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g Shift of Conduction Electrons in Sodium

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A simple procedure for estimating the wave-vector-dependent g shift of conduction electrons in sodium metal is described. The conduction-electron wave functions are approximated by single orthogonalized plane waves (SOPW), orthogonal to the $2p$, $2s$, and $1s$ ion-core wave functions. All the core wave functions are determined variationally in terms of a two-parameter ion-core potential. The binding energy and spin-orbit splitting of the $2p$ core state are adjusted to experimental values. It is found that the core functions have negligible amplitude at the boundary of the cellular polyhedron. The g shift is then approximately given by $2/\hbar$ times the expectation value of the orbital angular momentum in a unit cell, plus two small relativistic terms. The calculated Fermi-surface average of the g shift is -5×10^{-4}. Since the experimental values are $(-6\pm2)\times10^{-4}$, $(-8\pm2)\times10^{-4}$, and $(-10\pm2)\times10^{-4}$, it is concluded that a large part of the g shift in sodium can be accounted for by using the SOPW method.

I. INTRODUCTION

The g shift of conduction electrons in metals is caused by the spin-orbit interaction with the periodic crystal potential. The theory of this effect was initiated by Yafet,[1] reformulated, and generalized by Roth[2] and by Blount,[3] and recently simplified and corrected by the present authors.[4] According to this theory, the expression for the wave-vector-dependent g shift in metals with inversion symmetry can conveniently be divided in three parts, in previous work[4] denoted by $(\delta g)'$, $(\delta g)''$, and $(\delta g)^P$, respectively. We shall give, for completeness, the explicit expressions of these three contributions to the g shift. The first part is

$$(\delta g)' = (2mc^2)^{-1}\int_\Omega \left(x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y}\right)\psi^\dagger\psi\, d^3r\ , \quad (1)$$

which represents the contribution of the spin-dependent part of the velocity operator, namely, $(\hbar/4m^2c^2)\vec{\sigma}\times(\vec{\nabla}V)$, to the expectation value of the z component of the orbital angular momentum (times $2/\hbar$) in the crystalline unit cell Ω. Here, V is the crystal potential, and $\psi=\psi_{\vec{k}\uparrow}$ is the wave function of a conduction electron with wave vector $\vec{k}$ and spin direction ↑. The second part is the relativistic contribution

$$(\delta g)'' = -(m^2c^2)^{-1}\int_\Omega \psi^\dagger\vec{p}^{\,2}\psi\, d^3r\ , \quad (2)$$

where $\vec{p}$ is the momentum. This term was first crudely estimated by Yafet,[1] and was believed to be negligibly small. However, it has recently been shown that this term contributes significantly to the g shift in lithium.[4] It will be shown that also in sodium $(\delta g)''$ dominates $(\delta g)'$ and still contributes about 10% of the total g shift. Finally, the last part is given by

$$(\delta g)^P = (2/\hbar)\int_\Omega \psi^\dagger (xp^y - yp^x)\psi\, d^3r + S \ , \qquad (3)$$

where S stands for terms containing integrals over the surface of the cellular polyhedron. The term containing the volume integral is $2/\hbar$ times the expectation value of the z component of $\vec{r}\times\vec{p}$ in the unit cell. Actually, there are two other terms. One of these, δg^α, makes the wave-vector-dependent g shift independent of the choice of phase of the conduction-electron wave function. Since the Fermi-surface average of δg^α is always zero, it need not be considered here.[4] The other term, $\delta g'''$, corresponds to the average tilt of the intrinsic magnetic moment of the conduction electron and is at least second order in spin-orbit coupling. Since we calculate the g shift only to first order in spin-orbit coupling, $\delta g'''$ will also not be retained.

The first theoretical estimate of the g shift in sodium metal was given by Yafet.[5] He calculated $(\delta g)^P - S$, Eq. (3), using the Bardeen method including spin-orbit-coupling effects. The result was $(\delta g)^P - S = (-3.7\sin^2\theta_0)\times 10^{-4}$, where θ_0 is the angle between the Fermi wave vector $\vec{k}_F$ and the applied magnetic field. The corresponding Fermi-surface average is -2.5×10^{-4}. Brooks[6] calculated the same term using the quantum defect method. He obtained $(\delta g)^P - S = (-3.2\sin^2\theta_0)\times 10^{-4}$, the Fermi-surface average being -2.1×10^{-4}. The most complete calculation, however, has been reported by Bienenstock and Brooks,[7] also using the quantum defect method. These authors calculated in four ways the Fermi-surface average of $(\delta g)^P$, Eq. (3), see Table I. For $(\delta g)'$ they obtain 0.6×10^{-5}.[8] The contribution $(\delta g)''$, Eq. (2), was, however, not included in their calculation. In Table I we summarize the results of the various theoretical calculations. These may be compared with the values[9–11] as obtained from conduction-electron spin-resonance experiments: $(6\pm 2)\times 10^{-4}$, $(-8\pm 2)\times 10^{-4}$, and $(-10\pm 2)\times 10^{-4}$. The results of the calculation to be described in the present paper have also been included.

The agreement between theory and experiment is rather good, and another attempt to calculate the g shift in sodium seems hardly warranted. However, the derivations and computations underlying the treatment of Bienenstock and Brooks are so complex that no real understanding of the g shift in sodium can readily be gained from their work. The purpose of the present paper is to describe a simple method of estimating the g shift, which is nevertheless capable of giving reasonably accurate results.

TABLE I. Summary of g-shift calculations in sodium. Only averages over the Fermi surface are shown.

δg^P (10^{-4})	$(\delta g)'$ (10^{-4})	$(\delta g)''$ (10^{-4})	Ref.
-2.5	...	...	5
-2.1	...	...	6
-4.6 to -7.0	0.06	...	7
-4.5	0.11	-0.56	Present work

Our method is based on the observation that the spin-orbit interaction is strongest for electrons in the ion cores. This suggests that one would obtain a simple physical theory of the g shift in sodium by approximating the conduction-electron wave functions by single orthogonalized plane waves (SOPW), orthogonal to the $1s$, $2s$, and $2p$ core states. It will be shown that this is indeed the case. The core wave functions are determined by a procedure which will be described in detail in Sec. II. It is found that the amplitude of the core wave functions is negligible at the crystalline cell boundary. Therefore, the contribution of S, Eq. (3), can be neglected for our SOPW wave function. (For exact Bloch functions, S may not be negligible.) Once the core wave functions are known $(\delta g)'$, $(\delta g)''$, and $(\delta g)^P$ can be calculated as a function of wave vector $\vec{k}$. The quantity to be compared with the experimentally measured g shift is then the Fermi-surface average of the sum of Eqs. (1)–(3). The g shift of a conduction electron with Fermi wave vector $\vec{k}_F$ is found to be (Sec. III)

$$\delta g(\vec{k}_F) = -(0.5 + 6.7\sin^2\theta_0)\times 10^{-4} \ . \qquad (4)$$

The $\vec{k}_F$-dependent $\sin^2\theta_0$ term is due to $(\delta g)^P - S$, Eq. (3), whereas the small constant term is the contribution of $(\delta g)'$ and $(\delta g)''$, Eqs. (1) and (2). The Fermi-surface average of Eq. (4) is -5.0×10^{-4}, which is to be compared with the experimental shifts $\delta g = (-6\pm 2)\times 10^{-4}$ to $(-10\pm 2)\times 10^{-4}$. We conclude that a major part of the g shift in sodium can be understood by using the SOPW method.

II. CONDUCTION-ELECTRON WAVE FUNCTIONS

The conduction-electron wave functions needed to estimate numerically Eqs. (1)–(3) will be approximated by SOPW, orthogonal to the $1s$, $2s$, and $2p$ core states. As indicated in the Introduction, we need only the wave function of a conduction electron with spin predominantly in the direction of quantization, i.e., the z direction. The Hamiltonian of a conduction electron moving in a periodic potential $V(\vec{r})$ is

$$\mathcal{H} = p^2/2m + V(\vec{r}) + (\hbar/4m^2c^2)[\vec{\sigma}\times(\vec{\nabla}V)]\cdot\vec{p} \ , \qquad (5)$$

where the last term is the spin-orbit-coupling energy. Since the Hamiltonian depends explicitly on the Pauli spin operator $\vec{\sigma}$, the wave functions will be two-component spinors. The conduction-electron wave function of a conduction electron with wave vector $\vec{k}$ and spin predominantly up (designated by ↑) is then written as

$$\psi_{\vec{k}\uparrow}(\vec{r}) = N(\vec{k})\Big[e^{i\vec{k}\cdot\vec{r}}\begin{pmatrix}1\\0\end{pmatrix} - \sum_{n,s_z} \beta_{n,s_z}(\vec{k})\chi_{n,s_z}(\vec{r}) - \sum_{j,j_z} \alpha_{j,j_z}(\vec{k})\,\phi_{j,j_z}(\vec{r})\Big] , \tag{6}$$

where the functions $\chi_{n,s_z}(\vec{r})$ and $\phi_{j,j_z}(\vec{r})$ are the two-component core wave functions. The factor $N(\vec{k})$ normalizes $\psi_{\vec{k}\uparrow}$ in a unit cell. The coefficients $\alpha_{j,j_z}(\vec{k})$ and $\beta_{n,s_z}(\vec{k})$ are determined by the requirement that $\psi_{\vec{k}\uparrow}$ be orthogonal to all the core wave functions, i.e.,

$$\alpha_{j,j_z}(\vec{k}) = \int e^{i\vec{k}\cdot\vec{r}}\phi^{\dagger}_{j,j_z}(\vec{r})\begin{pmatrix}1\\0\end{pmatrix} d^3r \tag{7a}$$

and

$$\beta_{n,s_z}(\vec{k}) = \int e^{i\vec{k}\cdot\vec{r}}\chi^{\dagger}_{n,s_z}(\vec{r})\begin{pmatrix}1\\0\end{pmatrix} d^3r \ . \tag{7b}$$

The index n refers to the 1s and 2s states, and s_z is the expectation value of the z component of the spin angular momentum $\vec{S}$. The 1s and 2s core states are characterized by $s_z = \pm\frac{1}{2}$ (in units of $\hbar$). Since the spin-orbit interaction is large, one has to employ 2p two-component core wave functions which are eigenfunctions of $(\vec{L}+\vec{S})^2$ and $(L_z + S_z)$, $\vec{L}$ being the orbital angular momentum operator. The indices j and j_z are the total angular momentum quantum numbers. The 2p core states are then characterized by $j = \frac{1}{2}$ and $j_z = \pm\frac{1}{2}$, and $j = \frac{1}{2}$ and $j_z = \pm\frac{3}{2}$, $\pm\frac{1}{2}$. The $j = \frac{1}{2}$ and $j = \frac{3}{2}$ 2p core states are separated by the spin-orbit energy. We denote the normalized 1s and 2s core functions by $R_1(r)$ and $R_2(r)$, respectively. The normalized orbital parts of the $j = \frac{1}{2}$ and $j = \frac{3}{2}$ 2p core functions are denoted by $R_{1/2}(r)$ and $R_{3/2}(r)$, respectively. Of course, the orbital parts of the core wave functions will not depend on s_z or j_z. But the orbital function $R_{1/2}(r)$ will be different from the orbital function $R_{3/2}(r)$ on account of the spin-orbit splitting of the $j = \frac{1}{2}$ and $j = \frac{3}{2}$ states. The correct normalized two-component functions $\chi_{n,s_z}(\vec{r})$ and $\phi_{j,jz}(\vec{r})$, to be used in Eqs. (6), (7a), and (7b), are[12]

$$\chi_{1,1/2}(\vec{r}) = R_1(r)\begin{pmatrix}1\\0\end{pmatrix}, \quad \chi_{1,-1/2}(\vec{r}) = R_1(r)\begin{pmatrix}0\\1\end{pmatrix},$$

$$\chi_{2,1/2}(\vec{r}) = R_2(r)\begin{pmatrix}0\\1\end{pmatrix}, \quad \chi_{2,-1/2}(\vec{r}) = R_2(r)\begin{pmatrix}0\\1\end{pmatrix},$$

$$\phi_{1/2,1/2}(\vec{r}) = \frac{1}{\sqrt{3}} R_{1/2}(r)\begin{pmatrix}-Y_0\\ \sqrt{2}\,Y_{+1}\end{pmatrix},$$

$$\phi_{1/2,-1/2}(\vec{r}) = \frac{1}{\sqrt{3}} R_{1/2}(r)\begin{pmatrix}-\sqrt{2}\,Y_{-1}\\ Y_0\end{pmatrix},$$

$$\phi_{3/2,1/2}(\vec{r}) = \frac{1}{\sqrt{3}} R_{3/2}(r)\begin{pmatrix}\sqrt{2}\,Y_0\\ +Y_{+1}\end{pmatrix},$$

$$\phi_{3/2,-1/2}(\vec{r}) = \frac{1}{\sqrt{3}} R_{3/2}(r)\begin{pmatrix}-Y_{-1}\\ -\sqrt{2}\,Y_0\end{pmatrix},$$

$$\phi_{3/2,3/2}(\vec{r}) = R_{3/2}(r)\begin{pmatrix}Y_{+1}\\ 0\end{pmatrix},$$

$$\phi_{3/2,-3/2}(\vec{r}) = R_{3/2}(r)\begin{pmatrix}0\\ Y_{-1}\end{pmatrix} . \tag{8}$$

Here, $Y_{+1} = -(3/8\pi)^{1/2}\sin\theta\, e^{+i\phi}$, $Y_{-1} = (3/8\pi)^{1/2} \times\sin\theta\, e^{-i\phi}$, and $Y_0 = (3/4\pi)^{1/2}\cos\theta$ are normalized spherical harmonics, which describe the angular dependence of 2p atomic wave functions.

The purpose of the rest of this section is to determine $R_1(r)$, $R_2(r)$, $R_{1/2}(r)$, and $R_{3/2}(r)$, which are necessary to specify the wave function $\psi_{\vec{k}\uparrow}(\vec{r})$ completely. The potential appearing in the Hamiltonian, Eq. (5), will be assumed to have the form

$$V(r) = -2e^2/r - (\lambda e^2/r)e^{-\mu r} \ . \tag{9}$$

The first term represents the potential of two nuclear charges, whereas the second term is the potential due to λ nuclear charges, screened by the ion-core electrons (except the one we are considering). Ideally, λ would be nine in sodium, so that the potential close to the nucleus is due to just eleven nuclear charges. The parameters λ and μ are determined by fitting experimental data. Accordingly, $V(r)$ is phenomenological, and includes Hartree, exchange, and correlation contributions. It is found that $\lambda = 10.12$, which is reasonably close to the ideal value. Next, we assume that R_1, R_2, $R_{1/2}$, and $R_{3/2}$ have the form

$$\begin{aligned} R_1(r) &= N_1 e^{-Z_1 r/2} ,\\ R_2(r) &= N_2(e^{-Z_2 r/2} + t_2 r\, e^{-U_2 r/2}) ,\\ R_{1/2}(r) &= N_{1/2}\, r\,(e^{-Z_{1/2} r/2} + t_{1/2}\, e^{-U_{1/2} r/2}) ,\\ R_{3/2}(r) &= N_{3/2}\, r(e^{-Z_{3/2} r/2} + t_{3/2}\, e^{-U_{3/2} r/2}) \ . \end{aligned} \tag{10}$$

Here, N_1, N_2, $N_{1/2}$, and $N_{3/2}$ are normalizing factors. With the potential, Eq. (9), the spin-orbit energy to be used in the Hamiltonian, Eq. (5), takes the form

$$\mathcal{H}_{so} = (2m^2c^2)^{-1}\frac{1}{r}\frac{dV}{dr}\vec{L}\cdot\vec{S} \ . \tag{11}$$

We now calculate the expectation values of the Hamiltonian, Eq. (5), for the wave functions appearing in Eq. (8). These expectation values do not depend on s_z or j_z. They will be denoted by $E_i (i = 1, 2, \frac{1}{2}, \frac{3}{2})$, and are functions of the wave-function parameters Z_i, U_i, and t_i, and of the potential parameters λ and μ, hence, $E_i = E_i(Z_i, U_i, t_i; \lambda, \mu)$.

The functions E_i are minimized with respect to Z_i, U_i, and t_i, for each set of values of λ and μ. The parameters λ and μ are then chosen such that $E_{1/2}$ ($\approx E_{3/2}$) agrees with the experimental binding energy of the $2p$ state in sodium metal, and such that $E_{3/2} - E_{1/2}$ equals the experimental spin-orbit splitting of the $2p$ ion-core state. For $E_{3/2}$($\approx E_{1/2}$) we have used the value -2.45 Ry, which is equal to the sum of the x-ray absorption threshold[13] and the work function.[14] $E_{3/2} - E_{1/2} = 1.24\times10^{-2}$ Ry was obtained from spectroscopic data.[15] We find that $\lambda = 10.12$ and $\mu = 3.40$ (inverse Bohr radii). We do not display the explicit expressions for $E_i(Z_i, U_i, t_i; \lambda, \mu)$, since they are rather lengthy and not particularly illuminating. Finally, we collect in Table II all the wave-function parameters obtained in the way described above.

It should be noted that t_2 is not an independent parameter, but follows from the requirement that R_1 and R_2 be orthogonal,

$$t_2 = -\tfrac{1}{6}(Z_1 + U_2)^4/(Z_1 + Z_2)^3 \quad .$$

Finally, we wish to point out that we still have an independent check on the core wave functions R_1 and R_2 at our disposal. Namely, using the parameters of Table II, we can compute E_1 and E_2. We find that

$$E_1 = -90 \text{ Ry and } E_2 = -4.89 \text{ Ry} \;,$$

in good agreement with the experimental binding energies of the $1s$ and $2s$ core states in the metal, -78.98 and -4.82 Ry, respectively.[13]

Having determined the conduction-electron wave function $\psi_{\vec k\uparrow}(\vec r)$, we are in a position to calculate Eqs. (1)–(3), and hence, the g shift. This will be done in Sec. III.

III. g SHIFT

We first direct our attention to the calculation of $(\delta g)'$, Eq. (1), and $(\delta g)''$, Eq. (2). It has recently been shown that the sum of these two contributions reduces correctly to the g shift of an atomic S state in the tight-binding limit.[4] It is worthwhile to recall at this point that the general theory, on which our calculations are based, is valid only for electrons in a band that is not degenerate (except for spin), in a crystal possessing inversion symmetry. Sodium metal satisfies this requirement. It is clear that also in the metal, $(\delta g)'$ and $(\delta g)''$ are different from zero in the absence of spin-orbit coupling.

TABLE II. Core wave-function parameters. Z_i, U_i, and t_i are in inverse Bohr radii.

i	Z_i	U_i	t_i
1	23.344	...	0
2	22.228	6.781	-3.319
$\frac{1}{2}$	11.589	4.461	0.2159
$\frac{3}{2}$	11.514	4.436	0.2155

Since the g shift we are computing is rather small, we need to carry out our numerical calculations only to first order in spin-orbit coupling. We will now show that there is no first-order contribution to $(\delta g)'$ and $(\delta g)''$. It is therefore sufficient to calculate these two terms in the absence of spin-orbit coupling. The proof makes use of the fact that, in the absence of spin-orbit coupling, the periodic part of the Bloch function of an electron in a crystal with inversion symmetry is the sum of a real even function $\mathcal{E}(\vec r)$ and i times a real odd function $\mathcal{O}(\vec r)$. It can then easily be shown that, to first order in spin-orbit coupling, the periodic part of the Bloch function of an electron with spin direction $\uparrow$ is given by

$$u_\uparrow(\vec r) = [\mathcal{E}(\vec r) + i\,\mathcal{O}(\vec r)] + i[\delta\mathcal{E}(\vec r) + i\delta\,\mathcal{O}(\vec r)] \;, \tag{12}$$

where $\delta\mathcal{E}$ and $\delta\mathcal{O}$ are again a real even and a real odd function, respectively. In arriving at Eq. (12), we have made use of first-order perturbation theory, treating the spin-orbit energy, i.e., the last term of the Hamiltonian $\mathcal{H}$, Eq. (5), as a perturbation. Next one must realize that $V(\vec r)$ is an even function in a crystal with inversion symmetry, so that $x\partial V/\partial x$ and $y\partial V/\partial y$ are even functions. The origin of coordinates must be taken at the center of the crystalline unit cell. Then, upon substituting Eq. (12) in Eqs. (1) and (2), one immediately verifies that all first-order terms vanish, thus proving the desired result.

Thus, as far as the calculation of $(\delta g)'$ and $(\delta g)''$ is concerned only the zeroth-order (spin-orbit-coupling-independent) part of $\psi_{\vec k\uparrow}(\vec r)$, Eq. (6), needs to be used. The zeroth-order conduction-electron wave function takes then the form

$$\psi^0_{\vec k\uparrow}(\vec r) = N^0(\vec k)\left[e^{i\vec k\cdot\vec r}\begin{pmatrix}1\\0\end{pmatrix} - \sum_{n,s_z}\beta_{n,s_z}(\vec k)\chi_{n,s_z}(\vec r) - \sum_{m} \alpha_m(\vec k)\,\phi_m(\vec r)\right] , \tag{13}$$

where the index m can have the values 0, +1, or −1. The $2p$ core functions $\phi_m(\vec r)$ are now eigenfunctions of $\vec L^2$ and L_z, and are given by

$$\phi_m(\vec r) = R_p(r)\,Y_m(\theta,\phi)\begin{pmatrix}1\\0\end{pmatrix} , \tag{14}$$

where $R_p(r)$ equals the zeroth-order part of $R_{1/2}$ or $R_{3/2}$. The coefficients

$$\alpha_m(\vec k) = \int e^{i\vec k\cdot\vec r}\phi_m^\dagger(\vec r)\begin{pmatrix}1\\0\end{pmatrix} d^3r \tag{15}$$

ensure that $\psi^0_{\vec{k}\uparrow}(\vec{r})$ is orthogonal to the $2p$ core functions $\phi_m(\vec{r})$.

The potential $V(r)$, Eq. (9), is not realistic near the boundary of the crystalline unit cell. This is indicated by the fact that the derivative of $V(r)$ at the boundary is not zero. This is not important, except in one instant. Namely, most integrals which arise after substitution of $\psi^0_{\vec{k}\uparrow}$, Eq. (13), in Eqs. (1) and (2) contain $e^{-\mu r}$, $\chi_{n,s_z}(\vec{r})$, or $\phi_m(\vec{r})$, which fall off sufficiently fast towards the boundary of the unit cell. However, this is not true for the term

$$-(2mc^2)^{-1}[N^0(\vec{k})]^2\int_\Omega \left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}\right)\frac{2e^2}{r}\,d^3r\ , \tag{16}$$

which is the contribution of the plane-wave parts of $\psi^0_{\vec{k}\uparrow}$ and $\psi^{0\dagger}_{\vec{k}\uparrow}$, and of the first term of $V(r)$, Eq. (9), to $(\delta g)'$. In order to estimate this term it is actually better to replace $(-2e^2/r)$ in the potential $V(r)$ by

$$-[(a/r)+\tfrac{1}{2}(r/a)^2-\tfrac{3}{2}]\,2e^2/a\ , \tag{17}$$

which represents the potential of two nuclear charges screened by an electronic charge distributed uniformly throughout the Wigner-Seitz sphere of radius a. Equation (16) was estimated in this way.

One should of course calculate $(\delta g)'$ and $(\delta g)''$ for $\vec{k}=\vec{k}_F$. The calculation of $(\delta g)'$ is, however, rather cumbersome for arbitrary $\vec{k}$. We have therefore calculated $(\delta g)'$ for $\vec{k}=0$, after having convinced ourselves that $\delta g'(\vec{k}_F)-\delta g'(0)$ is small compared to $\delta g'(0)$. On the other hand, $(\delta g)''$ was expanded in powers of $\vec{k}$, and only the $\vec{k}$-independent term and the term quadratic in $\vec{k}$ were kept. There is no term linear in $\vec{k}$, and terms of order higher than the second are small.

Finally, $R_p(r)$ was approximated by $R_{1/2}(r)$, Eq. (10) and Table II. We find that

$$(\delta g)'=1.1\times 10^{-5} \tag{1$'$}$$

and

$$(\delta g)''=-5.6\times 10^{-5}\ . \tag{2$'$}$$

The lattice parameter of sodium, used in calculating (1′) and (2′), is 4.225 Å, at $T=4$ °K.[16]

We now turn to the calculation of $(\delta g)^P$, the remaining but major contribution to the g shift. As was mentioned in the Introduction, the contribution of the surface integrals over the cellular polyhedron can be neglected, because the amplitude of the core wave functions at the boundary of the crystalline unit cell is negligibly small. Thus, $(\delta g)^P$ is then effectively given by the expectation value of the z component of the angular momentum (times $2/\hbar$) in the unit cell. It is now imperative to use the complete wave function $\psi_{\vec{k}\uparrow}(\vec{r})$, Eq. (6), since the expectation value of the angular momentum in the unit cell vanishes in the absence of spin-orbit coupling. The calculation of $(\delta g)^P$ is, in addition, simplified due to the fact that the 1s and 2s core wave functions χ_{n,s_z} do not contribute, except through the normalizing factor

$$N(\vec{k})=\Big(\Omega-\sum_{n,s_z}\beta^*_{n,s_z}\beta_{n,s_z}-\sum_{j,j_z}\alpha^*_{j,j_z}\alpha_{j,j_z}\Big)^{-1/2}\ . \tag{18}$$

As in the case of $(\delta g)'$ and $(\delta g)''$, we will calculate $(\delta g)^P$ only to first order in spin-orbit coupling.

Making use of the fact that

$$\begin{aligned} R_{1/2}(r)&=R_p(r)+2\Delta(r)\ ,\\ R_{3/2}(r)&=R_p(r)-\Delta(r)\ , \end{aligned} \tag{19}$$

where $\Delta(r)=\tfrac{1}{3}[R_{1/2}(r)-R_{3/2}(r)]$, it can easily be verified that $N(\vec{k})$ is not affected by spin-orbit coupling to first order. Substituting Eq. (6) in Eq. (3), we find to first order in spin-orbit coupling that

$$\delta g^P(\vec{k})=6[N^0(\vec{k})]^2\{[\alpha^0_{1/2,-1/2}(\vec{k})]^*\,\alpha^\Delta_{1/2,-1/2}(\vec{k})+\text{c.c.}\}, \tag{20}$$

where

$$\begin{aligned} \alpha^0_{1/2,-1/2}(\vec{k})&=-(\sqrt{\tfrac{2}{3}})\int e^{i\vec{k}\circ\vec{r}}R_p(r)\,Y^*_{-1}(\theta,\phi)\,d^3r\ ,\\ \alpha^\Delta_{1/2,-1/2}(\vec{k})&=-(\sqrt{\tfrac{2}{3}})\int e^{i\vec{k}\circ\vec{r}}\,\Delta(r)\,Y^*_{-1}(\theta,\phi)d^3r\ . \end{aligned} \tag{21}$$

The coefficients $\alpha^0{}_{1/2,-1/2}(\vec{k})$ and $\alpha^\Delta_{1/2,-1/2}(\vec{k})$ are to first order in $\vec{k}$ given by

$$\begin{aligned} \alpha^0_{1/2,-1/2}(\vec{k})&=-\tfrac{2}{3}\pi^{1/2}\int r^3R_p(r)dr\,[ik_x-k_y]\ ,\\ \alpha^\Delta_{1/2,-1/2}(\vec{k})&=-\tfrac{2}{3}\pi^{1/2}\int r^3\Delta(r)dr\,[ik_x-k_y]\ . \end{aligned} \tag{22}$$

Using Eq. (22) and the fact that $R_p(r)=\tfrac{1}{3}[R_{1/2}(r)+2R_{3/2}(r)]$, we find to second order in $\vec{k}$ that

$$\delta g^P(\vec{k})=\tfrac{16}{27}\pi(k_x^2+k_y^2)\,[N^0(0)]^2\,(I_{1/2}+2I_{3/2})(I_{1/2}-I_{3/2})\ , \tag{23}$$

where

$$\begin{aligned} I_{1/2}&=\int r^3R_{1/2}(r)\,dr\ ,\\ I_{3/2}&=\int r^3R_{3/2}(r)\,dr\ . \end{aligned} \tag{24}$$

The normalizing factor at $\vec{k}=0$ is given by

$$N^0(0)=[\Omega-16\pi^2(I_1^2+I_2^2)]^{-1/2}\ , \tag{25}$$

with

$$I_1=\int r^2R_1(r)\,dr\ ,\quad I_2=\int r^2R_2(r)\,dr\ . \tag{26}$$

Finally, after performing the integrations in Eqs. (24) and (26) with the help of Eq. (10) and Table II, Eq. (23) becomes (for $\vec{k}=\vec{k}_F$)

$$\delta g^P(\vec{k}_F)=(-6.7\times 10^{-4})\sin^2\theta_0\,. \tag{3$'$}$$

Combining Eqs. (1′), (2′), and (3′), the final result, Eq. (4), is obtained.

We conclude by noting that the origin of a major contribution to the g shift of conduction electrons in sodium metal (in our calculation) lies in the difference between the orbital parts $R_{1/2}$ and $R_{3/2}$ of the $2p$ core wave functions, caused by the spin-orbit splitting of the $j=\frac{1}{2}$ and $j=\frac{3}{2}$ $2p$ core states. This leads to a conduction-electron g shift proportional to the difference in amplitude of these core functions in the orthogonalized plane wave. This is most clearly expressed by Eqs. (23) and (24).

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de Haas-van Alphen Effect in Dilute Beryllium-Copper Alloys*

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The de Haas–van Alphen effect was investigated in pure beryllium and in Be-Cu alloys containing up to 0.34 at.% Cu. The extremal cross-sectional areas of the cigar-shaped third-band electron pieces of Fermi surface decreased with alloying. The areas of the coronet-shaped second-band hole piece increased with alloying. The magnitude of the area changes were compared with rigid-band-theory predictions. Corrections for lattice-parameter changes were included when possible. In the low-concentration limit, the theory is able to account for the observed area changes. For the highest-concentration alloy, there are deviations, for all areas measured, to greater changes than are predicted by the theory. However, further data in the higher-concentration region ($\gtrsim 0.3$ at.% copper) are needed to verify this trend. Amplitude measurements were made to obtain cyclotron masses and scattering temperatures. Within experimental error, the masses were found to be independent of alloying. A significant anisotropy over the Fermi surface was observed in the rate of change of scattering temperature with respect to copper concentration. An analysis was made to determine the scattering rate due to copper impurities for the four orbits studied. The results indicate that this scattering rate is considerably larger for the two cigar orbits than it is for the two coronet orbits. The relative values of the scattering times as determined by the de Haas–van Alphen effect and residual-resistivity measurements were compared with the free-electron theory of Brailsford. Only order-of-magnitude agreement was found.

I. INTRODUCTION

The rigid-band model (RBM) as introduced by Jones[1] was the first attempt to explain the change in the electronic state of a pure metal upon alloying. This model proposed that the effect of alloying was to change the electron density by just the difference between the valence of the solute atom and the solvent atom, scaled by the atom fraction of solute. Later Friedel[2] used simple perturbation theory to show that the screening of the solute ions produces a shift of all the energy states of the electrons. In a first approximation this shift is independent of the wave vector and the