Conduction-electron g factors in the noble metals

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The conduction-electron g factor has been calculated at points on the Fermi surfaces of copper, silver, and gold by a relativistic linearized muffin-tin orbital method in the atomic-sphere approximation. The orbital g factors for principal extremal orbits on the Fermi surface of each metal have been deduced. A comparison with experimental g-factor data makes it possible to estimate the exchange-correlation enhancement factor for electrons on the Fermi surface of copper. The Fermi-surface average of the enhancement factor is in agreement with the predictions of a first-principles calculation, and the data suggest a weak anisotropy. Experimental data for silver and gold prove to be insufficiently accurate to yield reliable values of the exchange-correlation enhancement factor. A g-factor anomaly on the neck orbit in gold is discussed.

I. INTRODUCTION

The splitting of otherwise-degenerate electronic states at a point on the Fermi surface of a metal in an applied magnetic field is conveniently expressed in terms of the g factor. The extent to which the experimental value of the g factor differs from the free-electron value ($g_0=2.0023$) is governed by the spin-orbit interaction, and is modified by many-body effects.[1] The possibility of extracting information about many-body interactions on the Fermi surface accounts for the current interest in measuring and analyzing the g factors of conduction electrons in metals.

The g factors of conduction electrons at the Fermi surface can be measured by studying either conduction-electron spin resonance (CESR) or de Haas–van Alphen (dHvA) quantum oscillations. The g factors deduced from CESR experiments are local g factors averaged over the Fermi surface, and are unaffected by quasiparticle interactions,[1,2] whereas those derived from dHvA experiments are local g factors averaged over extremal orbits[3,4] and are renormalized by quasiparticle interactions. Early first-principles calculations focused on the variation from metal to metal in the Fermi-surface average that is observed in CESR experiments.[2,5] Recent advances in experimental techniques for studying the dHvA effect, which for the first time have made it possible to obtain reliable values of orbital g factors,[3,6–9] have stimulated theoretical calculations of orbital g factors for metals of the platinum group[10,11] and a preliminary calculation for gold.[11]

Each extremal orbit on each sheet of the Fermi surface gives rise to a component of magnetization that is oscillatory when plotted as a function of the reciprocal of the magnetic field. The theory of Lifshitz and Kosevich,[12] in which quasiparticle interactions are neglected, shows that the amplitude of the rth harmonic of the oscillatory magnetization of a nonferromagnetic metal includes a spin-splitting factor R_r first proposed by Dingle,[13]

$$R_r=\cos(\pi r S) \ . \tag{1}$$

Physically, S represents the ratio of spin splitting to Landau-level splitting in a plot of the density of states at the Fermi level as a function of the reciprocal of the magnetic field. S is related to the orbital g factor g_c by

$$S=g_c\frac{m_c}{2m_0} \ , \tag{2}$$

where m_c is the cyclotron mass and m_0 is the free-electron mass. S can be determined by measuring either the absolute amplitudes of dHvA oscillations or the ratios of the amplitudes of different harmonics, as discussed in recent reviews.[1,14] Samples used for such measurements must be free of magnetic impurities, small amounts of which can shift S significantly.

There is an ambiguity in the value of S deduced by inverting (1). The dHvA data are usually interpreted to yield the smallest positive value S_0 in (1), but the periodicity of the trigonometric function allows additional values $S=m\pm S_0$ for integer values of m. It is sometimes possible to establish whether m is an odd or an even integer by measuring the infinite field phase of the oscillation, but this is not always feasible. In view of this uncertainty, the experimental data must be supplemented by theoretical arguments to establish the correct value of the orbital g factor.

When many-body effects are taken into account, the quantity that is directly comparable to the experimental orbital g factor is $g_c^*=S_{\rm xc}g_c^{\rm band}/(1+\lambda_c^{ep})$, where $g_c^{\rm band}$ is the orbital average of the calculated g factor,[4] $S_{\rm xc}$ is the orbital average of the exchange-correlation enhancement factor, and $(1+\lambda_c^{ep})$ is the electron-phonon enhancement of the cyclotron mass. The Fermi-surface average of the exchange-correlation enhancement factor, which determines the spin susceptibility, is frequently termed the

Stoner factor. Assuming that the electron-phonon enhancement factor is known from other experiments, it is in principle possible to determine the orbital average of the exchange-correlation enhancement factor for nonferromagnetic metals by comparing the experimental and calculated values of the orbital g factor.

The combined CESR and NMR method of Schumacher and Slichter,[15] and studies of spin-wave propagation in association with CESR,[16] yield Fermi-surface averages of the exchange-correlation enhancement factor, but are applicable only to those few metals in which CESR has been observed. It is in principle possible to check the band calculation of the g factor by comparing an appropriate Fermi-surface average with the g factor deduced from CESR data, because the spin-resonance value is known to be unaffected by many-body effects. The analysis of experimental orbital g-factor data is the only way known to us to determine the anisotropy of the exchange-correlation enhancement factor for real metals.

The purpose of the present paper is to describe our approach to the calculation of orbital g factors, to discuss the influence of quasiparticle interactions, and to interpret experimental data on the noble metals copper, silver, and gold. Section II describes the theoretical calculation of the orbital g factor. In Sec. III, the results of the calculation are compared with the experimental CESR and dHvA data, and the Fermi-surface average of the exchange-correlation enhancement factor for copper is estimated. Finally, in Sec. IV, the conclusions of the present work are summarized.

II. THEORY

In a real metal in the absence of spin-orbit interaction, two degenerate electronic states, each an eigenstate of spin, are associated with every element of volume in the Brillouin zone. The effect of an applied magnetic field H is to remove the degeneracy. As in the free-electron metal, the energy splitting is given by $g_0\mu_B H$. When the spin-orbit interaction is taken into account, the energy levels remain doubly degenerate (Kramers degeneracy) if the crystal structure has an inversion center, but the energy eigenstates are no longer pure spin states.

Even though the electronic states in a uniform magnetic field are Landau levels rather than states of well-defined $\mathbf{k}$, it is possible to define a local g factor in terms of the difference between the expectation values of the energy operator for wave packets narrowly localized in momentum space.[17,18] By analogy with the free-electron case, the local g factor for an electron in the nth band at the point $\mathbf{k}$ in the Brillouin zone may be defined[2,5] in terms of the energy-level splitting of the otherwise-degenerate eigenstates in an applied magnetic field H along a direction $\hat{\alpha}$,

$$E_n^+(\mathbf{k})-E_n^-(\mathbf{k})=g_n^{\hat{\alpha}}(\mathbf{k})\mu_B H \ . \tag{3}$$

The energy-level splitting at the point $\mathbf{k}$ depends on the direction of $\mathbf{H}$, and therefore $g_n^{\hat{\alpha}}(\mathbf{k})$ is a tensor. It follows that there is no simple way to invert experimental g factors measured on several different orbits to yield the anisotropy of the local g factor.

A. The local g factor

The relativistic linearized muffin-tin orbital (LMTO) method in the atomic-sphere approximation has been used to calculate the energy eigenvalues needed in Eq. (3). This approach is expected to yield reliable eigenvalues within approximately 0.5 Ry above and below the Fermi energy. The relativistic problem was solved by the Pauli method, rather than by the Dirac method, in order to reduce the size of the secular matrix. A direct comparison between energy eigenvalues for conduction-band states of gold determined by the two techniques[18] gave agreement within 1 mRy.

The nonrelativistic Hamiltonian for an electron gas in external electric and magnetic fields has been discussed by White.[19] In the LMTO approximation, introducing relativistic corrections[20] and retaining only the magnetic field terms, the Hamiltonian can be expressed in the form

$$\mathcal{H}=\mathcal{H}_{\rm LMTO}+\mathcal{H}_{\rm so}+\mathcal{H}_Z \ . \tag{4}$$

The semirelativistic LMTO Hamiltonian is

$$\mathcal{H}_{\rm LMTO}=-\frac{\hbar^2\nabla^2}{2m}+V-\frac{1}{2mc^2}\left[(E-V)^2+\frac{\hbar^2}{2m}\frac{\partial V}{\partial r}\frac{\partial}{\partial r}\right] . \tag{4a}$$

For simplicity, the crystal potential $V(\mathbf{r})$ was taken to be spherically symmetric within overlapping atomic spheres, and correction structure constants were included.[20] The spin-orbit Hamiltonian is written in the form appropriate to a spherical potential

$$\mathcal{H}_{\rm so}=\frac{\hbar^2}{2m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\mathbf{S}\cdot\mathbf{L} \ , \tag{4b}$$

where for a single electron $\mathbf{S}=\boldsymbol{\sigma}/2$, and the σ_i are Pauli matrices. $\mathbf{L}$ is the angular momentum operator. The external field $\mathbf{H}$ is introduced to first order through the Zeeman Hamiltonian

$$\mathcal{H}_Z=\frac{e\hbar}{2mc}(\mathbf{L}+\boldsymbol{\sigma})\cdot\mathbf{H} \ , \tag{4c}$$

where e is the magnitude of the electronic charge.

In deriving the Hamiltonian (4), a term of the form

$$\frac{e^2\hbar}{8m^2c^3}\boldsymbol{\sigma}\cdot\nabla V\times(\mathbf{H}\times\mathbf{r}) \tag{5}$$

was neglected. This term is similar in form to the Zeeman term, and numerical estimates show that it is smaller than the Zeeman term by at least 2 orders of magnitude. In addition a diamagnetic term of the form

$$\frac{e^2H^2(x^2+y^2)}{8mc^2} \tag{6}$$

was neglected. This term is quadratic in H, and is therefore expected to shift both of the eigenvalues in (4) to higher energy, giving no contribution to the g factor.

The first step in the calculation of the local g factor is to find the potential self-consistently by solving the Schrödinger equation iteratively in the semirelativistic approximation. The calculations were done for a mesh of

505 points in the irreducible part of the Brillouin zone; s, p, d, and f orbitals were included. Exchange and correlation effects were taken into account in the approximation of von Barth and Hedin.[21] A substantial economy of computer time was achieved by introducing the spin-orbit and Zeeman terms only in the last cycle of iteration. At each $\mathbf{k}$ point, the last cycle of iteration yields two energy eigenvalues for each band, from which the local g factor is calculated according to Eq. (3).

Several checks were made to test the calculational procedure. When the Zeeman term was set to zero, the resulting eigenvalues were found to be in good agreement with relativistic LMTO and augmented plane-wave (APW) results.[18] In addition, the value of the g factor was found to be independent of the magnetic field strength for variations over 8 orders of magnitude. Finally, the spin-orbit parameter was set equal to zero, and the resulting value of the g factor was found to be equal to the free-electron value for all directions of the magnetic field.

B. The orbital g factor

It is convenient to express the result of a first-principles g-factor calculation as an orbital g factor that can be compared directly with experiment. Holtham[4] has shown that the g factor appropriate to a given orbit on the Fermi surface is the time-weighted average of the local g factor $g^{\hat{\alpha}}(\mathbf{k})$ around that orbit,

$$g_c^{\text{band}} = \oint_c g^{\hat{\alpha}}(\mathbf{k}) v^{-1}(\mathbf{k}) d\mathbf{k} \Big/ \oint_c v^{-1}(\mathbf{k}) d\mathbf{k} \ , \tag{7}$$

where $\hat{\alpha}$ denotes the direction of the magnetic field $\mathbf{H}$. Since the orbital g factor is known to be unaffected by the electron-phonon interaction,[22] consistency requires that, contrary to the assertion of Holtham,[4] the velocity in Eq. (7) should not be renormalized when the electron-phonon interaction is taken into account.

Equations (1) and (2), on which the experimental determination of the orbital g factors is based, remain valid when the electron-electron and electron-phonon interactions are taken into account, but the magnitude of the orbital g factor in (2) is modified by exchange and correlation effects, which enhance the time-weighted average of the local g factor by the exchange-correlation enhancement factor S_{xc}. If the Fermi surface is approximately spherical, the exchange-correlation enhancement factor can be written

$$S_{\text{xc}} = 1/(1+B_0^{ee}) \ , \tag{8}$$

where B_0^{ee} is the Landau parameter that represents the spin-antisymmetric $l=0$ component of the quasiparticle interaction.[23]

Since the electron-phonon interaction does not affect either the magnitude of the orbital g factor or the ratio S between the spin splitting and the Landau-level splitting,[22] the value of m_c that should be substituted in Eq. (2) is the band cyclotron mass unenhanced by the electron-phonon interaction. However, it is usual to extract the experimental value of the orbital g factor from S by substituting instead the experimental cyclotron mass, which is enhanced relative to the band mass by a multiplicative factor $1+\lambda_c^{ep}$ as a consequence of the electron-phonon interaction. If this procedure is followed, then the calculated quantity that is directly comparable with the experimental value of the orbital g factor is

$$g_c^* = \frac{S_{\text{xc}} g_c^{\text{band}}}{1+\lambda_c^{ep}} \ , \tag{9}$$

where g_c^{band} is given by Eq. (7).

C. Determination of Fermi-surface parameters

If the electron-phonon enhancement factor is known, the orbital average exchange-correlation enhancement factor S_{xc} can be determined by comparing the experimental orbital g factor with the value deduced from the band calculation. To evaluate the line integral of the orbital g factor in Eq. (7), it is essential to know both the shape of the orbit and the variation of the unrenormalized velocity around the orbit. To determine the electron-phonon enhancement is is necessary to know the variation of the quasiparticle and unrenormalized velocities over the Fermi surface. First-principles calculations alone yield neither the quasiparticle velocity nor the electron-phonon enhancement factor. Moreover, for the noble metals, the shapes of orbits on the Fermi surface predicted by the self-consistent relativistic LMTO calculations differ significantly from those observed by experiment. Therefore, the orbital characteristics were obtained by fitting experimental Fermi-surface area data by means of a phase-shift parametrization based on the Korringa-Kohn-Rostoker (KKR) method of band-structure calculation. The anisotropy of the quasiparticle velocity was determined by interpolating experimental cyclotron mass data, and the electron-phonon enhancement factor was deduced by comparing the experimental masses with band masses deduced from a self-consistent band-structure calculation.

The KKR method of band-structure calculation yields an implicit equation for the electronic energy eigenvalues at a point $\mathbf{k}$ in the first Brillouin zone, which takes the form

$$\Lambda(\mathbf{k}, E, \eta(E)) = 0 \ , \tag{10}$$

where Λ is an eigenvalue of the KKR secular matrix. In a first-principles band-structure calculation the crystal potential $V(\mathbf{r})$ is constructed, the energy-dependent phase shifts $\eta(E)$ are deduced by integrating the radial Schrödinger or Pauli equation, and the Fermi energy E_F is determined as that energy below which there are just enough electron states to accommodate all of the valence electrons in the metal. Finally, the shape of the Fermi surface is calculated by finding the locus of points in $\mathbf{k}$ space that satisfy Eq. (10) at the Fermi energy. In the present work, self-consistent LAPW band-structure calculations were used to estimate the magnitude of the Fermi energy and the unrenormalized velocity on the Fermi surface, to determine the electron-phonon enhancement of the cyclotron mass, and to estimate the spin-orbit parameters for gold. The self-consistent band-structure calculations for copper and silver were carried out nonrela-

tivistically, whereas the calculations for gold were carried out relativistically. In each case, exchange and correlation was represented by the local effective potential of Vosko *et al.*[24]

In the phase-shift pseudopotential method, the phase shifts at the Fermi energy $\eta_l(E_F)$ are adjusted iteratively to bring the extremal cross-sectional areas of orbits on the constant energy surface calculated from Eq. (10) into agreement with those deduced from experimental dHvA frequency data. For copper and silver, excellent agreement with the experimental data was achieved in a nonrelativistic calculation with three phase shifts η_l, corresponding to $l=0$, 1, and 2. The fit to the Fermi-surface data for gold was carried out relativistically, because relativistic effects are known to be important in gold. The relativistic KKR secular equation for $l \leq 2$ involves a set of five phase shifts $\eta_{l,j}$. Excellent agreement with the experimental Fermi-surface data for gold was achieved by adjusting the three phase-shift parameters $\eta_{0,1/2}$, $\eta_{1,3/2}+\eta_{1,1/2}$, and $\eta_{2,5/2}+\eta_{2,3/2}$. The remaining two parameters $\eta_{1,3/2}-\eta_{1,1/2}$ and $\eta_{2,5/2}-\eta_{2,3/2}$ are a measure of the strength of the spin-orbit interaction. The spin-orbit parameters for gold were calculated by integrating the radial Pauli equation with the self-consistent potential, because the shape of the constant energy surface in gold is not sufficiently sensitive to the magnitudes of the spin-orbit parameters to make it possible to determine them by fitting Fermi-surface data.

The Fermi energy is also a parameter in a phase-shift fit to the shape of the Fermi surface. The Fermi energy for each of the noble metals was estimated from a self-consistent LAPW band-structure calculation, because the shapes of orbits on the calculated Fermi surface prove to be almost independent of E_F, making it impossible to deduce E_F by fitting Fermi-surface data. Small angular-momentum-dependent corrections, constant within the muffin-tin sphere, were added to each self-consistent potential. The magnitudes of the corrections were adjusted to bring the calculated phase shifts at energy E_F into exact agreement with those deduced by fitting the Fermi-surface data. This procedure ensures that the corrected potential reproduces the shape of the Fermi surface to the accuracy with which it is known from experiment, so that the orbits around which the band velocities are calculated are identical to those to which the experimental cyclotron masses correspond. It also ensures that the band velocities calculated from the potential are independent of the value of the Fermi energy parameter. This proves to be essential if the ratio of the experimental mass to the band mass is to yield a reliable measure of the electron-phonon mass enhancement.

The most accurate way to evaluate the Fermi velocity and the cyclotron mass by the KKR method is to calculate the energy derivative of the KKR secular matrix $\mathcal{H}$ analytically and to use the Hellman-Feynman theorem to deduce the energy and wave-vector derivatives of the eigenvalue, using the relations

$$\frac{\partial \Lambda}{\partial E}=\left\langle \mathbf{k}\left|\frac{\partial \mathcal{H}}{\partial E}\right|\mathbf{k}\right\rangle \tag{11}$$

and

$$\nabla_{\mathbf{k}}\Lambda=\langle \mathbf{k}|\nabla_{\mathbf{k}}\mathcal{H}|\mathbf{k}\rangle \ . \tag{12}$$

The Fermi velocity is calculated from

$$v_k=\frac{1}{\hbar}|\nabla_{\mathbf{k}}E|=\frac{-|\nabla_{\mathbf{k}}\Lambda|}{\hbar(\partial\Lambda/\partial E)} \ , \tag{13}$$

and the cyclotron mass is calculated by evaluating the line integral

$$m_c=\frac{\hbar^2}{2\pi}\frac{\partial A}{\partial E}=-\frac{\hbar^2}{2\pi}\oint\frac{(\partial\Lambda/\partial E)dl}{|\nabla_{\mathbf{k}}\Lambda|\sin\theta} \ , \tag{14}$$

where θ is the angle between the normal to the Fermi surface and the direction of the magnetic field.

The energy derivatives $\partial\mathcal{H}/\partial E$ and $\partial\Lambda/\partial E$ involve the energy derivatives of the phase shifts. If the energy derivatives of the phase shifts are calculated from a self-consistent potential, then Eq. (14) yields the band cyclotron masses. If the energy derivatives of the phase shifts are determined by adjusting them to fit experimental cyclotron mass data for orbits on the Fermi surface, then Eq. (14) yields the quasiparticle cyclotron masses. Once the energy derivatives of the phase shifts have been determined, the unrenormalized velocity and the quasiparticle velocity at each point on the Fermi surface can be deduced by evaluating Eq. (13). This procedure proves to be an accurate and reliable way of inverting experimental cyclotron mass data to determine the quasiparticle velocity. Just as in fitting the area data, a complication arises in the relativistic case because the cyclotron mass data prove to be insensitive to the energy derivatives of the spin-orbit parameters. Therefore the energy derivatives of the p and d wave spin-orbit parameters for gold were calculated from the self-consistent potential, and were held constant in fitting the experimental cyclotron mass data.

The orbital average of the electron-phonon mass enhancement λ_c^{ep} was evaluated by combining the cyclotron masses deduced from the best fit to experimental data for a set of orbits on the Fermi surface with those deduced from the band-structure calculation, using the relationship

$$1+\lambda_c^{ee}+\lambda_c^{ep}=m_c^*/m_c \ . \tag{15}$$

For a given metal, calculations based on self-consistent potentials involving different treatments of exchange and correlation gave generally consistent results for the variation of $\lambda_c^{ee}+\lambda_c^{ep}$ from orbit to orbit, but the absolute magnitude of $\lambda_c^{ee}+\lambda_c^{ep}$ was found to vary slightly for different potentials. This is because the extent to which the spin-symmetric component of the electron-electron interaction is folded into the crystal potential varies from potential to potential, resulting in a small variation in λ_c^{ee}. Since λ_c^{ee} is not accurately known, it was assigned the constant value necessary to ensure that the value of λ^{ep} is greater than or equal to zero at every point on the Fermi surface; the resulting values of λ_c^{ee} are -0.032 (Cu), -0.024 (Ag), and -0.162 (Au). For comparison, the maximum values of λ_c^{ep} were found to be 0.198 (on the neck in copper), 0.264 (on the neck in silver), and 0.512 (on the dog bone in gold

in the direction of the minimum radius). This arbitrary procedure underestimates the value of λ_c^{ep}. The uncertainty in the value of λ_c^{ep} that results from the uncertainty in the extent to which the electron-electron interaction is folded into the potential is an important factor limiting the accuracy with which the exchange-correlation enhancement factor can be deduced from experimental orbital g-factor data.

III. RESULTS

The noble metals copper, silver, and gold have topologically similar multiply connected Fermi surfaces. A Fermi-surface average of the g factor has been calculated for each metal. Table I compares these and other[5] theoretical values with experimental values of the CESR g factor.[25–28] The Fermi surfaces of the noble metals support five principal orbits, the belly (B_{111}) and neck (N) for directions of **H** near ⟨111⟩, the belly (B_{100}) and rosette (R) for **H** near ⟨100⟩, and the dog bone (D) for **H** near ⟨110⟩.[1] Table II lists the calculated values of the orbital g factors and the electron-phonon enhancement factors determined in this work, together with the experimental values of the orbital g factors g_c^{expt} deduced from dHvA data,[3,6–8] and the resulting estimates of the exchange-correlation enhancement factor S_{xc}.

A. Copper

The experimental CESR g factor for copper has been determined independently by several groups, and the value listed in Table I is representative of results of measurements under conditions expected to yield an average of g over all states on the Fermi surface. A simple Fermi-surface average of the local g factor is significantly larger (by about 2%) than the experimental value. While there have been several theoretical treatments of CESR (see, for example, the works of Lamb[34] or Janossy[35]

TABLE I. Experimental values g^{CESR} of the g factor for the noble metals derived from CESR experiments, compared with values g^{av} derived from a Fermi-surface average of the local g factor calculated in the present work, and with values g^{sph} calculated by Schober *et al.* (Ref. 5) assuming a spherical wave function.

	g^{CESR}	g^{av}	g^{sph}
Cu	2.033(1)[a,b]	2.08	
Ag	1.983(1)[a,c]	2.06	1.97
Au[d]	2.11(1)[e]	2.26	2.02

[a]Reference 25.
[b]Reference 26.
[c]Reference 27.
[d]For Au, CESR has not been detected in conventional experimental configurations; the value listed was obtained by plating thin ferromagnetic films on both sides of foils cut from single crystals. CESR has also been seen in tiny Au particles; the results from two different groups are contradictory, 2.26(2) (Ref. 29) and 2.0024(4) (Ref. 30). Size effects are expected (Ref. 27) to alter the measured CESR g factor in small particles. Plated foil experiments in Cu (Ref. 31) have shown that g is unchanged from the value measured in conventional experiments (although line shape and amplitude are altered), so that the plated Au foil experiments (Ref. 28) are taken to be reliable.
[e]Reference 28.

TABLE II. Theoretical and experimental values of g and S_{xc} for principal orbits in the noble metals. Error estimates for g take into account uncertainties in calibrations, curvature factors, and effective masses, as well as experimental scatter. The resulting uncertainties in S_{xc} do not take into account possible systematic errors in λ_c^{ep}. Reasonable alternative values allowed by the ambiguity of inverting $\cos\pi S$ are given in brackets [ ]. The values listed from Ref. 8 are those based on curvature factors calculated (Ref. 32) from a KKR model, which we have verified by computing orbital integrals of geometric properties of the Fermi surface up to second order using our KKR parametrization. Average values of S_{xc} calculated by MacDonald *et al.* (Ref. 33) are 1.096 (Cu), 1.073 (Ag), and 1.063 (Au).

	Orbit	g_c^{band}	$1+\lambda_c^{ep}$	g_c^{expt} Ref. 3	Ref. 6	Ref. 7	Ref. 8	S_{xc}
Cu	B⟨100⟩	2.13	1.052	2.24(5)			2.24(3)[a]	1.11(2)
	R⟨100⟩	2.05	1.071	2.08(5)				1.09(2)
	D⟨110⟩	2.09	1.091	2.11(2)			2.14(2)	1.11(1)
	B⟨111⟩	2.12	1.034	2.12(2)			2.13(2)	1.04(1)
	N⟨111⟩	2.04	1.198	1.90(4)				1.12(2)
Ag	B⟨100⟩	2.09	1.057				2.14(20)	1.08(10)
	R⟨100⟩	2.04	1.109					
	D⟨110⟩	2.07	1.122				2.24(10) [1.77]	1.21(5) [0.96]
	B⟨111⟩	2.10	1.041				2.43(15) [1.91]	1.20(7) [0.95]
	N⟨111⟩	2.01	1.264	1.92(5)				1.21(3)
Au	B⟨100⟩	2.40	1.111			2.29(4)	2.03(4)	1.06(2) or 0.94(2)
	R⟨100⟩	2.13	1.103			2.26(10)		1.17(5)
	D⟨110⟩	2.19	1.167		2.04(28)	2.35(10)	2.03(20)	1.25(5) or 1.08(10)
	B⟨111⟩	2.43	1.051			2.42(13)	2.21(7)	1.05(6) or 0.96(3)
	N⟨111⟩	2.20	1.370	1.22(12)	1.04(3)	1.15(5)		0.70(5)
	B zero	2.34	1.114			2.35(5)[b]		1.18(3)

[a]Extrapolated from 12°.
[b]Recalculated in Ref. 8, using revised mass data, to be 2.49. For consistency, S_{xc} has been calculated from the latter value.

which provide comprehensive references to earlier work), they all make important simplifying assumptions, and no theoretical treatment of transmission CESR has yet fully taken into account the variation of g with field direction. Our calculations show that, in the noble metals, the local g-factor component for magnetic field parallel to the velocity tends to be smaller than the other components. Assuming that electron states with velocities along the field direction make the dominant contribution to the transmitted signal, this would explain why a simple Fermi-surface average overestimates the g factor observed in CESR. Further theoretical development, perhaps along the direction of Lamb's work[34] but including the experimental geometry and skin effect (the skin depth is generally less than the electron mean free path between momentum scattering events), is needed for a more accurate comparison between theoretical g factors and experimental CESR data.

The small value of the spin-splitting factor of the fundamental[8] and the existence of spin zeros[3] combine to ensure that $g_c^{\rm expt}$ can be determined with an experimental uncertainty of the order $\pm 1\%$. Thus the experimental dHvA data for copper yield reliable values of the orbital g factors. It has been noted[8] that the earlier estimates of the g factors[3] may be slightly too low, by amounts which we estimate to be between 1 and 2%, because the cyclotron masses used in the analysis were systematically too high.

The local g factor calculated in the present work is lower on the necks than on the belly, leading to corresponding differences between $g_c^{\rm band}$ for the neck and belly orbits; the rosette and dog bone orbits, which sample both regions, have intermediate values of $g_c^{\rm band}$. The anisotropy of the electron-phonon renormalization makes a significant contribution to the anisotropy of $g_c^{\rm expt}$, and is the main reason for the low value on the necks. Combining the experimental and calculated orbital g factors with the electron-phonon mass enhancement factor according to Eq. (9) yields an estimate of the orbital average of the exchange-correlation enhancement factor. The results presented in Table II indicate that the anisotropy of the exchange-correlation enhancement factor over the Fermi surface is weak. The mean value of 1.094 is in excellent agreement with the results of a first-principles calculation by MacDonald *et al.*[33]

B. Silver

A simple Fermi-surface average of the local g factor $g_n^{\hat{\alpha}}(\mathbf{k})$ was found to be significantly larger than the experimental value of the CESR g factor for silver. In view of the questions raised above concerning the appropriate Fermi-surface average, the interpretation of this result must await further theoretical developments.

For the principal orbits in silver, the cosine factor of Eq. (1) is close to unity.[8] This introduces a large uncertainty in the determination of $g_c^{\rm expt}$ from dHvA data. For the same reason, even a small systematic error in the measurement of the oscillatory amplitude would introduce a large error in $g_c^{\rm expt}$. The fact that the value of the cosine derived from the $\langle 100 \rangle$ belly data exceeds unity suggests a possible systematic error; in this case the maximum value of unity was assigned.[8] The $\langle 111 \rangle$ belly and the dog bone data are consistent with either of two reasonable alternative values of $g_c^{\rm expt}$. The value of $g_c^{\rm expt}$ for the neck is more precisely determined,[3] but is thought to be slightly too low because of a small error in the value of the cyclotron mass. Since m_c enters the analysis in other ways besides Eq. (2), it is impossible to correct the orbital g factor for the mass error without having access to the complete original data.

The experimental uncertainty in the orbital g factor for the $\langle 100 \rangle$ belly is as large as the calculated variation among the major orbits. Moreover, for the dog bone and the $\langle 111 \rangle$ belly orbits, the uncertainty in the experimental value of the orbital g factor is so large that the calculated values offer no guidance in resolving the ambiguity in inverting the cosine factor. Given the uncertainties in extracting $g_c^{\rm expt}$ from the experimental data and the likelihood of large systematic errors, the exchange-correlation enhancement factors reported in Table II for silver must be regarded with caution.

C. Gold

CESR experiments for gold show that the g factor is generally higher than in the other noble metals, presumably because the spin-orbit interaction is stronger. Again, a simple Fermi-surface average of the local g factor significantly overestimates the experimental value of the CESR g factor. The interpretation of CESR data is subject to the same uncertainties as for the other noble metals, and a quantitative analysis must await further theoretical developments.

The uncertainties in the orbital g factors deduced from dHvA data for principal orbits on the Fermi surface of gold are large. Moreover, the results of absolute amplitude measurements at different laboratories are in conflict; it has been suggested[8] that the results reported in Ref. 7 may be unreliable because the data suffer from magnetic interaction effects. A spin zero has been observed[7] on the belly of the Fermi surface of gold with **H** in the (110) plane 71.6° from [001]; the resulting value of $g_c^{\rm expt}$ was originally estimated to be 2.35, but a subsequent calculation with a revised mass[8] gave 2.49. This result casts doubt on dHvA data in Ref. 8, which indicate that $g_c^{\rm expt}$ on the belly orbits in gold is lower than in copper or silver, and supports the generally higher values obtained from dHvA data in Ref. 7. The large positive CESR g shift adds further support to this conclusion.

The band calculations for gold indicate a strong positive g shift, with a larger anisotropy than for the other noble metals. The results of the present calculation are in excellent agreement with those of an independent calculation by Ohlsen,[36] the differences are small and random, with a standard deviation of less than 0.02. Only on the spin-zero orbit and on the neck are the experimental g factors determined with sufficient accuracy to make it possible to estimate the exchange-correlation enhancement factor.

In the vicinity of the neck, the electronic energy band at the Fermi surface is strongly hybridized with an ener-

gy band at a slightly higher energy. A simple argument based on second-order perturbation theory predicts that such a configuration of bands will induce a negative g shift. This is believed to account for the generally small values of the g factors on the necks of the noble metals. At the symmetry point L (the center of the neck orbit) in gold the calculation predicts a negative g shift ($g_c^{\text{band}}=1.80$), which is consistent with the perturbation theory argument. However, the g shift on the neck orbit in gold is large and opposite in sign to that at the L point. This surprising result may arise from the strong admixture of d character to the electron states on the neck in gold. It is also surprising that the calculated g shift on the neck orbit is larger than on the rosette and dog bone, whereas in the other noble metals the g shifts on the rosette and dog bone are intermediate between the belly and the neck.

The experimental data are no less surprising than the results of the band calculations. Independent measurements by several groups are consistent in showing that the g factor on the neck in gold is unusually low, with a minimum at $\langle 111 \rangle$. Interpreting these results on the basis of Eq. (9) yields an exchange-correlation enhancement factor for the neck orbit that is significantly less than unity. While correlation is expected to offset the exchange enhancement of the g factor, the resulting exchange-correlation enhancement is expected to be greater than unity.[37] The applicability of this result to real metals is borne out by first-principles calculations.[38] A value less than unity must be considered unphysical.

A possible explanation of the unphysical estimate of S_{xc} on the neck in gold is that the choice of $S=S_0$ implicit in the interpretation of neck g-factor measurements[3,6,7] is incorrect. The ambiguity in inverting the cosine function allows $S=m\pm S_0$, where m is zero or a positive integer. Infinite field phase measurements[39] rule out odd integers for the $\langle 111 \rangle$ neck orbits in the noble metals. The next higher possible g factor comes from choosing $S=2-S_0$, which implies an orbital g factor of 13.1 at $\langle 111 \rangle$, decreasing to 12.4 for orbits that are barely viable on the neck. The dHvA data show that the g factor varies smoothly over the necks, while the CESR results show that g must be generally just over 2 on most of the Fermi surface. It seems unlikely that the exchange-correlation enhancement would increase almost discontinuously by an order of magnitude from the belly to the adjoining neck regions in gold.

A more likely explanation of the unphysically low value deduced for S_{xc} for the necks in gold is that the present calculations seriously underestimate the electron-phonon mass enhancement in the region of the neck. The calculated anisotropy of λ^{ep} over the Fermi surface is similar in copper and silver, but qualitatively different in gold, where the maximum value occurs on the dog bone orbit rather than on the neck. This is consistent with the possibility that the present estimate of λ^{ep} on the neck in gold is too low. Ultrasonic attenuation data[40] provide another indication that this may be so. The attenuation in the limit of long electron mean free path is proportional to the square of the electron-phonon enhancement $(1+\lambda^{ep})$.[41] In gold (but not in copper or silver) the experimentally observed attenuation of ultrasonic waves propagating along $\langle 111 \rangle$ is more than twice the free-electron prediction. A simple estimate of the contribution from the neck can be obtained by subtracting the belly contribution as calculated by MacFarlane and Rayne,[40] but corrected by the present value of the electron-phonon enhancement factor for the $\langle 111 \rangle$ belly. By interpreting the neck contribution on the basis of an average strain derivative of the Fermi surface deduced from area-derivative data[42] and curvatures calculated from our KKR parametrization, we estimate that $1+\lambda^{ep}\approx 1.9$ for the neck effective zone in gold, which is essentially identical to the dHvA orbit. If this value is used as an estimate of the orbital mass enhancement to interpret the neck g-factor data in gold, the resulting value of the exchange-correlation enhancement is $S_{\text{xc}}\approx 1.0$. This result is physically reasonable, and taken together with the result from the spin-zero orbit on the belly, yields an average exchange-correlation enhancement that is in reasonable agreement with the result of the first-principles calculation by MacDonald *et al.*[33] (see Table II). However, as the estimate of the electron-phonon enhancement on which the present result is based involves several approximations, further studies are needed to establish a reliable value for S_{xc} on the neck in gold. With this in mind, work is in progress to evaluate the strain derivatives of the Fermi surface and hence to determine the various contributions to the ultrasonic attenuation with greater precision.

IV. DISCUSSION AND CONCLUSIONS

In this paper, a novel approach to the theoretical calculation of the g factors of conduction electrons is described, and results of calculations in the noble metals are presented. The role of quasiparticle interactions in experimental orbital g-factor data is discussed, and experimental data for the noble metals are interpreted. An ambiguity in the value of the electron-phonon enhancement λ_c^{ep} arises from the uncertainty in the extent to which the electron-electron interaction is folded into the self-consistent crystal potential. This ambiguity was resolved by arbitrarily setting the minimum value of the electron-phonon enhancement over the Fermi surface equal to zero. This procedure is expected to underestimate the value of λ_c^{ep} and hence S_{xc}. The uncertainty in the electron-phonon enhancement is an important factor limiting the accuracy with which the exchange-correlation enhancement factor can be deduced from experimental orbital g-factor data.

The most reliable and complete experimental data are those for copper. It is probable that the present calculations for copper do not underestimate the values of λ_c^{ep} and S_{xc} by more than 0.05. The good agreement between the average value of S_{xc} over the various orbits and the theoretical estimate of MacDonald *et al.* gives confidence in the validity of the present approach. The results indicate little anisotropy in the exchange-correlation enhancement in copper. The g factors for the large orbits in silver and gold are generally not well established by the experimental data; the exception is that the spin-zero or-

bit on the belly in gold yields a reliable value of the g factor.

The g factor deduced from dHvA measurements on the $\langle 111 \rangle$ neck orbit in gold is unexpectedly low. This is because the experimental cyclotron mass has been used instead of the unrenormalized mass in deducing g from the experimentally determined value of S. Ultrasonic attenuation data indicate that the electron-phonon enhancement factor for this orbit is approximately 1.9, and hence that the true value of the g factor for the $\langle 111 \rangle$ neck orbit is comparable to values of g on the rest of the Fermi surface. A comparison between the experimental cyclotron mass and the calculated band mass significantly underestimates the electron-phonon enhancement on the $\langle 111 \rangle$ neck orbit in gold. The failure of the band calculation to yield an accurate estimate of the unrenormalized mass on the $\langle 111 \rangle$ neck orbit in gold will be the subject of further work. The present work suggests that in such cases λ^{ep} can be determined from an analysis of ultrasonic attenuation data.

An important motivation for this work is the hope that it will prove possible to determine the exchange-correlation enhancement factors in metals by analyzing experimental quantum oscillation data. Because the de Haas–van Alphen effect is observable in almost every metallic element, the present method is more widely applicable than methods based on CESR, and in addition it may make it possible to determine the anisotropy of the exchange-correlation enhancement. Even if the inversion of dHvA amplitude data for principal orbits on the Fermi surface proves to be unreliable, the exchange-correlation enhancement can be determined on those orbits and at those orientations where the dHvA amplitude shows a spin zero. High-purity samples are essential for such work, since magnetic impurities present even in minute concentrations can alter the relative amplitudes of the harmonic components of the quantum oscillations, and can induce field-dependent shifts in the orientations at which the spin zeros are observed.[43] In conditions of significant magnetic interaction, magnetic impurities can also induce spurious field-dependent zeros in all but the fundamental component of the quantum oscillations. Only by demonstrating their field dependence can the spurious zeros be distinguished from true spin zeros.[44]

The accuracy with which the exchange-correlation enhancement can be determined is limited by the accuracy of the estimate of electron-phonon enhancement. If, as in the noble metals, the uncertainty in λ_c^{ep} is comparable to $S_{xc}-1$ it is impossible to extract the exchange-correlation enhancement with great accuracy. However, there is every reason to hope that the analysis of quantum oscillation data will prove to be a practical technique for determining the exchange-correlation enhancement for conduction electrons on the Fermi surfaces of those metals in which the enhancement is strong.

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