the metal differ from their free atom values and here is the largest uncertainty that enters into the computations. For the $s$ electrons this problem has received considerable attention.[23] As a reasonable estimate for $\xi=H_{\text{hf}}{}^{\text{metal}}(s)/H_{\text{hf}}(s)$ we take 0.7, giving for $\alpha_s$ the value in Table I. Since relativistic corrections are not entirely negligible for the spin-dipolar and orbital-hyperfine interactions, we must estimate an average value of $F_j$ for the $5d$ electrons in the metal. Assuming the two states to be populated according to their statistical weight, we find $\bar{F}_j=1.086$. Since we

TABLE I. The hfs interaction parameters determined from optical data[a] on the neutral platinum atom (see Sec. I). The second column gives the hyperfine field per spin for the $s$ contact hyperfine interaction, the hyperfine field per spin resulting from core polarization (obtained from analysis of the metal Knight shift), and the hyperfine field per unit angular momentum for a $d$ electron; $\langle 1/r^3\rangle\bar{F}_j=11.7$ au.

| | | | |
|---|---|---|---|
| $\alpha_s$ | $27.6\ \times10^3$ | $H_{\text{hf}}(s)$ | $33.9\ \times10^6$ Oe |
| $\alpha_d$ | $-\ 1.92\times10^3$ | $H_{\text{hf}}(d)$ | $-\ 2.36\times10^6$ Oe |
| $\beta'\bar{F}_j$ | $2.41\times10^3$ | $2\beta\langle 1/r^3\rangle\bar{F}_j$ | $1.47\times10^6$ Oe |

[a] See Ref. 21.

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know that the $d$ wave functions are expanded in the metal we take, as in the case of $V^{(1)}$, the value $\frac{3}{4}\langle r^{-3}\rangle_{\text{ion}}$ as a reasonable one for $\langle r^{-3}\rangle$ in the metal. The value of $\beta'$ times $\bar{F}_j$ is given in Table I.

The procedure employed here for obtaining $\langle 1/r^3\rangle$ differs from the one employed in the case of $V$, since in that case no measured values of the hfs parameters existed but we had reliable Hartree-Föck calculations.[24] No such calculations exist for the $5d$ ions at the present time but a useful check on the magnitude of $\langle 1/r^3\rangle$ is obtained from the empirical relation for $\langle 1/r^3\rangle$ obtained from the fine structure splitting[22] $\lambda$ using screened hydrogen-like wave functions;

$$\lambda=(2l+1)Z_iH\langle 1/r^3\rangle'\times 2.0\ \text{cm}^{-1}, \qquad \text{(I.13)}$$

where $Z_i$ is the "interior charge" defined as $Z_i=Z-Z_s$ and $H$ is a relativistic correction factor. For the $5d$ shell we have found from an analysis of the hfs and fine structure of La and Lu that the values of $\langle 1/r^3\rangle'$ derived from (I.12) and (I.13) are brought into coincidence for $Z_s\simeq 20$. Furthermore, it may be shown that in the $3d$ shell, $Z_s$ is surprisingly constant as one crosses the shell and, if we assume the same to be true for the $5d$ shell, we may use $Z_s=20$ in (I.13) for platinum. For $H=1.05$[22] and $\lambda=8419.9$ cm$^{-1}$ for the fine structure splitting[25] of the configuration $5d^9$ of Pt$^{\text{II}}$, we find $\langle 1/r^3\rangle'=9.5$.

$\delta K_{\text{dia}}$: in comparing the shift of the NMR in the metal with respect to a chloroplatinic acid solution, one has to correct for the *differential* diamagnetic shift. That this is unimportant relative to the other large shifts that we are considering may be seen as follows. The metal and the acid platinum configurations correspond roughly to core $+5d^{10}$ and core $+5d^6$, respectively; hence[26]

$$\delta K_{\text{dia}}\cong -\frac{1}{3}\frac{e^2}{mc^2}\sum_{\delta}\left\langle\frac{1}{r}\right\rangle=-\frac{r_0}{3a_0}\sum_{\delta}\left\langle\frac{a_0}{r}\right\rangle, \qquad \text{(I.14)}$$

where $r_0$ and $a_0$ are the classical electron and first Bohr radii, respectively, and the $\delta$ indicates the sum extends over four of the $5d$ electrons. Now quite generally $\langle a_0/r\rangle < \langle (a_0/r)^3\rangle$. In particular for the isoelectronic Ni$^{\text{I}}$ Hartree-Fock calculations[27] give $\langle a_0/r\rangle \approx \frac{1}{3}\langle (a_0/r)^3\rangle$. Using the same ratio for Pt we find that $\langle a_0/r\rangle \sim 3$ and hence $\delta K_{\text{dia}}\simeq -4(r_0/a_0)=-0.02\%$. This number is so small when compared to the uncertainties in the other quantities, observed and estimated, that we shall omit all reference to it from now on.

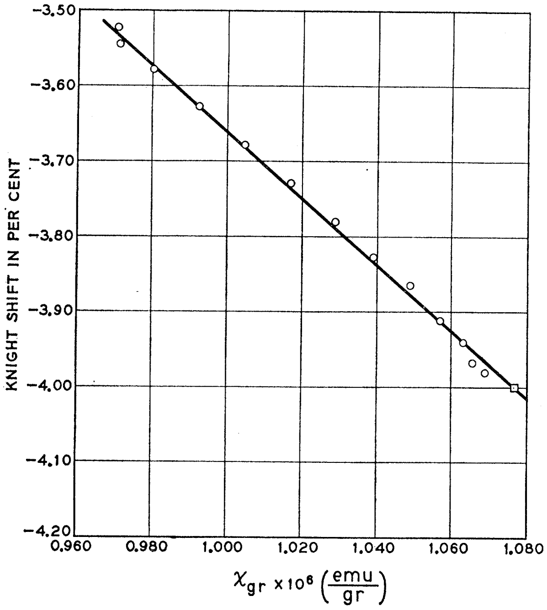

FIG. 1. The experimentally observed Knight shift of the Pt$^{195}$ NMR in platinum metal versus the susceptibility, with temperature the implicit parameter, is shown by the open circles. The straight line is a best fit to this data. The open square is a low-temperature measurement of $K$ which is arbitrarily placed on the straight line. The value of $1/\chi$ corresponding to this is shown as a cross in Fig. 3.

### (c) Construction of the K versus χ Diagram

If one plots the raw measurements of $K$ (9) versus $\chi$ (15), with temperature the implicit variable, one finds the result shown in Fig. 1. The figure also includes more recent measurements of $K$ at lower temperatures.[28] It is to be noted that $K$ versus $\chi$ is linear with the exception of the lowest temperature region. We shall offer evidence in the susceptibility versus temperature analysis later on which indicates that the effects of a paramagnetic impurity on $\chi$ might be responsible for this departure from linearity in the $K$ versus $\chi$ plot. From the partitioning of $K$ and $\chi$ in Eqs. (I.2) and (I.8) we see that the slope of the $K$ versus $\chi$ plot determines $\alpha_d$; the value so obtained[29] is given in Table I. It appears, as in the $3d$ group, that $|\alpha_d|\simeq\beta'$ and both are an order of magnitude smaller than $\alpha_s$.

The chloroplatinic acid has one drawback as a reference solution; the Pt$^{4+}$ ion in PtCl$_6$ is in $5d^6$ configuration in a strong crystal field and not a closed $d$ shell. Although the level $(5d)^6\,{}^1\Gamma_1$ lies lowest, there is an appreciable Van Vleck paramagnetism to be expected. This problem has been treated in detail for the $3d^6$ Co$^{3+}$ case and an empirical procedure followed[30] which utilizes the optical measurements of the cubic field

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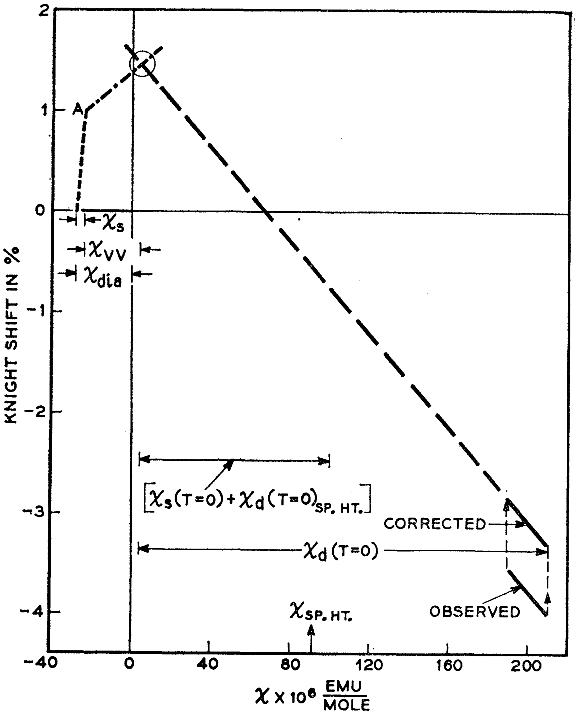

FIG. 2. A diagram of the Knight shift of the $Pt^{195}$ NMR in platinum metal versus the susceptibility. The solid line marked "observed" is the experimental datum shown in Fig. 1, only much reduced because of the scale change. The solid line immediately above marked "corrected" is the same data corrected for the positive NMR shift in the chloroplatinic acid reference solution. The remaining features of the $K$ versus $\chi$ diagram are discussed in detail in the body of the paper.

splitting $({}^1\Gamma_1-{}^1\Gamma_4)$ and NMR shifts in the same compounds to extrapolate a "zero shift" value. It appears somewhat more difficult to do this for different $5d^6$ Pt compounds because the ${}^1\Gamma_1-{}^1\Gamma_4$ optical transition in many cases overlaps the intense charge transfer bands. Nevertheless, Drain[28] has estimated the $VV$ shift for the $PtCl_6$ ion to be about +0.7% and an examination of the optical data of Jorgensen[31] on platinum complexes would seem to support this value.[32]

Assuming now that we have all contributions to $K$ and $\chi$ we construct the diagram in Fig. 2. The $\chi_{\text{dia}}$ corresponds to the horizontal line starting from the origin of the $K$-$\chi$ axis. The $K_s$ contribution is added to this and from the point $A$ a line with slope $\beta'$ is drawn. The observed $K$ versus $\chi$ data are shown in the lower right-hand part of the figure and the same data, displaced vertically by 0.7% for reasons discussed in the paragraph above, are then extrapolated until it intersects the line extending from point A. The extrapolation procedure provides all of the information concerning $\chi$ that we need. In particular, it shows that $\chi_{P^s}+\chi_{VV}$ nearly cancels $\chi_{\text{dia}}$ so that all of the *observed* $\chi\approx\chi_{P^d}$. The magnitudes of the individual contributions to the susceptibility are indicated by the horizontal lines in Fig. 2. Although the $H_{\text{hf}}(d)$ resulting from core polarization is an order of magnitude larger than the corresponding fields observed in the $3d$ transition metals, the ratio of $H_{\text{hf}}(d)/H_{\text{hf}}(s)\simeq0.1$ does not change appreciably.

The fact that $\chi_{VV}$ in platinum is substantially less than the value of $211\times10^{-6}$ emu/mole deduced for $\chi_{\text{orb}}$ in vanadium[1] is in keeping with the expected qualitative dependence of $\chi_{VV}$ on the position of the Fermi level in the $d$ band. Equation (I.5) would suggest that, apart from the detailed consideration of the symmetries of the $d$ functions and their energy distribution in the band, $\chi_{VV}\sim N_oN_u$ where $N_o$ and $N_u$ are the numbers of occupied and unoccupied states, respectively, in the $d$ band, subject to $N_o+N_u=10$/atom. For vanadium, $N_o\simeq4$, $N_u\simeq6$, whereas platinum (as we shall see from the analysis of the temperature dependence of the susceptibility) has $N_o\simeq9.8$ and $N_u\simeq0.2$. The ratio $(N_oN_u)_{\text{V}}/(N_oN_u)_{\text{Pt}}=12$ is to be compared with the ratio deduced; $(\chi_{VV})_{\text{V}}/(\chi_{VV})_{\text{Pt}}\simeq7.5$.

## 2. Estimate of the $d$-Band Parameters

Having seen that the observed susceptibility is in fact equal to the $d$-spin susceptibility, it is possible to interpret the temperature dependence of the susceptibility in terms of the derivatives of the density of states at the Fermi level.[2] In addition, platinum, being the heaviest transition metal, has the largest spin-orbit coupling. It is of interest to see whether the values of the band parameters deduced from experiment are appreciably modified by spin-orbit coupling. To do this we make the usual parabolic band approximation for the $d$ holes, being aware that this is a gross approximation to the actual band structure. Let $\chi(T)\equiv\chi_{P^d}(T)$. Then the reciprocal susceptibility is[3]

$$\frac{1}{\chi(T)}=\frac{1}{\chi_0(T)}-\frac{k_BT_{\text{ex}}}{n\beta^{*2}}. \tag{I.15}$$

$k_B$ is the Boltzmann constant, $T_{\text{ex}}$ an effective exchange temperature $n$, the number of $d$ holes per unit volume and $\beta^*=(g/2)\beta$, the effective spin moment with a $g$ factor determined by spin-orbit interaction. $\chi_0(T)$ is given by

$$\chi_0(T)=\frac{3}{2}\frac{n\beta^{*2}}{k_BT_0}\left[1-\frac{\pi^2}{12}\left(\frac{T}{T_0}\right)^2\right], \tag{I.16}$$

where $T_0$ is the Fermi temperature, $\zeta=k_BT_0$.

The electronic specific heat per unit volume $C_v$ is

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[31] K. Jorgensen, Acta. Chem. Scand. **10**, 518 (1956).

[32] In this regard an additional piece of evidence to support the $VV$ correction to the $PtCl_6^{--}$ shift comes from the NMR measurements (Ref. 10) on the $PtAl_2$, $PtGa_2$, $PtIn_2$ metals. The susceptibility of these metals is much smaller than Pt metal indicating, in a crude sense, that the $d$ band is filled. The observed Knight shifts, though positive ($K\sim+0.4\%$) with respect to the $PtCl_6^{--}$ reference are not as large as would be expected on a free-electron calculation for the $6s$ band. Again one must subtract at least 0.7% from the reference (or add it to the metals) to obtain anywhere near a reasonable value of $K_s$. Since the $d$ band is filled, $\chi_{VV}$ and $K_{VV}\simeq0$.

TABLE II. $d$-band parameters determined from the analysis of the electronic specific heat and the temperature dependence of the "corrected" susceptibility of platinum. The two columns of numerical values correspond to (1) zero spin-orbit coupling and (2) ratio of spin-orbit coupling to mean band width equal to 0.1. The quantity $N(\zeta)V$ is discussed in Sec. III.

| $n$ — No. of holes / atoms | 0.20 | 0.18 |
|---|---|---|
| $T_0$ (°K) | 1206 | 1096 |
| $T_{\text{ex}}$ (°K) | 454 | 345 |
| $m^*/m$ | 19.2 | 19.9 |
| $N(\zeta)V$ | 0.565 | 0.472 |

given by

$$C_v=\tfrac{1}{2}(\pi^2)(nk_B/T_0)T\equiv\gamma T. \qquad \text{(I.17)}$$

(For simplicity in the above analysis we have not differentiated between the "bare" $N(\zeta)$ and the modification that results from electron-phonon self-energy corrections; see section III.) The last three equations contain three unknowns, $T_0$, $T_{\text{ex}}$ and $n$ ($\beta^*$ will be discussed below), which may be determined experimentally, provided $\chi$ varies as $T^2$.

However, the observed $1/\chi$ versus $T$ exhibits an anomalous decrease at the low-temperature end of the plot (see Fig. 3) although no such behavior is present in the Knight shift. Since $K(T)=\text{constant}\times\chi(T)$ above 80°K, it would appear reasonable to assume that some paramagnetic impurity could be responsible for the low-temperature behavior of $1/\chi$ and at the same time not affect the Knight shift. If we use the Knight shift at 20°K as a measure of $1/\chi(20°\text{K})$, we find the point indicated by a cross on Fig. 3. The dashed line is an extrapolation of the high-temperature data to $T=0$ subject to the condition $[\partial(1/\chi)/\partial T]_{T=0}=0$. We shall call this the "corrected" $1/\chi(T)$. In Fig. 4 we plot the "corrected" $1/\chi$ versus $T^2$. The linearity of this plot shows that the density of states does not vary rapidly in the vicinity of the Fermi level and this, at least, is consistent with our simple model.

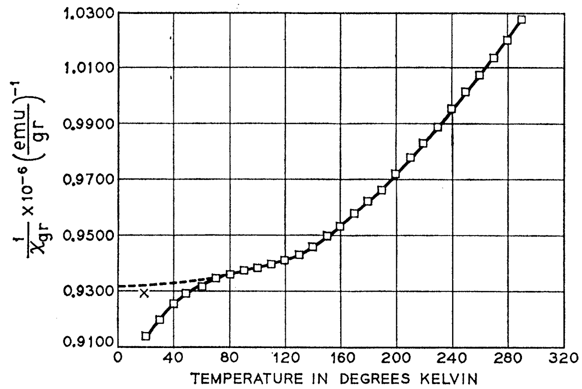

FIG. 3. The reciprocal of the mass susceptibility versus temperature is shown by the open squares. The point marked by a cross is the value of $1/\chi$ determined using the Knight shift as a measure of the susceptibility in this low-temperature region. The dashed line is an extrapolation of the high-temperature $1/\chi$ data subject to $\partial(1/\chi)/dT=0$.

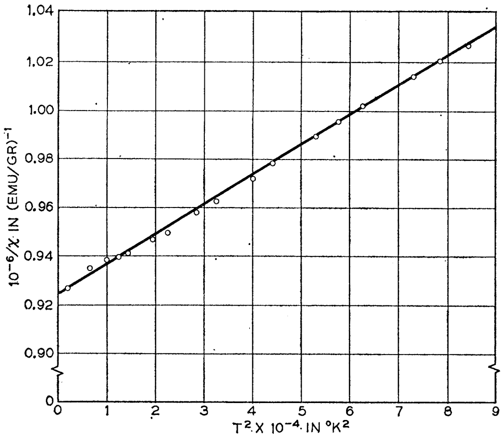

FIG. 4. The reciprocal of the mass susceptibility versus $T^2$ using only the data above 80°K in the previous figure. The lowest temperature point is derived from the Knight shift found at 20°K as explained in the text.

In Table II values of $n$, $T_0$, $T_{\text{ex}}$, and $m^*/m$ are given for two values of $\beta^*$; $\beta^*=\beta$ corresponding to no spin-orbit coupling and $\beta^*=1.1\beta$. This latter value is obtained as follows: If $\lambda$ is the atomic spin-orbit coupling for the platinum ion and $\Delta$ the mean width of the $5d$ band in platinum, then the *fractional* increase in $g$ would be of order[13] $\lambda/\Delta$. From the observed[25] fine structure splitting of 8400 cm$^{-1}$ for Pt$^{\text{II}}$ $5d^9\,{}^2D$, and a value of $\Delta\simeq4$ eV, we find $\lambda/\Delta\simeq0.1$.

### 3. Temperature Dependence of Orbital Paramagnetism

In the preceding section we have neglected the temperature dependence of the orbital paramagnetism, $\chi_{VV}$. For platinum this can be justified as follows.

From Eq. (I.5) it is easy to show, if one assumes that the holes have mostly $\Gamma_3$ orbital character, that the change in $\chi_{VV}$ for small $T$, $\delta\chi_{VV}=\chi_{VV}(T)-\chi_{VV}(0)$ is of order

$$\delta\chi_{VV}\simeq\chi_{VV}(0)(N(\zeta)/n)(k_BT)^2/\Delta. \qquad \text{(I.18)}$$

In fact they will be a mixture of $\Gamma_3$ and $\Gamma_5$ so that the energy denominator should be somewhat smaller than the bandwidth $\Delta$ and probably of the order of $\zeta$. As we have seen, the change in $\chi_P{}^d$ is of order

$$\delta\chi_P{}^d\simeq\chi_P{}^d(0)(k_BT/\zeta)^2, \qquad \text{(I.19)}$$

and since $\chi_{VV}(0)\ll\chi_P{}^d(0)$ and $\zeta\ll\Delta$, the change in $\chi_{VV}$ can be neglected.

It may be noted that the temperature dependence of $\chi_{VV}$ must be taken into account, along with that of $\chi_P{}^d$ when $\chi_{VV}\gtrsim\chi_P{}^d$, as is the case in the first half of the transition series. Thus an appreciable part of the temperature dependence of $\chi$ in lanthanum and scandium could be attributed to $\chi_{VV}$. This appears to be borne out by the fact that the Knight shift of these metals[33] increases with decreasing temperature, as does the susceptibility,[34] indicating that the changes in the susceptibility and in the hyperfine field are of the same sign, as would be the case for a field of orbital origin.

## II. THEORY OF THE ORBITAL KNIGHT SHIFT IN TRANSITION METALS

The orbital Knight shift resulting from orbital electronic currents, can be conveniently split into two parts.[35,36] First, there is a long-range contribution, $(\Delta H/H)=(4\pi-D)\chi$, where $\chi$ is the total susceptibility and $D$ the demagnetizing tensor. Second, there is the contribution of the short-range part of the orbital hyperfine interaction, which is very similar to the interaction in an isolated atom. As will be seen below, in metals with partly filled $d$ shells this contribution is expected to be much larger than the former. Recently, Hebborn[36] [Eq. (25) of his paper] has given an exact expression for this term, in a form which is simple enough that numerical calculations could be carried out if the $d$-band wave functions were known.

We give here an alternative and direct derivation of this term, which is based on the work of Blount[11] and Roth[12] and makes use of the similar character of the orbital-hyperfine and spin-orbit interactions, resulting from the fact that both interactions are velocity-dependent. Our result is given in a form different from Hebborn's but it too is amenable to computation; it explicitly reduces to the atomic value in the tight-binding limit and it can be generalized to include the effect of spin-orbit coupling, which, as we have seen, is not negligible in platinum.

### 1. No Spin-Orbit Coupling

Consider the interaction of a band electron with a periodic array of nuclear moments $\boldsymbol{\mu}$, located at the lattice sites and parallel to one another. The periodic Hamiltonian is

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}', \tag{II.1}$$

where $\mathcal{H}_0$ is the sum of the kinetic and electrostatic energies, and $\mathcal{H}'$ is the short-range part of the orbital hyperfine interaction, given by[36]

$$\begin{aligned}\mathcal{H}'&=\left(\frac{e}{mc}\right)\sum_{K_m\neq 0}\frac{4\pi}{i\Omega}e^{i\mathbf{K}_m\cdot\mathbf{r}}\frac{\boldsymbol{\mu}\times\mathbf{K}_m}{K_m^2}\cdot\mathbf{p} \qquad \text{(II.2)}\\ &\equiv(e/mc)\mathbf{A}'\cdot\mathbf{p},\end{aligned}$$

where $\mathbf{K}_m$ is a reciprocal lattice vector and $\mathbf{p}$ the momentum.

To find the orbital hyperfine field, we apply a magnetic field $\mathbf{H}$ parallel to the direction of $\boldsymbol{\mu}$ and calculate the free-energy $F$ to first order in $\mu$. The hyperfine field is then given by $\Delta H=-(1/N)(\partial F/\partial\mu)$. The free energy was calculated in Refs. 11 and 12. We now briefly describe this result and then use it, replacing the spin-orbit interaction by $\mathcal{H}'$ of Eq. (II.2).

In the presence of an external field $\mathbf{H}=\boldsymbol{\nabla}\times\mathbf{A}$, the Hamiltonian of the system described by Eq. (II.1) is written as a symmetric function of the noncommuting variables $\kappa_\alpha=k_\alpha+eA_\alpha(i\boldsymbol{\nabla}_{\mathbf{k}})/\hbar c$, where $\mathbf{k}$ is the wave vector. A power series in the field is obtained,

$$\mathcal{H}_n(\boldsymbol{\kappa})=\mathcal{H}_n^{(0)}(\boldsymbol{\kappa})+\mathcal{H}_n^{(1)}(\boldsymbol{\kappa})+\cdots, \tag{II.3}$$

where $\mathcal{H}_n^{(1)}$ is first order in $H$; $n$ is the band index, including the spin state. To this order the free energy per unit volume is

$$F=F_0+\frac{1}{(2\pi)^3}\sum_n\int\mathcal{H}_n^{(1)}(\mathbf{k})g(E_{n\mathbf{k}})dk, \tag{II.4}$$

where $F_0$ is the field-independent part, and $g(E)$ is the Fermi function. Had we not imposed the condition that the direction of $\boldsymbol{\mu}$ be fixed, the second term of (II.4) would have vanished on summing over the directions of $\boldsymbol{\mu}$. The orbital hyperfine field $\Delta H$ is given in terms of $\mathcal{H}^{(1)}$ by

$$-\mu\Delta H=\left(\frac{1}{N}\right)\frac{1}{(2\pi)^3}\sum_n\int\mathcal{H}_n^{(1)}(\mathbf{k})g(E_{n,\mathbf{k}})d\mathbf{k}, \tag{II.5}$$

where $N$ is the number of atoms per unit volume. $\mathcal{H}^{(1)}$ itself is given by

$$\mathcal{H}_n^{(1)}(\mathbf{k})=\frac{\beta\mathbf{H}}{\hbar}\cdot\Big[\sum_{n'\neq n}\mathbf{X}_{nn'}\times\boldsymbol{\pi}_{n'n}+2\mathbf{X}_{nn}\times\boldsymbol{\pi}_{nn}+\hbar(\boldsymbol{\sigma})_{nn}\Big], \tag{II.6}$$

where $\boldsymbol{\sigma}$ is the Pauli spin operator, $\mathbf{X}$ is the periodic part of the coordinate, and $\boldsymbol{\pi}$ is the velocity times the electron mass, $\boldsymbol{\pi}=(im/\hbar)[\mathcal{H},\mathbf{x}]$; the matrix elements over the Bloch states, $\boldsymbol{\sigma}_{nn}$, $\mathbf{X}_{nn'}$, $\boldsymbol{\pi}_{nn'}$ are functions of $\mathbf{k}$. Since spin-orbit coupling is neglected, $\boldsymbol{\sigma}_{nn}$ is a constant matrix, independent of any orbital effect and thus does not contribute to the hyperfine field. The first two terms of Eq. (II.6) represent the interaction of the periodic part of the electronic orbital moment induced by the nuclear moment with the external field. Equation (II.6), like Hebborn's Eq. (25), is valid not only for nondegenerate bands, but also for the degenerate bands in the transition metals, except along lines of symmetry where the band states are degenerate. Since these form a set of measure zero the application of (II.6) to the $d$ bands is valid.

We now transform Eq. (II.6) into an expression which is very similar to that of the orbital hyperfine interaction of an isolated atom with one difference in that it has a contribution from the surface of the atomic cell. This is small in the tight binding approximation. The

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[33] W. E. Blumberg, J. Eisinger, V. Jaccarino, and B. T. Matthias, Phys. Rev. Letters **5**, 52 (1960).

[34] J. M. Lock, Proc. Phys. Soc. (London) **B70**, 566 (1957).

[35] Y. Yafet, Phys. Chem. Solids **21**, 99 (1961).

[36] J. E. Hebborn, Proc. Phys. Soc. (London) **80**, 1237 (1962); J. E. Hebborn and M. J. Stephen, *ibid.* **80**, 991 (1962).

details of the transformation, which essentially eliminates $\mathbf{X}$ and replaces it by the ordinary coordinate $\mathbf{r}$, have been given elsewhere[37] and here we give only the result:

$$\mathcal{H}_n^{(1)}(\mathbf{k})=\frac{\beta H}{\hbar}\Bigg\{\int_\Omega \psi_n^*(xp_y-yp_x)\psi_n d\tau+\left(\frac{e}{c}\right)\int_\Omega \psi_n^*(xA_y'-yA_x')\psi_n d\tau$$
$$-\frac{i}{2}\int_S\left[u_n^*p_\nu+(p_\nu u_n)^*+2u_n^*\left(\hbar k_\nu+\left(\frac{e}{c}\right)A_\nu'\right)\right]\left(x\frac{\partial u_n}{\partial k_y}-y\frac{\partial u_n}{\partial k_x}\right)dS$$
$$-\frac{\partial E_n/\partial k_y}{4\partial E_n/\partial k_x}\int_S\left[\frac{\partial\psi_n^*}{\partial k_x}\pi_\nu\frac{\partial\psi_n}{\partial k_x}+\left(\pi_\nu\frac{\partial\psi_n}{\partial k_x}\right)^*\frac{\partial\psi_n}{\partial k_x}\right]dS+\frac{\partial E_n/\partial k_x}{4\partial E_n/\partial k_y}\int_S\left[\frac{\partial\psi_n^*}{\partial k_y}\pi_\nu\frac{\partial\psi_n}{\partial k_y}+\left(\pi_\nu\frac{\partial\psi_n}{\partial k_y}\right)^*\frac{\partial\psi_n}{\partial k_y}\right]dS\Bigg\}. \qquad (\text{II.7})$$

The magnetic field has been assumed to lie in the $z$ direction; $\mathbf{A}'$ is the periodic part of the vector potential due to the nuclear moment and is defined in (II.2); the Bloch state $\psi_{n\mathbf{k}}$ is normalized over the unit cell and $u_{n\mathbf{k}}$ is its cell-periodic part. $\psi_{n\mathbf{k}}$ is assumed known to first order in the hyperfine interaction $\mathcal{H}'$; i.e.,

$$\psi_{n\mathbf{k}}=\varphi_{n\mathbf{k}}+\sum(\mathcal{H}')_{n'n}\varphi_{n'\mathbf{k}}/(E_n-E_{n'}),$$

where the $\varphi_{n\mathbf{k}}$'s are the eigenfunctions of $\mathcal{H}_0$. The last three terms of Eq. (II.7) are integrals over the surface of the unit cell; the first one originates from the first term in Eq. (II.6) and the other two from the terms in $\mathbf{X}_{nn}$ of the same equation.

It is to be expected that in transition metals where the Van Vleck paramagnetism is likely to be important the surface terms will be small because of the localization of the $d$ functions. In this limit the two volume terms in Eq. (II.7) acquire simple physical meanings as will be more apparent if we first give an alternative expression for the interaction $\mathcal{H}'$.

The summation over $\boldsymbol{\kappa}_m$ in Eq. (II.2) is rather inconvenient. It can be eliminated and converted into a summation over lattice points $\mathbf{R}_s$ by using the theta function transformation of Ewald.[38] We obtain

$$\mathcal{H}'=\frac{e}{mc}\boldsymbol{\mu}\cdot\sum_s\frac{(\mathbf{r}-\mathbf{R}_s)}{|\mathbf{r}-\mathbf{R}_s|^3}\times\mathbf{p}, \qquad (\text{II.8})$$

where the summation over $s$ (which would be conditionally convergent if the order were not specified) is to be effected in the order of increasing distance from the origin. The summation converges rapidly. Thus the term from $\mathbf{R}_s=0$ is of order $r^{-3}l_z$ while in a cubic metal the contribution from the nearest neighbors is of order $\nu(r^2/a^5)l_z$, $a$ being the distance and $\nu$ the number of nearest neighbors. In the case of vanadium, $a$ is about 5 au while calculated values[27] of $\langle r^n\rangle$ in the free ion are: for the $d^3$ configuration, $\langle r^{-3}\rangle'=2.747$; $\langle r^2\rangle'=2.07$; and for the $d^5$ configuration, $\langle r^{-3}\rangle'=1.835$; $\langle r^2\rangle'=4.576$. These figures suggest that only the contribution from the central cell is of importance in Eq. (II.8) [when $\mathbf{A}'$ occurs in the surface terms of Eq. (II.7), the contribution from the nearest neighbors can of course not be neglected].

Returning now to the volume terms in Eq. (II.7), and using Eq. (II.8) and the perturbation expansion of $\psi_{n\mathbf{k}}$, we see that if only the central cell contribution to $\mathcal{H}'$ is retained, the first term becomes

$$\int_\Omega \psi_n^*(xp_y-yp_x)\psi_n d\tau$$
$$=\sum_{n'\neq n}\left\{(n|l_z|n')\left(n'\left|\frac{e\mu}{mc}\frac{l_z}{r^3}\right|n\right)+\text{c.c.}\right\}\frac{1}{(E_n-E_{n'})}. \qquad (\text{II.9})$$

Except for the $1/r^3$ factor this expression is identical, within a proportionality factor, with the contribution of the electron in the state $\varphi_{n\mathbf{k}}$ to the Van Vleck susceptibility of the material; this can be seen from Eq. (103) in Ref. 12 and the discussion following it, provided the spin-orbit interaction is neglected. If the further approximation is made that the radial functions of the states $\varphi_{n\mathbf{k}}$ and $\varphi_{n'\mathbf{k}}$ are identical and Eq. (II.5) is used, we find for the Knight shift arising from this term:

$$K_{VV}\equiv(\Delta H/H)_{VV}=2\chi_{VV}\langle 1/r^3\rangle\Omega. \qquad (\text{II.10})$$

This was to be expected by continuity from Ramsey's[39] result for molecules.

Similarly, the second volume term of Eq. (II.7) can be seen to give the diamagnetic contribution to the Knight shift. In the tight-binding limit this can be related, in analogy to (II.10), to the atomic diamagnetism $\chi_{\text{dia}}$ of the material, and we find

$$K_{\text{dia}}\equiv\left(\frac{\Delta H}{H}\right)_{\text{dia}}=\frac{2\chi_{\text{dia}}\langle r^{-1}\rangle\Omega}{\langle r^2\rangle}. \qquad (\text{II.11})$$

Whenever the $d$ shell is partly filled the paramagnetic contribution exceeds the diamagnetic contribution because $\chi_{VV}\gg\chi_{\text{dia}}$. In the beginning of this section it was stated that under the same condition the long-range contribution is small compared to the short-range contribution. From (II.10) it is seen that the ratio of the two is of order $(\Omega/\pi)\langle 1/r^3\rangle$ and since $\Omega\approx 10^2$ au, the short-range term dominates.

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[37] Y. Yafet, Phys. Rev. **106**, 679 (1957).

[38] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954), p. 248.

[39] N. Ramsey, Phys. Rev. **78**, 699 (1950).

### 2. Effect of Spin-Orbit Coupling

We now turn to the effect of spin-orbit coupling, and, more generally, to the relativistic effects, assuming the nuclear moment to be concentrated at a point. If $\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}$ is the solution of the Dirac equation, it is convenient to eliminate the small component part $\psi_2$ and to express the result in terms of the large component spinor $\psi_1$. The energy of interaction[40] to first order in the nuclear moment is then given by the expectation value over $\psi_1$ of the operator $\mathcal{H}_\mu$,

$$\begin{aligned}\mathcal{H}_\mu=&\left(1+\frac{W+e\varphi}{2mc^2}\right)^{-1}\\ &\times\left[\frac{8\pi}{3}\beta\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\delta(\mathbf{r})+\beta\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}\boldsymbol{\mu}\cdot\boldsymbol{\nabla}\left(\frac{1}{r}\right)+2\beta\frac{\boldsymbol{\mu}\cdot\mathbf{l}}{r^3}\right]\\ &+\left(1+\frac{W+e\varphi}{2mc^2}\right)^{-2}\left[\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}(-e\varphi)\times\frac{e(\boldsymbol{\mu}\times\mathbf{r})}{cr^3}\right].\end{aligned}\tag{II.12}$$

Here $W=E-mc^2$, $E$ is the energy, and $\varphi$ is the electrostatic potential. Of the three terms in the first square bracket, the first (which nonrelativistically is the contact interaction) gives a vanishing result because of the $e\varphi/mc^2$ term in the first factor, the second is the dipole-dipole interaction with the electron spin, and the third is the orbital interaction. The term in the second square bracket is a part of the spin-orbit interaction $(\hbar/4m^2c^2)\boldsymbol{\sigma}\times\boldsymbol{\nabla}(-e\varphi)\cdot(\mathbf{p}+e\mathbf{A}'/c)$, where $\mathbf{A}'=\boldsymbol{\mu}\times\mathbf{r}/r^3$ is the vector potential of the nuclear moment. This term by itself is of order $r^{-2}$ and hence it would diverge for $s$ states. The factor $[1+(W+e\varphi)/2mc^2]^{-2}$ makes it finite, which restores the contact interaction. For an $s$ state only this term contributes; for $l\neq 0$, the other two terms of (II.12) contribute as well.

We do not intend to give a formal relativistic treatment and so we consider the large component of the Bloch function $\psi_{1,nk}$ to be decomposed into eigenstates of the angular momentum. Especially in heavy metals, the largest relativistic effects are those for $s$ and $p_{1/2}$ states, and their contributions to the energy are to be calculated by the usual methods[22,40] used in atomic hyperfine calculations. For the $j\neq\frac{1}{2}$ part of the wave function the relativistic corrections are less important and can be treated in the lowest approximation, i.e., by including the spin-orbit coupling into the Schrödinger Hamiltonian. We will consider in turn the hyperfine-orbital and the hyperfine-spin interactions.

#### (*a*) *Orbital Interaction*

The Hamiltonian of Eq. (II.1) is modified as follows: $\mathcal{H}_0$ includes the spin-orbit interaction

$$\mathcal{H}_{\mathrm{so}}=(\hbar/4m^2c^2)\boldsymbol{\sigma}\times\boldsymbol{\nabla}(-e\varphi)\cdot\mathbf{p};$$

$\mathcal{H}'$ includes (for non-$s$ states only) the last term of (II.12) but without the convergence factor, i.e.,

$$\mathcal{H}'=\frac{e}{mc}\mathbf{A}'\cdot\left[\mathbf{p}+\frac{\hbar}{4mc^2}\boldsymbol{\sigma}\times\boldsymbol{\nabla}(-e\varphi)\right].\tag{II.13}$$

Again we only treat the short-range part of the interaction in which case $\mathcal{H}'$ is periodic. It is assumed that the energy levels and wave functions of $\mathcal{H}$ have been found to the first order in $\mu$. We note that as a result of the spin-orbit coupling the Bloch states now have an additional energy $\mu E_{n\mathbf{k}\rho;\rho'}{}'$ proportional to $\mu$, which depends on the relative direction of $\boldsymbol{\sigma}$ and $\boldsymbol{\mu}$,

$$\mu E_{n\mathbf{k}\rho;\rho'}{}'=(\psi_{n\mathbf{k}\rho},\mathcal{H}'\psi_{n\mathbf{k}\rho'}),\tag{II.14}$$

where $\rho$ is the spin index of the Bloch state. Both terms of $\mathcal{H}'$ contribute to (II.14) and it is likely, as is the case when $\mathbf{A}'$ is the vector potential of an externally applied field, that the contribution from the first term is by far the most important. In the presence of a magnetic field Eqs. (II.4)–(II.6) are valid, but because of the dependence of the energy on the spin, the Fermi function in Eq. (II.5) is no longer symmetric in the two spin directions. Let us assume that the spin states $\rho$, $\rho'$ have been chosen such that the energy (II.14) is diagonal in $\rho$, and let $E_{n\mathbf{k}\rho}=E_{N\mathbf{k}\rho}{}^{(0)}+\mu\rho\epsilon_{n\mathbf{k}}$, where $E_{n\mathbf{k}\rho}{}^{(0)}$ is the energy in the absence of hyperfine interactions; $\rho$ has the two values ±1 corresponding to the spin directions ↑ and ↓. We rewrite Eq. (II.5), making the summation over $\rho$ explicit, as follows:

$$\begin{aligned}-\mu(\Delta H_1+\Delta H_2)=&\frac{1}{N}\frac{1}{(2\pi)^3}\sum_n\sum_\rho\int\mathcal{H}_{n\rho}{}^{(1)}(\mathbf{k})\\ &\times\left[g[E_{n\mathbf{k}\rho}{}^{(0)}]+\mu\rho\epsilon_{n\mathbf{k}}\frac{\partial g}{\partial E_{n\mathbf{k}\rho}{}^{(0)}}\right]d\mathbf{k}.\end{aligned}\tag{II.15}$$

The field $\Delta H_1$, from the first term on the right is formally given by the same expression as in the no spin-orbit case, i.e., using Eq. (II.7), but with the Bloch states modified by spin-orbit coupling. Let $\mathcal{H}_{\mu n\rho}{}^{(1)}(\mathbf{k})$ denote the part of $\mathcal{H}_{n\rho}{}^{(1)}(\mathbf{k})$ that is linear in $\mu$. From the fact that for fixed $\boldsymbol{\mu}$, $\mathcal{H}'$ changes sign under time reversal, it can easily be shown that $\mathcal{H}_{\mu n\uparrow}{}^{(1)}(\mathbf{k})=\mathcal{H}_{\mu n\downarrow}{}^{(1)}(-\mathbf{k})$. If the crystal has a center of inversion, it is also true that $\mathcal{H}_{\mu n\downarrow}{}^{(1)}(+\mathbf{k})=\mathcal{H}_{\mu n\downarrow}{}^{(1)}(-\mathbf{k})$. It then follows that $\mathcal{H}_\mu{}^{(1)}$ cannot have a term that is linear in the spin-orbit interaction because, such a term being proportional to $\sigma_z$, it would have to be of opposite signs for $\psi_{nk\uparrow}$ and $\psi_{nk\downarrow}$. Thus the spin-orbit corrections to $\Delta H_1$ are of second and higher orders. In contrast, $\Delta H_2$ is of first order in the spin-orbit interaction because $\epsilon_{n\mathbf{k}}=\epsilon_{n-\mathbf{k}}$. Thus for small spin-orbit coupling, it is sufficient in calculating $\Delta H$ to first compute the contribution from the filled states, ignoring spin-orbit interaction and then to calculate the expectation value of $\mathcal{H}'$ [Eq. (II.14)] at the Fermi surface. Using (II.15) and (II.6), we find in this

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[40] H. Kopferman, *Nuclear Moments* (Academic Press Inc., New York, 1958), English translation, p. 199.

approximation:

$$\frac{\Delta H_2}{H}=\frac{2\beta\Omega}{(2\pi)^3}\sum_n\int\epsilon_{n\mathbf{k}}\frac{dS_k}{|\nabla_{\mathbf{k}}E_{n\mathbf{k}}|},\qquad\text{(II.16)}$$

the integral being over the Fermi surface.

Because the spin-orbit coupling in the *d* shells is small compared to the bandwidth, even in the heaviest transition metals, the major part of the effect of spin-orbit interaction will be given by (II.16).

### (*b*) *Spin-Spin Interaction*

The periodic part of the electron-nucleus spin-spin interaction is

$$\mathcal{H}''=\sum_s\beta\boldsymbol{\sigma}\cdot\nabla\boldsymbol{\mu}\cdot\nabla\frac{1}{|\mathbf{r}-\mathbf{R}_S|},\qquad\text{(II.17)}$$

where, as in (II.8), the summation is to be made over lattice points within spherical concentric shells.

In absence of spin-orbit interaction only the electrons with unpaired spin at the Fermi surface contribute. The hyperfine field is then given by an expression identical to (II.16), except that $\epsilon_{n\mathbf{k}}$ is now calculated using $\mathcal{H}''$ instead of $\mathcal{H}'$ in Eq. (II.14). In cubic symmetry, as is well known, this term vanishes; in lower symmetry it is finite but usually small compared to the orbital interaction term.

When spin-orbit interaction is taken into account $\mathcal{H}''$ contributes a hyperfine field even in cubic metals. As in the case of the orbital interaction, this is given by Eq. (II.7), but with the Bloch states determined to first order in the spin-spin interaction. It is informative to examine the character of this contribution in the case of small spin-orbit coupling. To first order in $\mathcal{H}_{\mathrm{so}}$ the expectation value of $\mathcal{H}''$ over a Bloch state is $\mu\sigma_z\epsilon_{n\mathbf{k}}$ and arises from the $\sigma_+$ and $\sigma_-$ terms in $\mathcal{H}_{\mathrm{so}}$ and $\mathcal{H}''$, respectively, according to $[\sigma_+,\sigma_-]=\sigma_z$. The order of magnitude of $\epsilon_{n\mathbf{k}}$ is $\beta\langle 1/r^3\rangle(\mathcal{H}_{\mathrm{so}}/\Delta E)$ where $\Delta E$ is an interband energy and, from (II.16), the corresponding Knight shift is of order

$$\frac{\Delta H_2{}^{(s)}}{H}\sim\Omega N(\zeta)\beta^2\left(\frac{1}{r^3}\right)\frac{\mathcal{H}_{\mathrm{so}}}{\Delta E}.\qquad\text{(II.18)}$$

In addition the filled part of the band also contributes in this order. Since $\mathcal{H}''$ and $\mathcal{H}'$ behave in the same way under time-reversal, the argument following Eq. (II.15) is applicable to $\mathcal{H}''$ and hence $\mathcal{H}_{\mu n\uparrow}{}^{(1)}(-\mathbf{k})=\mathcal{H}_{\mu n\downarrow}{}^{(1)}(\mathbf{k})$. However, in contrast with the orbital case, there is no reason why this should vanish because it includes a term that is even in $\sigma_z$. In the case of a paramagnetic ion this would be written as $\lambda\mu_z l_z$ where $\lambda$ is of the order of $\epsilon_{n\mathbf{k}}$ given above. It arises as a cross term in the elimination of the $\sigma_z$ components of $\mathcal{H}''$ and $\mathcal{H}_{\mathrm{so}}$. $\langle l_z\rangle$ vanishes in the absence of an external field but in its presence it gives rise to a Knight shift,

$$\Delta H_1{}^{(s)}/H\sim\beta^2\langle 1/r^3\rangle\mathcal{H}_{\mathrm{so}}/(\Delta E)^2.\qquad\text{(II.19)}$$

This is of the same order as (II.18), except when the density of states at the Fermi surface is large.

## III. SPIN SUSCEPTIBILITY AND SUPERCONDUCTIVITY OF AN ELECTRON GAS

The Pauli spin susceptibility of a noninteracting electron gas is given by the well-known formula $\chi=\frac{1}{2}g^2\beta^2N(E_f)$, where $\beta$ is the Bohr magneton and $N(E_f)$ is the density of states at the Fermi surface. In the case of Coulomb interaction between the electrons the susceptibility is enhanced by exchange. In this case a useful approximation to $\chi$ has been obtained by Wolff[41] using the random-phase approximation. If the interparticle potential is $G(r-r')$, then the interaction term in the Hamiltonian is

$$H_{\mathrm{int}}=-\frac{1}{2\nu}\sum_{\mathbf{k}\mathbf{k}'\mathbf{q}\sigma\sigma'}G(\mathbf{k}-\mathbf{k}')c_{\mathbf{k},\sigma}{}^*c_{\mathbf{k}'+\mathbf{q},\sigma'}{}^*c_{\mathbf{k}',\sigma}c_{\mathbf{k}+\mathbf{q},\sigma'},\qquad\text{(III.1)}$$

where

$$G(\mathbf{k}-\mathbf{k}')=\int e^{-i\mathbf{k}'\cdot\mathbf{r}}G(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r},\qquad\text{(III.2)}$$

and $\nu$ is the sample volume. In this case Wolff finds for the uniform susceptibility

$$\chi=\frac{\frac{1}{2}g^2\beta^2N(E_f)}{1-N(E_f)(1/4\pi)\int G(\mathbf{k}_f-\mathbf{k}_f')d\Omega'},\qquad\text{(III.3)}$$

where $\mathbf{k}_f$ and $\mathbf{k}_f'$ lie on the Fermi surface and $d\Omega'$ is the element of solid angle centered on $\mathbf{k}_f'$. $N(E_f)$ is now the density of states per unit volume corrected for the exchange self-energy according to the relation

$$E_{\mathbf{k}}=E_{0\mathbf{k}}-\frac{1}{8\pi^3}\int G(\mathbf{k}-\mathbf{k}')d\mathbf{k}',\qquad\text{(III.4)}$$

where $E_{0\mathbf{k}}$ is the free electron energy. If $G(\mathbf{r})$ is represented by a screened Coulomb potential

$$G(\mathbf{r})=(e^2/r)e^{-\alpha r},\qquad\text{(III.5)}$$

then

$$G(\mathbf{k}-\mathbf{k}')=4\pi e^2/(|\mathbf{k}-\mathbf{k}'|^2+\alpha^2).\qquad\text{(III.6)}$$

The Thomas-Fermi approximation for $\alpha$ is $\alpha^2=8\pi e^2N(E_f)$ which gives

$$\left(\frac{\alpha}{k_f}\right)^2=\left(\frac{24}{\pi}\right)^{1/3}\frac{e^2/a}{E_f},\qquad\text{(III.7)}$$

where $a$ is the average distance between electrons. For values of $a$ and $E_f$ encountered in a $d$-band metal $\alpha$ is of order $4k_f$.

In the case of metals that are superconductors, the lattice-induced interactions introduce an attractive potential between the electrons. If retardation effects are ignored, the interaction Hamiltonian may be written[42]

$$H_{\mathrm{int}}=-\frac{1}{2\nu}\sum_{\mathbf{k}\mathbf{k}'\mathbf{q}\sigma\sigma'}G(\mathbf{k},\mathbf{k}')c_{\mathbf{k},\sigma}{}^*c_{\mathbf{k}'+\mathbf{q},\sigma'}{}^*c_{\mathbf{k}',\sigma}c_{\mathbf{k}+\mathbf{q},\sigma'},\qquad\text{(III.8)}$$

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[41] P. A. Wolff, Phys. Rev. **120**, 814 (1960).

[42] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

where

$$G(\mathbf{k},\mathbf{k}')=\frac{2g^2(\hbar\omega_{\mathbf{k}-\mathbf{k}'})^2}{(E_{\mathbf{k}}-E_{\mathbf{k}'})^2-(\hbar\omega_{\mathbf{k}-\mathbf{k}'})^2}+\frac{4\pi e^2}{|\mathbf{k}-\mathbf{k}'|^2+\alpha^2}. \tag{III.9}$$

$G(\mathbf{k},\mathbf{k}')$ is no longer solely dependent on $\mathbf{k}-\mathbf{k}'$ but is still independent of their absolute orientation.

A procedure exactly similar to that followed by Wolff[41] gives for the spin susceptibility

$$\chi=\frac{\frac{1}{2}g^2\beta^2N(E_f)}{1-N(E_f)(1/4\pi)\int G(\mathbf{k}_f,\mathbf{k}_f')d\Omega'}, \tag{III.10}$$

with $N(E_f)$ corrected for the exchange self-energy.

$$E_{\mathbf{k}}=E_{0\mathbf{k}}-(1/8\pi^3)\int G(\mathbf{k},\mathbf{k}')d\mathbf{k}'. \tag{III.11}$$

Let us define a quantity $\chi_{\text{sp.ht.}}=\frac{1}{2}g^2\beta^2N(E_f)$ which is a measure, in susceptibility units, of the density of states for the interacting gas, as would be determined by an experimental measurement of specific heat. The susceptibility will then be given by

$$\chi=\frac{\chi_{\text{sp.ht.}}}{1-N(E_f)\frac{1}{4\pi}\int G(\mathbf{k}_f,\mathbf{k}_f')d\Omega'}. \tag{III.12}$$

If we represent the phonon spectrum by the ionic-plasma frequency screened by the electron dielectric constant, we get $g^2=2\pi e^2/(|\mathbf{k}-\mathbf{k}'|^2+\alpha^2)$. Then from Eq. (III.9) we find

$$\frac{1}{4\pi}\int G(\mathbf{k}_f,\mathbf{k}_f)d\Omega'=-\frac{\pi e^2}{k_f^2}\ln\left[1+\left(\frac{k_D}{\alpha}\right)^2\right]+\frac{\pi e^2}{k_f^2}\ln\left[1+\left(\frac{2k_f}{\alpha}\right)^2\right], \tag{III.13}$$

where $k_D$ is the Debye cutoff for the phonons. Compared to $\chi_{\text{sp.ht.}}$, $\chi$ is thus reduced by the electron-phonon interaction and increased by the electron-electron interaction.

Since the density of states at the Fermi level can be written as $N(E_f)=(k_f^2/2\pi^2)(dk/dE)_{E_f}$, we have

$$N(E_f)=\frac{N_0(E_f)}{1-\left(\frac{\partial E_{0k}}{\partial k}\right)_{E_f}^{-1}\left[\frac{\partial}{\partial k}\frac{1}{8\pi^3}\int G(\mathbf{k},\mathbf{k}')d\mathbf{k}'\right]_{E_f}}. \tag{III.14}$$

If we define $\chi_0=\frac{1}{2}g^2\beta^2N_0(E_f)$ to be the susceptibility of the noninteracting electron gas, we have

$$\chi=\left[1-\left(\frac{\partial E_{0k}}{\partial k}\right)_{E_f}^{-1}\left(\frac{\partial}{\partial k}\frac{1}{8\pi^3}\int G(\mathbf{k},\mathbf{k}')d\mathbf{k}'\right)_{E_f}-N_0(E_f)\frac{1}{4\pi}\int G(\mathbf{k}_f,\mathbf{k}_f')d\Omega'\right]^{-1}\chi_0. \tag{III.15}$$

From Eq. (III.9) we obtain

$$\left[\frac{\partial}{\partial k}\frac{1}{8\pi^3}\int G(\mathbf{k},\mathbf{k}')\right]_{E_f}=\frac{e^2}{2\pi}\ln\left[1+\left(\frac{k_D}{\alpha}\right)^2\right]+\frac{e^2}{\pi}\left\{1-\frac{1}{2}\left[1+2\left(\frac{\alpha}{2k_f}\right)^2\right]\ln\left[1+\left(\frac{2k_f}{\alpha}\right)^2\right]\right\}. \tag{III.16}$$

If Eqs. (III.16) and (III.13) are substituted into Eq. (III.15) we obtain

$$\chi=\left(1-N_0(E_f)\frac{2\pi e^2}{k_f^2}\left\{1-\left(\frac{\alpha}{2k_f}\right)^2\ln\left[1+\left(\frac{2k_f}{\alpha}\right)^2\right]\right\}\right)^{-1}\chi_0. \tag{III.17}$$

Thus the electron-phonon interaction does not change the susceptibility of the noninteracting gas, as noted by Quinn.[43] $\chi$ however is always enhanced above $\chi_0$ by the electron-electron interaction.

If the susceptibility of the interacting electron gas is calculated thermodynamically taking account of the exchange self-energy, Eq. (III.11), one easily obtains

$$\chi=\left(1-\left(\frac{\partial E_{0k}}{\partial k}\right)_{E_f}^{-1}\frac{\partial}{\partial k_f}\left[\frac{1}{8\pi^3}\int G(\mathbf{k}_f,\mathbf{k}')d\mathbf{k}'\right]\right)^{-1}\chi_0. \tag{III.18}$$

As must necessarily be the case this is identical with Eq. (III.15).

In the BCS theory of superconductivity[42] the temperature-dependent energy gap $\Delta_k$ is given by the integral equation

$$\Delta_k=-\frac{1}{16\pi^3}\int\frac{G(\mathbf{k},\mathbf{k}')(1-2f_{\mathbf{k}'})\Delta_{\mathbf{k}'}}{e_{\mathbf{k}'}} \tag{III.19}$$

where $f_k=[\exp(e_k/kT)+1]^{-1}$ and $e_k=(E_k^2+\Delta_k^2)^{1/2}$. In the simplest form of the theory, $G(\mathbf{k},\mathbf{k}')$ is replaced by its average value over the Fermi surface. If $V=-(1/4\pi)\int G(\mathbf{k}_f,\mathbf{k}_f')d\Omega'$ and the integral is carried over an energy range $\hbar\omega_D$ above and below the Fermi level, one finds the BCS formulas,

$$\sinh\frac{1}{N(E_f)V}=\frac{\hbar\omega_D}{\Delta}, \tag{III.20}$$

and

$$kT_c=1.14\hbar\omega_De^{-1/N(E_f)V}. \tag{III.21}$$

Restating Eq. (III.12) in terms of $V$ we have

$$\chi=\frac{\chi_{\text{sp.ht.}}}{1+N(E_f)V}, \tag{III.22}$$

so that the same quantity $N(E_f)V$ appears in both Eqs. (III.20) and (III.21), and Eq. (III.22).

Recognizing the shortcomings of the simple BCS theory which neglects retardation effects, and overlooking the crude treatment of the gap equation which leads to Eqs. (III.20) and (III.21), it is still interesting

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[43] J. J. Quinn in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (J. Wiley & Sons, Inc., New York, 1960).

to see if any experimental relations exist between the susceptibilities and superconducting transition temperatures such as those suggested by Eqs. (III.21) and (III.22). We have, in fact, evidence[1] which shows that $\chi$ for the intermetallic compounds $V_3Si$ and $V_3Ga$, and the metal vanadium, is less than $\chi_{\mathrm{sp.ht.}}$ in approximately the degree predicted by Eq. (III.22) and the observed transition temperatures. In the case of Pt metal discussed in this paper for which we find $\chi > \chi_{\mathrm{sp.ht.}}$, we conclude that $N(E_f)V$ is negative. According to Eq. (III.20), no energy gap would then exist at absolute zero and we would conclude that Pt would not be a superconductor at any temperature. Thus if superconductivity exists it must arise from considerations not included in the simple BCS theory.[44]

## CONCLUSIONS

It has been shown that a consistent interpretation of the Knight shift and susceptibility in platinum metal may be given and that the contributions to each from spin and orbit may be separated. The dominant contribution to $K$ is that of core polarization resulting from the spins of $d$-band electrons. Both the orbital and $s$-electron paramagnetism are small as a result of the small number of $s$ electrons and $d$ holes. To construct our $K$ versus $\chi$ diagram (Fig. 2) we have used a free-electron estimate for the $s$-electron susceptibility neglecting $s$-$s$ and $s$-$d$ interactions. Since both $\chi_{VV}$ and $\chi_P^s$ are positive, our graphical procedure puts an upper bound on both, from which we conclude that neither one can be increased by more than a factor of 2 from the values given. The relative value of orbital and spin contributions in platinum as compared with those in vanadium is clearly consistent with the position of the Fermi level in the $d$ band in each case.

Spin-orbit coupling, which might be thought to be important for the heavy transition metals, has been seen to have a minor effect on the band parameters determined from an analysis of the susceptibility and electronic specific heat.

In Sec. II we have given a formal treatment of the orbital and dipolar hyperfine fields in transition metals including the effects of spin-orbit coupling. The result is obtained in a form particularly suitable for calculations in the tight binding approximation which should be adequate for the $d$ electrons in these metals.

The last section shows that the quantity $N(E_f)V$, which determines the energy gap and transition temperature in the BCS theory, also determines, in the random phase approximation the relation between the measured density of states $N(E_f)$, and the measured spin paramagnetism. Within these approximations, for $V$ positive, a finite energy gap exists and $\chi < \chi_{\mathrm{sp.ht.}}$, whereas, for $V$ negative, no energy gap exists and $\chi > \chi_{\mathrm{sp.ht.}}$. Since, for Pt $\chi \sim 2\chi_{\mathrm{sp.ht.}}$ our theory predicts it not to be superconducting.

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[44] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958), [English transl.: Soviet Physics—JETP **7**, 505 (1958)]. G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **38**, 966 (1960), [English transl.: Soviet Physics—JETP **11**, 696 (1960)]. P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

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# Faraday Rotations of Divalent Rare-Earth Ions in Fluorides. III*

Y. R. Shen
*Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts*

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A large rotatory power for $Eu^{2+}$ in cubic fluoride lattices has been observed in the visible range. At frequencies sufficiently removed from the absorption bands, the rotation is proportional to the magnetization. This suggests that the upper levels in the allowed optical transitions are of the $P_J$ character. Measurements on $CaF_2$ and $SrF_2$ crystals doped with very low concentrations of Eu ($\sim$0.005%) also suggest some possible structure for the strong, sharp characteristic line of $Eu^{2+}$ near 4000 Å. The rotatory powers of several other divalent rare-earth ions in fluorides have also been measured.

In a previous paper,[1] we reported results of rotation measurements on several rare-earth ions in $CaF_2$. In particular, we found that the divalent europium ion ($Eu^{2+}$) in $CaF_2$ has enormous rotatory power, which appears proportional to the magnetization at frequencies sufficiently removed from the absorption bands. These facts are well explained theoretically.[2] Van Vleck and Penney[3] first suggested that for $S$-state ions in a cubic field, both $S_J$ and $P_{J'}$ levels in the allowed $S_J \rightarrow P_{J'}$ transitions are only slightly perturbed, and hence the rotation should be proportional to the magnetization.

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[1] Y. R. Shen and N. Bloembergen, Phys. Rev. **133**, A515 (1964).

[2] Y. R. Shen, Phys. Rev. **133**, A511 (1964).

[3] J. H. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934).