If the exchange interaction is quite small, the pair spectrum is not sufficiently different from the single-ion spectrum to be recognized.)

On the other hand, the ground state of the Fe^{2+} ion at either the $M1$ or $M2$ site involves the d_ϵ orbitals indicated in Fig. 7. Consequently, there may be nearly equal interaction between the metal ions and each of their six ligands. Thus, the exchange interaction between n.n. $M1$ ions would be comparable to that between an $M1$ and an $M2$ yielding a cooperative transition involving all the ions at the same time.

In a similar manner, the behavior of the Ni^{2+} salt might be explained by noting that the ground state in a cubic field consists of a "hole" in each of the d_γ orbitals and that any tetragonal elongation along the z axis will tend to concentrate the "hole" wave function in the xy plane. This could lead, again, to a greater exchange interaction between two $M1$'s than between an $M1$ and an $M2$.

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Magnetic Field Dependence of the Knight Shift*

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The apparent inconsistencies among the theories of de Haas–van Alphen oscillations in the Knight shift due to Das and Sondheimer, to Stephen, and to Dolgopolov and Bystrik are resolved. The calculation of the Knight shift is treated by a method which goes beyond the semiclassical approximation used by these authors. It is found that for polyvalent metals the dominant magnetic field dependence may be due to the behavior of the electronic wave function, rather than to the density of states.

I. INTRODUCTION

A STRONG field dependence of the Knight shift has been observed in tin.[1] Since the magnitude of the effect is considerably larger than previous theoretical estimates would indicate, and since there are apparent disagreements among these theories a survey and appraisal of this work seems timely. In addition to serving these ends, some additional considerations are advanced leading to a field dependence whose nature lies outside the scope of the previous theories, and which may be important for the interpretation of experiments.

We begin with a rederivation of the magnetic shielding constant followed by an examination of validity of the usual expression for the zero-field limit. The earlier work on the oscillatory behavior of the Knight shift is then discussed and, beginning with Sec. II, a different theory for this phenomenon is presented.

The vector potential due to a nuclear magnetic moment may be written

$$\mathbf{A}(\mathbf{r})=\boldsymbol{\mu}_n\times r^{-3}\mathbf{r}.$$

When this is placed in the Hamiltonian for an electron in a magnetic field it gives rise to the terms

$$\begin{aligned}&\mathcal{H}_n=\mathcal{H}_d+\mathcal{H}_p,\\&\mathcal{H}_d=(2\mu_0\mu_n/\hbar r^3)L_z+(e^2H\mu_n/2mc^2r^3)(x^2+y^2),\\&\mathcal{H}_p=(16\pi/3)\mu_0\mu_n\delta(\mathbf{r})S_z+2\mu_0\mu_n[(3z^2-r^2)/r^5]S_z,\end{aligned}\tag{1.1}$$

(the nuclear moment has been taken in the z direction and L_z is the component of angular momentum about the z axis). The first term of the paramagnetic part is the Fermi contact interaction, the only term ordinarily considered in discussions of the Knight shift. The second term of $\mathcal{H}_p$ vanishes for cubic crystals and is responsible for the so-called anisotropic Knight shift. The diamagnetic terms are generally dismissed on the grounds that the orbital momentum of conduction electrons is quenched and that the diamagnetic shielding term is small compared to the singular Fermi term.

The Knight shift is given essentially by the magnetic shielding constant

$$\sigma=-H^{-1}(\partial F/\partial\mu_n)_{\mu_n=0},\tag{1.2}$$

where F is the free energy and H is the applied magnetic field. We consider the independent-particle model for a metal and in addition neglect lattice vibrations.

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[1] J. M. Reynolds, R. Goodrich, and S. Kahn, Phys. Rev. Letters 16, 609 (1966).

Thus, for a nontransition metal the Hamiltonian may be written, if we retain only the Fermi contact hyperfine term,

$$\begin{aligned}&\mathcal{H}=\mathcal{H}_0+\mathcal{H}_n+\mathcal{H}_z,\\&\mathcal{H}_0=\frac{1}{2m}\left(\mathbf{p}-\frac{e}{c}\mathbf{A}\right)^2+V(\mathbf{r}),\\&\mathcal{H}_n=(16\pi/3)\mu_0\mu_n\mathbf{I}\cdot\mathbf{S}\delta(\mathbf{r}),\\&\mathcal{H}_Z=2\mu_0\mathbf{H}\cdot\mathbf{S},\end{aligned}\tag{1.3}$$

where $\mathbf{A}$ is the vector potential for the external magnetic field, $V(\mathbf{r})$ is the periodic lattice potential, μ_0 and μ_n are the electronic and nuclear magnetons, $\mathbf{I}$ is the nuclear spin (unit) vector, and $\mathbf{S}$ is the electronic spin operator in units of $\hbar$. We first calculate the partition function

$$Z(s)=\mathrm{Tr}\{e^{-s\mathcal{H}}\},$$

and then evaluate the (zero-temperature) free energy by the formula

$$F-n\zeta=\Phi=-\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}s^{-2}Z(s)e^{\zeta s}ds,\quad c>0.\tag{1.4}$$

Tr denotes the trace over spin and space variables and ζ is the Fermi level.

$Z(s)$ is required only to first order in μ_n and may be obtained by using the Schwinger trace formula. Taking $\mathbf{I}$ and $\mathbf{H}$ along the z axis, we find for the "nuclear" partition function

$$Z_n(s)=-(16\pi/3)s\mu_0\mu_n\,\mathrm{Tr}\{S_z\delta(r)e^{-s(\mathcal{H}_0+\mathcal{H}_z)}\}.$$

Thus,

$$\sigma=-(16\pi/3)(\mu_0/H)\,\mathrm{Tr}\{S_z\delta(r)\theta(\zeta-\mathcal{H}_0-\mathcal{H}_Z)\},$$

where

$$\theta(x)=0,\quad x<0;\ =1,\ x>0.$$

The performance of the spin trace is elementary and leads to the expression

$$\sigma=(8\pi\mu_0/3H)\,\mathrm{Tr}\{\delta(\mathbf{r})X_{\mu_0H}(\zeta-\mathcal{H}_0)\},$$

where Tr denotes a trace over spatial states and $X_a(x)$ is the characteristic function of the interval $-a<x<a$. Taking the eigenstates of $\mathcal{H}_0$ as $\langle\mathbf{r}|\lambda\rangle=\psi_\lambda(\mathbf{r})$, E_λ, we obtain quite generally

$$\sigma=(8\pi\mu_0/3)\lim_{H\to0}H^{-1}\textstyle\sum_\lambda|\psi_\lambda(0)|^2X_{\mu_0H}(\zeta-E_\lambda),$$

where it should be kept in mind that $\psi_\lambda(0)$ is field-dependent.

In the usual calculations of the Knight shift this is evaluated, in effect, simply by setting $H=0$, which gives

$$\sigma=(16\pi\mu_0^2/3)\sum_{\mathbf{k},n}|\psi_{\mathbf{k},n}(0)|^2\delta(\zeta-E_n(k)),\tag{1.5}$$

where $\mathbf{k}$, n denote the field-free band states. This may be written

$$\sigma=(8\pi/3)\chi_p\langle|\Psi(0)|^2\rangle\tag{1.6}$$

which is Towne, Herring, and Knight's expression.[2] However, $\psi_\lambda(0)$ is nonanalytic at $H=0$ and the very structure of the sum is field-dependent; consequently, taking the limit in this manner is highly suspect. We have been unable to find a rigorous derivation of (1.6), but the following simple model and the results of Sec. III lend confidence to its general validity.

If we assume that $V(\mathbf{r})=V(z)$, then $\mathcal{H}_0$ is separable

$$\begin{aligned}&\mathcal{H}_0=\mathcal{H}_\perp+\mathcal{H}_{11},\ [\mathcal{H}_\perp,\mathcal{H}_{11}]=0,\\&H_\perp=(1/2m)\{[p_x-(e/c)A_x]^2+[p_y-(e/c)A_y]^2\},\\&\mathcal{H}_{11}=(1/2m)p_z^2+V(z).\end{aligned}$$

For a suitable choice of gauge, $\lambda=(n,k_x,k=k_z,\nu)$,

$$\begin{aligned}\psi_\lambda(\mathbf{r})&=(eH/\pi\hbar c)^{1/2}(2^nn!)^{-1/2}e^{-1/2(\eta-\eta_0)^2}\\&\quad\times H_n(\eta-\eta_0)e^{ik_xx}\Psi_{\nu,k}(z),\\\eta&=(eH/\hbar c)^{1/2}y,\quad\eta_0=-(\hbar c/eH)^{1/2}k_x,\\E_\lambda&=2\mu_0H(n+\tfrac12)+E_\nu(k).\end{aligned}$$

If we use the integral representation

$$X_a(x)=\frac{1}{\pi i}\int_{c-i\infty}^{c+i\infty}s^{-1}\sinh as\,e^{xs}\,ds,\quad c>0$$

and the identity (2.4) we find, quite straightforwardly, that

$$\sigma=(4\mu_0/3)(e/\hbar c)\lim_{H\to0}\sum_{k,\nu}|\psi_{k,\nu}(0)|^2\theta[\zeta-E_\nu(k)].\tag{1.7}$$

The $H=0$ limit is now quite trivial, for all the field dependence is in the chemical potential. The resulting sum is evaluated simply in terms of the one-dimensional density of states[3] and we find (1.6) except that the average is over the *entire* occupied one-dimensional band structure. However, in this model the sum in (1.5) may be written

$$\frac{1}{2\pi}\sum_{k_z,\nu}|\psi_{k_z,\nu}(0)|^2\int_0^\infty k_\perp dk_\perp\delta\left(\zeta-E_\nu(k_z)-\frac{\hbar^2}{2m}k_\perp^2\right),$$

where $k_\perp$ is the component of $\mathbf{k}$ in the x-y plane, which gives precisely (1.7).

Das and Sondheimer[4] have evaluated (1.5) for free electrons by perturbation theory (to first order in μ_n) retaining the entire nuclear Hamiltonian $\mathcal{H}_n$, and have obtained the steady part of σ. Their result is [for free electrons $\langle|\Psi_f(0)|^2\rangle=1$]

$$\sigma=(8\pi/3)(\chi_d+\chi_p).\tag{1.8}$$

[2] F. J. Milford, Am. J. Phys. **28**, 521 (1960).
[3] M. L. Glasser, J. Phys. Chem. Solids (to be published).
[4] T. P. Das and E. H. Sondheimer, Phil. Mag. **5**, 529 (1960).

Das and Sondheimer conjectured, further, that (1.8) would remain valid for the oscillatory as well as the steady part of the susceptibility and that an oscillatory Knight shift might therefore be observable. They, in effect, predicted density-of-states oscillation which have been subsequently commented on by Kaplan[5] and Rodriguez.[6]

Das and Sondheimer's speculations have been examined by Stephen[7] who calculated, in the scalar effective-mass approximation, the exact free energy including the complete hyperfine interaction $\mathcal{H}_n$. He found that (1.8) is not correct. For free electrons ($m=m^*$) Stephen's results are (at $T=0°\mathrm{K}$)

$$\sigma=\sigma_p+\sigma_d,$$

$$\sigma_p=(4\pi n\mu_0^2/\zeta_0)\{1+O[(\mu_0 H/\zeta_0)^2]\},$$

(no oscillatory terms),

$$\sigma_d=-(4\pi n\mu_0^2/3\zeta_0)\{1+9\sum_{k=1}^{\infty} I(k)k^{-1}\sin(k\pi\zeta_0/\mu_0 H)+O[(\mu_0 H/\zeta_0)^2]\},$$

where n and ζ_0 are the free-electron density and Fermi level, and[8] $I(k)=\int_0^1 ds\, s^{1/2}(1-s)^{1/2}|\sin k\pi s|\, ds$. For $m\neq m^*$, σ_p has an oscillatory term with amplitude proportional to $H^{1/2}$.

With these considerations in mind, we turn to the calculation of Dogolpolov and Bystrik.[9] These authors consider only the Fermi contact term in the hyperfine interaction; consequently, their considerations apply only to the paramagnetic shielding constant σ_p. The semiclassical calculation, which they employ, is a slight generalization of the effective-mass approximation; the effective mass is simply expressed in terms of the local curvature of the Fermi surface. For the special case of a parabolic band, their result for the oscillatory part of σ_p [Eq. (10) of Ref. 9] agrees exactly with Stephen's result [Eq. (27) of Ref. 7]. Both the calculations of Stephen and Dogolpolov and Bystrik contradict Das and Sondheimer's speculation concerning the amplitude of the oscillatory part of the Knight shift. What Dogolpolov and Bystrik in effect did was to equate their σ with Stephen's σ_d.

In the remainder of this paper this problem is considered from the point of view of the nearly-free-electron approximation. For simplicity, only the Fermi contact term in $\mathcal{H}_p$ is considered; the calculation can easily be extended to include the other terms, but the interesting features already occur in this approximation. From the previous work on this problem, one has the feeling that any oscillatory behavior of σ_p must somehow be related to the susceptibility factor in (1.6), and thus arise from the behavior of the density of states at the Fermi surface. However, the semiclassical approximation has severe limitations for Bloch electrons in a magnetic field. Peierls,[10] and Kohn[11] and others have shown that the correct Hamiltonian (for a magnetic field in the z direction) has the form $\mathcal{H}=E(H,\mathbf{k})$ where $\mathbf{k}$ is a (wave vector) operator whose components obey the commutation relations $[k_x,k_y]=ieH/\hbar c$, $[k_x$ or $k_y,k_z]=0$. For $H=0$, $\mathcal{H}$ gives the ordinary band structure. The semiclassical approximation in effect replaces $E(H,\mathbf{k})$ by $E(0,\mathbf{k})$. It is the field dependence which gives rise, for example, to the lattice banding of the Landau levels and magnetic breakdown. Pippard[12] has shown that the Landau level band structure, at least for nearly free electrons, depends sensitively on the magnetic field, and one is led to conjecture that some field dependence of σ_p might arise via the wave-function factor in (1.6), which lies outside of the effective-mass approximation. Furthermore, since the wave function depends on the lattice potential to the first order, while the density of states displays only a second-order dependence, such an effect should be of importance in a situation to which the nearly-free-electron approximation is applicable. The shielding constant has been treated more or less exactly for Bloch electrons by Hebborn[13] and Stephen,[14] but their treatments are limited to $H=0$ and the non-semiclassical effects are missed.

The nearly-free-electron approximation leads to an approach which has the advantages of comprehensiveness, as far as including quantum effects, and reasonable simplicity. The free energy is simply expanded, by thermodynamic perturbation theory, in powers of the lattice potential. Unfortunately, this procedure has the disadvantage that convergence depends on conditions sufficiently restrictive to limit the validity of the results to weak or to very high fields strengths, and we can obtain only the steady behavior for moderate magnetic fields, and oscillatory behavior only in the so-called magnetic breakdown limit in which the Zeeman energy exceeds the largest energy gap and where the deHaas–van Alphen effect is dominated by the giant orbit oscillation. This method has already been applied to the magnetic susceptibility.[15] The calculation, as described, bears out the above conjecture: A field dependence of σ_p is obtained to first order in the periodic lattice potential.

[5] J. I. Kaplan, J. Phys. Chem. Solids **23**, 826 (1962).
[6] S. Rodriguez, Phys. Letters **4**, 306 (1963).
[7] M. J. Stephen, Phys. Rev. **123**, 126 (1961).
[8] M. L. Glasser, J. Math. Phys. **43**, 158 (1964).
[9] D. G. Dolgopolov and P. S. Bystrik, Zh. Eksperim. i Teor. Fiz. **46**, 593 (1964) [English transl.: Soviet Physics—JETP **19**, 404 (1964)].
[10] R. Peierls, Z. Physik **80**, 763 (1933).
[11] W. Kohn, Phys. Rev. **115**, 1460 (1959); E. I. Blount, *ibid.* **126**, 1636 (1962); L. M. Roth, J. Phys. Chem. Solids **23**, 433 (1962).
[12] A. B. Pippard, Phil. Trans. Roy. Soc. (London) **A256**, 317 (1964).
[13] J. E. Hebborn, Proc. Phys. Soc. (London) **80**, 1237 (1962).
[14] M. J. Stephen, Proc. Phys. Soc. (London) **79**, 987 (1962).
[15] M. L. Glasser, Phys. Rev. **134**, A1296 (1964); M. L. Glasser (unpublished).

II. CALCULATION

We consider N noninteracting electrons moving in a weak potential $V(\mathbf{r})$, which occupies a large volume Ω, in the presence of a nuclear magnetic moment $\boldsymbol{\mu}_n$, oriented along an external magnetic field represented by the vector potential $\mathbf{A}=(-Hy,0,0)$. Each electron is, accordingly, described by the Hamiltonian $\mathcal{H}=\mathcal{H}_L+\mathcal{H}_n+V(\mathbf{r})$, where

$$\begin{aligned}\mathcal{H}_L&=(1/2m)[\mathbf{p}-(e/c)\mathbf{A}]^2+2\mu_0 HS_z,\\ V(\mathbf{r})&=\textstyle\sum_{\mathbf{K}} V_{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}},\\ \mathcal{H}_n&=(16\pi/3)\mu_0\mu_n\delta(\mathbf{r})S_z.\end{aligned}\tag{2.1}$$

The eigenstates of $\mathcal{H}_L$ are the free-electron Landau levels

$$\begin{aligned}\langle r|\lambda\rangle&\equiv\langle\mathbf{r}|k_x,n,k_z,\sigma\rangle\\ &=N_n e^{-1/2(\eta-\eta_0)^2}H_n(\eta-\eta_0)e^{i(k_x x+k_z z)}\chi_\sigma,\\ E_\lambda&\equiv E_\sigma(n,k_z)=2\mu_0 H(n+\tfrac{1}{2})+\hbar^2k_z^2/2m+\mu_0H\sigma,\\ \eta&=(eH/\hbar c)^{1/2}y,\quad \eta_0=-(\hbar c/eH)^{1/2}k_x,\\ N_n&=(eH/\pi\hbar c)^{1/4}\Omega^{-1/3}(2^{n+1}n\,!)^{-1/2};\end{aligned}\tag{2.2}$$

the H_n are Hermite polynomials and $\chi_\sigma(\sigma=\pm1)$ are spin states. We require the expansion of the partition function

$$Z(\beta)=\mathrm{Tr}\{\exp(-\beta\mathcal{H})\},\quad \beta=1/k_BT,$$

to second order in $V(\mathbf{r})$ and first order in $\mathcal{H}_n$. This is conveniently obtained by using Schwinger trace formula[16]

$$\mathrm{Tr}\{\exp\beta(A+B)\}=\mathrm{Tr}\{e^{-\beta A}\}-\beta\,\mathrm{Tr}\{Be^{-\beta A}\}+\beta\sum_{n=2}^{\infty}[(-1)^n/n]\,\mathrm{Tr}\left\{Be^{-\beta A}\int_0^\beta d\beta_1\cdots\int_0^{\beta_{n-2}}d\beta_{n-1}B(\beta_1)\cdots B(\beta_{n-1})\right\},$$

where $B(\beta)=e^{-\beta A}Be^{\beta A}$. Carrying this out to third order, we find that the relevant terms are

$$\begin{aligned}Z(\beta)\cong Z_0(\beta)\{1+\tfrac{1}{2}\beta^2\sum_{\mathbf{K}\neq0}G(\mathbf{K},\beta)V_{\mathbf{K}}^2\}&-\beta\,\mathrm{Tr}\{\mathcal{H}_n e^{-\beta\mathcal{H}_L}\}+\beta^2\,\mathrm{Tr}\left\{\int_0^1 du\mathcal{H}_n e^{-\beta(1-u)\mathcal{H}_L}V(\mathbf{r})e^{-\beta u\mathcal{H}_L}\right\}\\ -\beta^3\,\mathrm{Tr}\left\{\mathcal{H}_n\int_0^1 du_1\int_0^{u_1}du_2 e^{-\beta(1-u_1)\mathcal{H}_L}V(\mathbf{r})e^{-\beta(u_1-u_2)\mathcal{H}_L}V(\mathbf{r})e^{-\beta u_2\mathcal{H}_L}\right\}&=Z_2(\beta)+Z_n^{(0)}(\beta)+Z_n^{(1)}(\beta)+Z_n^{(2)}(\beta).\end{aligned}\tag{2.3}$$

$Z_2(\beta)$, which is independent of $\mathcal{H}_n$, is described in Ref. 15 and is not required here.

We first describe in detail the evaluation of

$$Z_n^{(0)}(\beta)=-(16\pi/3)\mu_0\mu_n\beta\,\mathrm{Tr}\{\delta(r)S_z e^{-\beta\mathcal{H}_L}\},$$

which gives the shielding factor for free electrons. If Landau states are used to evaluate the traces, we have for any operator A

$$\mathrm{Tr}\{Ae^{-\beta\mathcal{H}_L}\}=(8\pi^2)^{-1}(eH/\hbar\pi c)^{1/2}\sum_\sigma\int_{-\infty}^{\infty}dk_x\int_{-\infty}^{\infty}dk_z\sum_{n=0}^{\infty}(2^n n!)^{-1}M(k_x n k_z\sigma|A)e^{-\beta E_\sigma(n,k_z)},$$

where

$$M=\int d^3r\, e^{-1/2(\eta-\eta_0)^2}H_n(\eta-\eta_0)e^{-i(k_x x+k_z z)}\chi_\sigma^* A e^{-1/2(\eta-\eta_0)^2}H_n(\eta-\eta_0)e^{i(k_x x+k_z z)}\chi_\sigma.$$

The calculation of the free energy is referred to unit volume and all volume factors have been dropped; a summation over spin indices is implied in the integration in M. In the present case,

$$M(k_x n k_z\sigma|S_z\delta(r))=\tfrac{1}{2}\sigma e^{-\eta_0^2}H_n^2(-\eta_0).$$

The k_z integration and σ sum are trivial; the n summation is easily performed by use of the relation

$$\sum_{n=0}^{\infty}(2^n n!)^{-1}e^{-1/2(x^2+y^2)}H_n(x)H_n(y)e^{-n\alpha}=2^{-1/2}(\mathrm{csch}\alpha)^{1/2}e^{\alpha/2}\exp[-\tfrac{1}{4}\{(x+y)^2\tanh(\tfrac{1}{2}\alpha)+(x-y)^2\coth(\tfrac{1}{2}\alpha)\}].\tag{2.4}$$

The k_x integral now becomes Gaussian and we obtain

$$Z_n^{(0)}=(8\pi/3)\mu_0\mu_n(m/2\pi\hbar^2)^{3/2}\mu_0H\beta^{1/2},$$

[16] A. Saenz and R. O'Rourke, Rev. Mod. Phys. **26**, 381 (1955).

which agrees with Stephen's[7] $Z_p(\beta)$ for $m=m^*$. For $T=0°\mathrm{K}$ the thermodynamic potential is given by (1.4). Correspondingly, we obtain

$$\Phi_n{}^{(0)}=-\zeta^{1/2}(4\mu_0\mu_n/3\pi)(eH/\hbar c)(2m/\hbar^2)^{1/2}, \tag{2.5a}$$

$$\sigma_p{}^{(0)}=(8\pi/3)\chi_p, \tag{2.5b}$$

χ_p being the free-electron spin susceptibility. (2.5b) agrees with (1.6) since for free electrons $\langle|\psi_F(0)|^2\rangle=1$.

The evaluation of the first-order correction to $\sigma_p{}^{(0)}$ proceeds by a natural extension of the above calculation. We have simply to evaluate

$$Z_n{}^{(1)}(\beta)=\beta^2\int_0^1 du\sum_{\lambda,\lambda'}\langle\lambda|\mathcal{H}_n|\lambda'\rangle\langle\lambda'|V(\mathbf{r})|\lambda\rangle e^{-\beta[(1-u)E_{\lambda'}+uE_\lambda]}.$$

The matrix elements are, in this case,

$$\langle\lambda|\mathcal{H}_n|\lambda'\rangle=(16\pi/3)\mu_0\mu_n e^{-1/2(\eta_0^2+\eta_0'^2)}H_n(-\eta_0)H_{n'}(-\eta_0')N_nN_{n'},$$

$$\langle\lambda'|V(\mathbf{r})|\lambda\rangle=(2\pi)^2\sum_{\mathbf{K}}V_{\mathbf{K}}\delta(k_x-k_x'-K_x)\delta(k_z-k_z'-K_z)N_nN_{n'}\int_{-\infty}^{\infty}dy\ e^{-1/2[(\eta-\eta_0)^2+(\eta-\eta_0')^2]}H_n(\eta-\eta_0)H_{n'}(\eta-\eta_0')e^{ik_yy}.$$

As before, the k_z integrations and σ sums are trivial, the n, n' summations are carried out easily by using (2.4), and the remaining k_x, k_x' and y integrals are all Gaussian. Thus we obtain, after a great deal of simplification,

$$Z_n{}^{(1)}(\beta)=-\beta^{3/2}(eH/\hbar c)(2\pi m/\hbar^2)^{1/2}(\mu_0\mu_n/6\pi)\sum_{\mathbf{K}}V_{\mathbf{K}}\int_0^1 du\,F(u)e^{-\beta u(1-u)\epsilon_{11}(\mathbf{K})}e^{-[\epsilon_\perp(K)/\mu_0H]f(u)}, \tag{2.5}$$

where $\epsilon_{11}(\mathbf{K})=\hbar^2K_z^2/2m$, $\epsilon_\perp(\mathbf{K})=\hbar^2(K_x^2+K_y^2)/2m$, and

$$F(u)=1+\operatorname{csch}\beta\mu_0H\sinh\beta\mu_0H(1-2u),$$
$$f(u)=\tfrac{1}{2}\operatorname{csch}\beta\mu_0H[\cosh\beta\mu_0H-\cosh\beta\mu_0H(1-2u)].$$

Changing the variable of integration to $s=1-2u$ we find that the second term coming from $F(u)$ vanishes by symmetry and we are left with

$$Z_n{}^{(1)}(\beta)=\beta^{3/2}(eH/\hbar c)(2\pi m/\hbar^2)^{1/2}(\mu_0\mu_n/12\pi)\sum_{\mathbf{K}}V_{\mathbf{K}}G(\mathbf{K},\beta),$$
$$G(\mathbf{K},\beta)=\exp\{-\tfrac{1}{4}\beta\epsilon_{11}(\mathbf{K})-\tfrac{1}{2}[\epsilon_\perp(\mathbf{K})/\mu_0H]\coth\beta\mu_0H\}\times\int_0^1 ds\exp\{\tfrac{1}{4}\beta\epsilon_{11}(\mathbf{K})s^2+\tfrac{1}{2}[\epsilon_\perp(\mathbf{K})/\mu_0H]\operatorname{csch}\beta\mu_0H\cosh\beta\mu_0Hs\}. \tag{2.6}$$

The third-order term may be handled in a similar fashion and, indeed, can be simplified to a remarkable extent, but the result is still too complicated to justify its inclusion in the following analysis and will no longer be considered.

Expanding (2.6) to second order in the magnetic field strength leads to the expression

$$Z_n{}^{(1)}(\beta)=-\beta^{3/2}(eH/\hbar c)(2\pi m/\hbar^2)^{1/2}(\mu_0\mu_n/6\pi)\sum V_{\mathbf{K}}\left[{}_1F_1(1,\tfrac{3}{2};-\tfrac{1}{4}\beta\epsilon)+\frac{1}{90}\beta^3\epsilon_\perp(\mathbf{K})(\mu_0H)^2\,{}_1F_1(3,\tfrac{7}{2};-\tfrac{1}{4}\beta\epsilon)\right],$$

where $\epsilon(\mathbf{K})=\epsilon_{11}+\epsilon_\perp$. Hence the low-field shielding factor, to first order in the lattice potential, is (see Appendix)

$$\sigma_p=(8\pi/3)\chi_p\left\{\langle|\psi_F(0)|^2\rangle-\frac{16}{45}(\mu_0H)^2\sum_{\mathbf{K}}(V_{\mathbf{K}}/\zeta)\epsilon_\perp(\mathbf{K})\zeta^{1/2}[\epsilon(\mathbf{K})]^{-7/2}h(a)\right\}, \tag{2.7}$$

where

$$\langle|\psi_F(0)|^2\rangle=1-\tfrac{1}{4}\sum_{\mathbf{K}}(V_{\mathbf{K}}/\zeta)a^{1/2}\ln|(1+a^{1/2})/(1-a^{1/2})|,$$
$$h(a)=-(\partial^3/\partial a^3)a^{5/2}\,{}_2F_1(\tfrac{1}{2},3,\tfrac{7}{2};a),\qquad a<1,$$
$$h(a)=a^{-6}(\partial^3/\partial(a^{-1})^3)a^{-1/2}\,{}_2F_1(\tfrac{1}{2},3,\tfrac{7}{2};a^{-1}),\quad a>1,$$

and $a=4\zeta/\epsilon(\mathbf{K})$. In spite of its apparent complexity, $h(a)$ is a slowly varying function except near $a=1$ where it diverges logarithmically. This divergence corresponds to the usual breakdown of the nearly-free-electron approximation when $2k_F=K$.

The first-order contribution to the partition function, $Z_n^{(1)}(\beta)$, has singularities along the imaginary axis in the complex β plane and, therefore, gives rise to oscillatory terms in the free energy. For simplicity we assume that $V(\mathbf{r})$ has only Fourier components with wave vectors perpendicular to the magnetic field. Then, introducing the notation $\lambda=\zeta/\mu_0 H$, $b=\epsilon(\mathbf{K})/\mu_0 H$, the first-order contribution to the free energy may be written

$$\Phi_n^{(1)}=\tfrac{1}{4}(\mu_0 H)^{-1/2}\left[\frac{8\pi}{3}\mu_0\mu_n(m/2\pi\hbar^2)^{3/2}\mu_0 H\right]\sum_{\mathbf{K}} V_{\mathbf{K}} I(\mathbf{K});$$
$$2\pi i I(\mathbf{K})=\int_{c-i\infty}^{c+i\infty} ds\int_0^1 du\, s^{-1/2}\exp[\lambda s+b\,\mathrm{csch}s(\cosh su-\cosh s)]. \tag{2.8}$$

By the mean-value theorem

$$\int_0^1 du\exp[b\,\mathrm{csch}s\cosh su]=\exp[b\,\mathrm{csch}s\cosh su_0],$$

where $0<u_0(s)<1$. The singularities at $s=k\pi i$ are therefore essential; however, except at $s=0$, the integrand vanishes if they are approached in the right half-plane, as may be seen by expanding the exponential about one of these points. Consequently, the s contour may be taken to lie along the imaginary axis (the remaining singularity at the origin is integrable). We divide $I(K)$ into two parts $I=I_0+I_1$ where I_1 is the integral from $s=-\pi i$ to $s=\pi i$ and I_0 is the rest. We further break up I_0 into a sum of integrals from $k\pi i$ to $(k+1)\pi i (k\neq -1, 0)$ and by means of the substitution $s\to i(k\pi+s)$ we find that

$$I_0=\frac{1}{2\pi}\sum_{k\neq 0,-1}^{\infty}\exp(i\lambda\pi+\tfrac{1}{4}i\pi\,\mathrm{sgn}k)\int_0^{\pi} ds\int_0^1 du|s+k\pi|^{-1/2}\exp\{i\lambda s-ib(-1)^k\,\mathrm{csc}s[\cos u(s+k\pi)-(-1)^k\cos s]\}. \tag{2.9}$$

Now consider the u integration

$$U_k(s)=\int_0^1\exp[ibh_k(s,u)]du,$$

where $h_k(s,u)=(-1)^{k+1}\,\mathrm{csc}s\cos u(s+k\pi)$. Since b will be at least of order 10^4 or higher, this may be treated by the method of stationary phase, according to which

$$U_k(s)=\sum_j[2\pi/b|h_k''(s,u_j)|]^{1/2}e_j\exp[ibh_k(s,u_j)+\tfrac{1}{4}i\pi\,\mathrm{sgn}h_k''(s,u_j)]+O(b^{-1}).$$

The sum is over the roots of $h_k'(s,u)=0$ which lie in the range of integration and e_j is $\frac{1}{2}$ or 1 according as u_j is an endpoint or not. Now, $h_k'(s,u)=0$ has the roots $u_j=j\pi/(s+k\pi)$ for which

$$h_k(s,u_j)=(-1)^{j+k+1}\,\mathrm{csc}s,$$
$$h_k''(s,u_j)=(-1)^{j+k}(s+k\pi)^2\,\mathrm{csc}s,$$

and it is clear, by inspection, that $j=0, 1, \cdots, k$ for $k>0$ and $|j|=0, 1, \cdots, |k|-1$ for $k<0$. Also $e_0=\frac{1}{2}$ only. In this way we obtain

$$U_k(s)\sim(\mathrm{sgn}k)[2\pi/b(s+k\pi)^2]^{1/2}(\tfrac{1}{2}+k\,\mathrm{Re})\exp[\tfrac{1}{4}i\pi-ib\,\mathrm{csc}s], \tag{2.10}$$

where Re denotes the real part. Inserting (2.10) into (2.9), we find

$$2(2\pi b)^{1/2}I_0\cong\sum_{-\infty}^{\infty}{}'\exp[i\lambda k\pi+\tfrac{1}{4}\pi i\,\mathrm{sgn}k](\mathrm{sgn}k)\left\{e^{i\pi/4}(k+1)\int_0^{\pi} ds(\sin s)^{1/2}|s+k\pi|^{-3/2}e^{ibg_1(s)}\right.$$
$$\left.+e^{-i\pi/4}k\int_0^{\pi} ds(\sin s)^{1/2}|s+k\pi|^{-3/2}e^{ibg_2(s)}\right\}, \tag{2.11}$$

where $g_j(s)=\frac{1}{2}as+\cot s+(-1)^j\csc s$. Now in the second integral replace s by $\pi-s$ and in the corresponding term in the sum over k replace k by $-(k+1)$. Then the simple result

$$(2\pi b)^{1/2}I_0=\mathrm{Re}\sum_{k\neq 0,-1}\exp[i\lambda k\pi+(1+\mathrm{sgn}k)\pi i/4](k+1)\,\mathrm{sgn}k\int_0^\pi ds(\sin s)^{1/2}|s+k\pi|^{-3/2}e^{ibg_1(s)}$$

is obtained. When $a<1$, meaning that the corresponding zone plane does not interesect the Fermi surface, $g_1(s)$ has no stationary point in the range of integration. The dominant contribution to the integral in (2.11) comes, therefore, from the neighborhood of the origin where $g_1(s)\sim s$. The integral is thus of order $b^{-3/2}$, which is completely negligible. When $a>1$, on the other hand, $g_1(s)$ is stationary at $s=s_0$ where

$$\begin{aligned}\cos s_0&=(2-a)/a\,,\\ g_1(s_0)&=\tfrac{1}{2}as_0-(a-1)^{1/2}\,,\\ g_1''(s_0)&=-\tfrac{1}{2}a(a-1)^{1/2}.\end{aligned}\tag{2.12}$$

We find, again by the method of stationary phase,

$$\int_0^\pi ds(\sin s)^{1/2}|s+k\pi|^{-3/2}e^{ibg_1(s)}\sim[2\pi/b]^{1/2}(2/a)\,|s_0+k\pi|^{-3/2}\exp[ibg_1(s_0)-\tfrac{1}{4}\pi i],$$

which gives

$$I_0=\frac{2}{ab}\sum_{k=1}^{\infty}\left\{\frac{(k+1)}{|s_0+k\pi|^{3/2}}\cos[\lambda k\pi+bg_1(s_0)+\tfrac{1}{4}\pi]+\frac{(k-1)}{|k\pi-s_0|^{3/2}}\cos[\lambda k\pi-bg_1(s_0)+\tfrac{1}{4}\pi]\right\}.\tag{2.13}$$

We next require I_1 which may be written

$$\pi I_1=\mathrm{Im}\int_{c^+}ds\int_0^1 du\,s^{-1/2}\exp[\lambda s+b\,\mathrm{csch}s(\cosh su-\cosh s)],\tag{2.14}$$

where Im denotes the imaginary part and c^+ is a path, lying in the right-hand s plane, from anywhere on the real axis to πi. We now let

$$U=\int_0^1\exp[\chi h(s,u)]du\,,$$

where $|\chi|=|b\,\mathrm{csch}s|\gg 1$ on c^+ and $h(u,s)=\cosh su$. Considering U by the method of steepest descents, we find that $u=0$ is a saddle point of order unity. Writing $s=\sigma e^{i\theta}$ and $u=\alpha+i\beta$, it is not difficult to show that the steepest paths through this point, given by $\mathrm{Im}h(s,u)=0$, are

$$\begin{aligned}\beta&=\alpha\tan(\pi/2-\theta)\,,\\ \beta&=-\alpha\tan\theta.\end{aligned}$$

If we distort the u contour to run along the former, we find easily that

$$U\sim\tfrac{1}{2}i[2\pi/|\chi|]^{1/2}(e^{\chi}/s)\,,$$

and (2.14) becomes

$$(2nb)^{1/2}I_1\cong\mathrm{Re}\int_{c^+}dss^{-3/2}|\sinh s|^{1/2}e^{bg(s)},$$

where $g(s)=\frac{1}{2}as-\coth s+\mathrm{csch}s$. For $a<1$, $g'(s)=0$ has a real positive root σ_0 given by $\cosh\sigma_0=(2-a)/a$ which may be chosen as the end-point of c^+, so this term exhibits only steady behavior. For $a>1$, $\sigma_0=is_0$, where s_0 is described in (2.12), and in addition $g(ix)=ig_1(x)$. The steepest paths have zero slope on the imaginary s axis; so, distorting the contour to pass horizontally through $s=is_0$, we find

$$\int_{c^+}ds|\sinh s|^{1/2}s^{-3/2}e^{bg(s)}\sim\frac{2}{a}s_0^{-3/2}[2\pi/b]^{1/2}\exp[ibg_1(s_0)-3i\pi/4],$$

and

$$I_1 \cong -[2/abs_0^{3/2}]\cos[bg_1(s_0)+\tfrac{1}{4}\pi]. \tag{2.15}$$

Combining (2.13) and (2.15) with (2.8) we find that, for $a(K)>1$, the oscillatory part of $\sigma_n^{(1)}$ is given by

$$\sigma_n^{(1)} = \tfrac{1}{2}(\mu_0 H)^{1/2}\left[\frac{8\pi}{3}\mu_0^2(m/2\pi\hbar^2)^{3/2}\right]\sum_{\mathbf{K}}'(V_{\mathbf{K}}/\zeta)\left\{s_0^{-3/2}\cos[\pi\xi_0/\mu_0 H+\tfrac{1}{4}\pi]\right.$$
$$\left.-\sum_{k=1}^{\infty}\left\{\frac{(k+1)}{|k\pi+s_0|^{3/2}}\cos[\pi\xi_k^{+}/\mu_0 H+\tfrac{1}{4}\pi]+\frac{(k-1)}{|k\pi-s_0|^{3/2}}\cos[\pi\xi_k^{-}/\mu_0 H+\tfrac{1}{4}\pi]\right\}\right\}, \tag{2.16}$$

where

$$\xi_0=\frac{1}{2\pi}\epsilon(\mathbf{K})g_1(s_0) \quad \text{and} \quad \xi_k^{\pm}=k\zeta\pm\xi_0.$$

III. DISCUSSION

Equation (2.7) has some interesting consequences. In a previous study of the effect of a crystal potential on the magnetic susceptibility[15,17] it was found that the spin susceptibility is affected to only second order in $V_{\mathbf{K}}$. Since, furthermore, $\langle|\Psi_F(0)|^2\rangle$ has no expansion in ascending powers of the magnetic field, (2.7) is inconsistent with Eq. (1.6) and the latter can be correct only for $H=0$. The error is of order $(\mu_0 H/\epsilon)^2(\delta/\zeta)$, where δ is a typical band gap, and for $H\sim 10^5$ G, $\epsilon\sim 10$ eV, $\zeta\sim 5$ eV, $\delta\sim 0.1$ eV, the field dependence amounts to about one part in 10^{10}, which is completely negligible. Such a field dependence might possibly be detected in a metal having a low Fermi level, large lattice spacing and large band gaps.

In the effective-mass approximation,[7] σ_p does exhibit an oscillatory and steady field dependence and it might be argued that this is equivalent to the first-order dependence discussed in this paper. However, doubt is cast on this interpretation by the following considerations: The effective-mass approximation for nearly free electrons in a magnetic field has been examined by Zilberman,[18] as follows. The states of a free electron in a uniform magnetic field are highly degenerate in the quantum number k_x; this degeneracy may be lifted, however, by applying an infinitesimal field $W(x)$ so that ordinary perturbation theory can be applied to include $V(\mathbf{r})$. Referring to the Landau states given earlier (now labeled $E_\lambda^{(0)}$) we have

$$E_\lambda = E_\lambda^{(0)}+\langle\lambda|V(r)|\lambda\rangle+\sum_{\lambda'\neq\lambda}\frac{|\langle\lambda|V|\lambda'\rangle|^2}{E_\lambda^{(0)}-E_{\lambda'}^{(0)}},$$

where $E_\lambda^{(0)}=2\mu_0 H(n+\frac{1}{2})+\hbar^2 k_z^2/2m+W_{k_x k_x}$. After some rather tedious simplifications, Zilberman is able to express this in the form

$$E_\lambda=\frac{e\hbar H}{2m_1^* c}(2n+1)+\hbar^2 k_z^2/2m_3^*+V_0+\sum_l A_l\cos(4\pi\alpha_l k_x),$$

where $m_1^*=m(1-c_1)^{-1}$, $m_3^*=m(1-c_3)^{-1}$ and α_l is independent of $V(\mathbf{r})$. All that need concern us here is that V_0 is a constant and the quantities c_1, c_3 and A_l are all proportional to $V_{\mathbf{K}}^2$. Thus, if the m^* of Stephen's work is interpreted as some function of Zilberman's effective-mass coefficients, Stephen's expression (27) for σ_0 can only lead to a field dependence which is of second order in $V(\mathbf{r})$. Hence, the first-order effects we have obtained lie outside the scope of the effective-mass approximation.

To discuss the oscillatory effects, we require an interpretation of (2.16). This is easily obtained with reference to Fig. 1. We find from (2.12) that $\cos\frac{1}{2}s_0=(K/2k_F)$, and s_0 may be identified as the angular aperture of the overlap, or lens, surface as seen from the center of the zone. The area of the lens is clearly $A_L=k_F^2(s_0-\sin s_0)=\frac{1}{2}K^2 g_1(s_0)$. Consequently, the frequency f_L of the oscillation corresponding to the effective Fermi level ξ_0, is given by $(\hbar c/2\pi e)A_L$, and the oscillation may be identified as due to the lens orbit. The oscillation in ξ_k^+ is due to an electron making k circuits of the Fermi sphere before tunneling to the lens, and the oscillation in ξ_k^- corresponds to an electron circling the Fermi sphere $k-1$ times and then following orbit (c) in Fig. 2. The giant orbit oscillation also occurs, but its amplitude is smaller than the others by a factor of 10^4. To obtain oscillations corresponding to more complicated orbits, as well as the de Haas–van Alphen oscillation when $a(K)<1$, requires going to higher order in $V(\mathbf{r})$.

It is clear that in first order, the oscillatory behavior

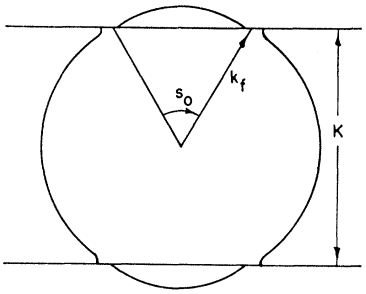

FIG. 1. Fermi-surface geometry for the case $a(\mathbf{K})>1$.

[17] R. Abe, Progr. Theoret. Phys. (Kyoto) **29**, 23 (1963).
[18] G. E. Zilberman, Zh. Eksperim. i Teor. Fiz. **23**, 49 (1952).

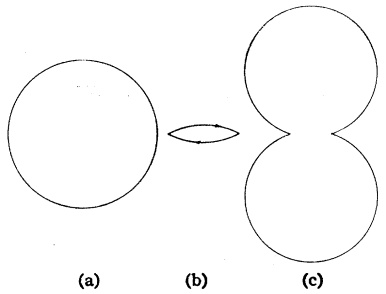

FIG. 2. Orbits corresponding to the oscillations which occur in first order. (a) Giant orbit, (b) Lens orbit, (c) Dumbbell orbit.

is dominated by the lens orbit oscillation σ_L for which we have

$$r=\frac{\text{amp}\sigma_L}{\sigma(H=0)}=\frac{\delta(\pi\mu_0 H)^{1/2}}{8(\zeta s_0)^{3/2}},$$

where δ is a typical band gap. Taking typical values of $\delta\cong 0.1$ eV, $\mu_0 H\cong 10^{-4}$ eV, $\zeta\cong 8$ eV, we find $r\cong s_0^{-3/2}\times 10^{-5}$. The effect will clearly be dominated by the oscillation for the zone plane which has the smallest overlap, and thus the smallest value of s_0. An overlap surface subtending an angle of a few degrees, which is not unreasonable to expect in tin, would give an r of the observed magnitude.

It should be pointed out that the limitation to a two-dimensionally periodic potential is not necessary, and the calculation can be extended to include the variation of $V(\mathbf{r})$ along the field with only a slight increase in complexity. On the other hand, the convergence of the nearly-free-electron approximation, as applied to the free energy, is extremely difficult to assess. The method has been used principally to bring out certain features of the shielding constant which are likely to be independent of the approximation scheme. Thus the extra labor in extending these results to more realistic potentials is probably not justified. For the same reason it is not proposed that (2.7) or (2.16) can be taken as a starting point for a numerical calculation from band-structure data.

APPENDIX

For example we evaluate the integral

$$J=-\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} z^{5/2}e^{-\lambda z}\,{}_1F_1(\tfrac{1}{2},\tfrac{7}{2};\lambda z)e^{\zeta z}dz.$$

Using the convolution theorem we find

$$J=-\lambda^{-7/4}\frac{\partial^3}{\partial\zeta^3}\left\{\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} z^{-1/2}\{z^{-7/4}e^{-1/2\lambda z}M_{5/4,5/4}(\lambda z)\}\times e^{\zeta z}dz\right\}$$

$$=-\lambda^{-7/4}\frac{\partial^3}{\partial\zeta^3}\int_0^{\zeta} f_1(u)f_2(\zeta-u)du,$$

where $M_{\kappa,\mu}(z)$ is a Whittaker function, and

$$f_1(u)=\mathfrak{L}_u^{-1}\{z^{-7/4}e^{-1/2\lambda z}M_{5/4,5/4}(\lambda z)\},$$

or

$$B(3,\tfrac{1}{2})f_1(u)=\lambda^{-3/4}u^2(\lambda-u)^{-1/2}\theta(\lambda-u)\theta(u),$$

and

$$f_2(u)=\mathfrak{L}_u^{-1}\{z^{-1/2}\}=\theta(u)(\pi u)^{-1/2}.$$

Hence,

$$\pi^{1/2}B(3,\tfrac{1}{2})J=\lambda^{-5/2}\frac{\partial^3}{\partial\zeta^3}\int_0^{\zeta} u^2\theta(\lambda-u)(\lambda-u)^{-1/2}(\zeta-u)^{-1/2}du.$$

Let

$$I=\int_0^d[(b-u)(d-u)]^{-1/2}u^2du.$$

If $u=dx$, then

$$b^{1/2}I=d^{5/2}\int_0^1[(1-x)(1+\alpha x)]^{-1/2}x^{s-1}dx,\qquad(\alpha=-d/b,\ s=3).$$

This may be obtained from a table of Mellin transforms, for example, and we find

$$b^{1/2}I=d^{5/2}B(3,\tfrac{1}{2})\,{}_2F_1[\tfrac{1}{2},3,\tfrac{7}{2};(d/b)],\quad d<b.$$

Thus,

$$\pi^{1/2}J=-\lambda^{-5/2}\frac{\partial^3}{\partial\zeta^3}\left[\zeta^{5/2}\lambda^{-1/2}\,{}_2F_1\left(\tfrac{1}{2},3,\tfrac{7}{2};\frac{\zeta}{\lambda}\right)\right],\quad \zeta<\lambda,$$

$$\pi^{1/2}J=-\lambda^{-5/2}\frac{\partial^3}{\partial\zeta^3}\left[\lambda^{5/2}\zeta^{-1/2}\,{}_2F_1\left(\tfrac{1}{2},3,\tfrac{7}{2};\frac{\lambda}{\zeta}\right)\right],\quad \lambda<\zeta.$$