Magnetic Shielding of a Nucleus by Free Electrons

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The magnetic-shielding constant of a nucleus by free electrons is evaluated by obtaining the classical partition function for a system of free electrons in a uniform magnetic field perturbed by the field of a nuclear magnet. Both diamagnetic and paramagnetic terms are included in the Hamiltonian. For a highly degenerate gas, the shielding constant has oscillatory terms similar to those in the magnetic susceptibility of a free-electron gas. The possibility of observing these terms is discussed.

1. INTRODUCTION

BESIDES the usual paramagnetic Knight shift[1] of the magnetic-resonance frequency of a nucleus in a metal, it was pointed out recently[2] that there may also be an appreciable diamagnetic shift in the opposite direction. Das and Sondheimer calculated the first field-independent term in the diamagnetic-shielding constant for free electrons and conjectured that oscillatory terms, similar to those found in the magnetic susceptibility, should exist. In this paper, it is shown that such oscillatory terms in the shielding constant may arise out of the paramagnetic and diamagnetic terms in the Hamiltonian. The paramagnetic oscillatory terms are merely a consequence of the fact that the density of states is an oscillatory function and are generally smaller than the corresponding diamagnetic terms.

The method employed here to evaluate the shielding constant is to expand the classical partition function of the electron gas in a magnetic field in terms of the perturbation due to the nuclear moment. Only the term linear in the perturbation is required. This expansion is most conveniently done using a Green's function and thus avoids the use of any basis set of functions. The Fermi-Dirac phenomena are derived from the analytical properties of the classical partition function. For an electron gas in a magnetic field, the classical partition function has poles along the imaginary axis and a branch point at the origin. In the case considered here, the poles are replaced by branch points. The branch point at the origin gives rise to the steady terms and the branch points along the imaginary axis to oscillatory terms in the shielding constant. In view of the interest of a number of groups in observing this phenomenon, it was decided to publish this work.

2. THEORY

To expand the partition function of a system in powers of a perturbation, we will use the standard Green's-function method.[3] The propagator $\Psi(\mathbf{r}_1, \mathbf{r}_2, \gamma_1-\gamma_2)$ is defined by

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \gamma_1-\gamma_2)=\eta(\gamma_1-\gamma_2) \textstyle\sum_i \psi_i^*(\mathbf{r}_2) \times\exp[-(\gamma_1-\gamma_2)\mathcal{H}]\psi_i(\mathbf{r}_1), \quad (1)$$

where $\eta(\gamma_1-\gamma_2)=1$ if $\gamma_1>\gamma_2$ and is zero otherwise. $\mathcal{H}$ is the complete Hamiltonian of the system and $\psi_i(\mathbf{r})$ are some complete set of states. The partition function $Z(\gamma)$ is given by

$$Z(\gamma)=\int d\mathbf{r}\, \Psi(\mathbf{r},\mathbf{r},\gamma), \quad (2)$$

where $\gamma=1/kT$. The propagator (1) satisfies the equation

$$\left(\frac{\partial}{\partial\gamma_1}+\mathcal{H}(\mathbf{r}_1)\right)\Psi(\mathbf{r}_1, \mathbf{r}_2, \gamma_1-\gamma_2)=\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(\gamma_1-\gamma_2). \quad (3)$$

The Hamiltonian $\mathcal{H}$ is taken to consist of two parts

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}', \quad (4)$$

and $\mathcal{H}'$ is treated as a perturbation. The Green's function for Eq. (3), $G(\mathbf{r}_1, \mathbf{r}_2, \gamma_1-\gamma_2)$, is defined as the solution of the equation

$$\left(\frac{\partial}{\partial\gamma_1}+\mathcal{H}_0(\mathbf{r}_1)\right)G(\mathbf{r}_1, \mathbf{r}_2, \gamma_1-\gamma_2) =\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(\gamma_1-\gamma_2). \quad (5)$$

Then it is easy to verify that the solution of (3) is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \gamma_1-\gamma_2)=G(\mathbf{r}_1, \mathbf{r}_2, \gamma_1-\gamma_2) -\int d\mathbf{r}_3 d\gamma_3\, G(\mathbf{r}_1, \mathbf{r}_3, \gamma_1-\gamma_3) \times\mathcal{H}'(\mathbf{r}_3)\Psi(\mathbf{r}_3, \mathbf{r}_2, \gamma_3-\gamma_2). \quad (6)$$

The Green's function with the appropriate boundary condition is

$$G(\mathbf{r}_1, \mathbf{r}_2, \gamma_1-\gamma_2)=\eta(\gamma_1-\gamma_2) \textstyle\sum_i \psi_i^*(\mathbf{r}_2) \times\exp[-(\gamma_1-\gamma_2)\mathcal{H}_0]\psi_i(\mathbf{r}_1). \quad (7)$$

In the present work, we will only require the term in the partition function linear in the applied perturbation. From (2) and (6), this is

$$Z'(\gamma)=-\int d\mathbf{r}\int d\mathbf{r}'d\gamma'\, G(\mathbf{r}, \mathbf{r}', \gamma-\gamma') \times\mathcal{H}'(\mathbf{r}')G(\mathbf{r}', \mathbf{r}, \gamma'). \quad (8)$$

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[1] C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. 77, 852 (1950).
[2] T. P. Das and E. H. Sondheimer, Phil. Mag. 5, 529 (1960).
[3] A. J. F. Siegert, J. Chem. Phys. 20, 572 (1952).

The system we consider here is a free-electron gas enclosed in a volume V in a uniform magnetic field H in the z direction. The gas is perturbed by a nuclear magnetic moment μ_N also in the z direction located in it. By fixing the nuclear magnet along the direction of the field H, terms leading to relaxation of the nucleus are neglected. The Hamiltonian $\mathcal{H}_0$ of (4) is that for an electron in a magnetic field H, i.e.,

$$\mathcal{H}_0=-\frac{\hbar^2}{2m^*}\nabla^2-i\mu_0^*H\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)+\frac{e^2H^2}{8m^*c^2}(x^2+y^2)+2\mu_0HS_z \quad (9)$$

and $\mathcal{H}'$ is the perturbation due to the moment μ_N. Separating diamagnetic and paramagnetic terms, $\mathcal{H}'$ is the sum of the two terms $\mathcal{H}_d$ and $\mathcal{H}_p$.

$$\mathcal{H}_d(\mathbf{r})=-2i\mu_0^*\mu_Nr^{-3}\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)+\frac{e^2H\mu_N}{2m^*c^2}\left(\frac{x^2+y^2}{r^3}\right), \quad (10)$$

$$\mathcal{H}_p=\mathcal{H}_p(\mathbf{r})S_z=(16\pi/3)\mu_0\mu_N\delta(\mathbf{r})S_z+2\mu_0\mu_N(3z^2-r^2/r^5)S_z. \quad (11)$$

The effective mass of the electron is denoted by m^*, and μ_0 is the Bohr magneton $(e\hbar/2mc)$.

It is convenient before using (8) to integrate over spin variables and then the coordinate propagator (1) is given by $(\gamma>0)$

$$\begin{aligned}\Psi(\mathbf{r}_1,\mathbf{r}_2,\gamma)&=\tfrac{1}{2}\exp(-\mu_0H\gamma)\textstyle\sum_i\psi_i^*(\mathbf{r}_2)\\&\quad\times\exp\{-\gamma[\mathcal{H}_0+\tfrac{1}{2}\mathcal{H}_p(\mathbf{r}_1)+\mathcal{H}_d(\mathbf{r}_1)]\}\psi_i(\mathbf{r}_1)\\&\quad+\tfrac{1}{2}\exp(\mu_0H\gamma)\textstyle\sum_i\psi_i^*(\mathbf{r}_2)\\&\quad\times\exp\{-\gamma[\mathcal{H}_0-\tfrac{1}{2}\mathcal{H}_p(\mathbf{r}_1)+\mathcal{H}_d(\mathbf{r}_1)]\}\psi_i(\mathbf{r}_1). \quad (12)\end{aligned}$$

Applying (8) to each term of (12) treating $\mathcal{H}_d\pm\frac{1}{2}\mathcal{H}_p$ as a perturbation, the required terms in the partition function are (again separating diamagnetic and paramagnetic contributions)

$$Z_d(\gamma)=-\gamma\cosh(\mu_0H\gamma)\int_0^1ds\int d\mathbf{r}d\mathbf{r}'\,G(\mathbf{r},\mathbf{r}',\gamma(1-s))\mathcal{H}_d(\mathbf{r}')G(\mathbf{r}',\mathbf{r},\gamma s), \quad (13)$$

$$Z_p(\gamma)=\tfrac{1}{2}\gamma\sinh(\mu_0H\gamma)\int_0^1ds\int d\mathbf{r}d\mathbf{r}'\,G(\mathbf{r},\mathbf{r}',\gamma(1-s))\mathcal{H}_p(\mathbf{r}')G(\mathbf{r}',\mathbf{r},\gamma s). \quad (14)$$

We only need consider these terms, which are linear in μ_N, to obtain the shielding constant of the nucleus. The Green's function in (13) and (14) is that for a spinless electron in a uniform magnetic field and is known from the work of Sondheimer and Wilson.[4] Thus,

$$\begin{aligned}G(\mathbf{r},\mathbf{r}',\gamma)=&\left(\frac{m^*}{2\pi\hbar^2}\right)^{\frac{3}{2}}\frac{\mu_0^*H\gamma}{\sinh(\mu_0^*H\gamma)}\\&\times\exp\Big[-\frac{m^*}{2\hbar^2\gamma}\{2i\mu_0^*H\gamma(xy'-yx')\\&+\mu_0^*H\gamma\coth(\mu_0^*H\gamma)[(x-x')^2+(y-y')^2]\\&+(z-z')^2\}\Big]. \quad (15)\end{aligned}$$

Substitution of (10), (11), and (15) in (13) and (14) followed by a number of integrations gives the results

$$Z_p(\gamma)=\frac{8\pi\mu_0\mu_N}{3}\left(\frac{m^*}{2\pi\hbar^2}\right)^{\frac{3}{2}}\mu_0^*H\gamma^{\frac{1}{2}}\frac{\sinh(\mu_0H\gamma)}{\sinh(\mu_0^*H\gamma)}, \quad (16)$$

$$\begin{aligned}Z_d(\gamma)=&-8\pi\mu_0^*\mu_N\left(\frac{m^*}{2\pi\hbar^2}\right)^{\frac{3}{2}}(\mu_0^*H)^2\frac{\gamma^{\frac{3}{2}}\cosh(\mu_0H\gamma)}{\sinh(\mu_0^*H\gamma)}\\&\times\int_0^1ds\,s(1-s)\{(A-1)^{-1}-A^{-\frac{1}{2}}(A-1)^{-\frac{3}{2}}\\&\times\ln[A^{\frac{1}{2}}+(A-1)^{\frac{1}{2}}]\}. \quad (17)\end{aligned}$$

It should be noted that, in obtaining (16), the second term of (11) vanishes indentically and the remaining integration is trivial. The integration of (13) is discussed in the Appendix. In (17)

$$A=\frac{\mu_0^*H\gamma s(1-s)\sinh(\mu_0^*H\gamma)}{\sinh(\mu_0^*H\gamma s)\sinh[\mu_0^*H\gamma(1-s)]}. \quad (18)$$

For Boltzmann statistics, the free energy is given by $F=-NkT\ln(Z_0+Z_p+Z_d)$, where Z_0 is the partition function of the free electrons in the magnetic field and N is the number of electrons. The nuclear-shielding constant is defined by

$$\sigma=-\frac{1}{H}\left(\frac{\partial F}{\partial\mu_N}\right)_{\mu_N=0}. \quad (19)$$

The differentiation here is with respect to μ_N rather than H because the shielding constant will in general depend on H. Equation (17) is easily expanded in power of $\mu_0H\gamma$ and the shielding constant is given by

$$\sigma_p=(8\pi N\mu_0/3VH)\tanh(\mu_0H\gamma), \quad (20)$$

$$\sigma_d=-(8\pi N\mu_0^{*2}\gamma/9V)[1-(4/75)(\mu_0^*H\gamma)^2\cdots]. \quad (21)$$

It is interesting to compare these results with what is obtained from a Lorentz sphere argument. As pointed out by Das and Sondheimer,[1] when the electron density is constant, the field at a nucleus contributed by elec-

[4] E. H. Sondheimer and A. H. Wilson, Proc. Roy. Soc. (London) **A210**, 173 (1951).

trons within a Lorentz sphere is just

$$(8\pi/3)(\chi_p+\chi_d), \tag{22}$$

where χ_p and χ_d are the paramagnetic and diamagnetic susceptibility, respectively. For a free-electron gas,[4]

$$\chi_p=(N\mu_0/VH)\tanh(\mu_0 H\gamma), \tag{23}$$

$$\chi_d=-(N\mu_0{}^*/VH)(\coth(\mu_0{}^*H\gamma)-1/\mu_0{}^*H\gamma). \tag{24}$$

Thus, $\sigma_p=(8\pi/3)\chi_p$ but the relation (22) is true only for the first terms of (21) and (24). The first term of (21) was obtained by Das and Sondheimer.

3. FERMI-DIRAC STATISTICS

In order to obtain the free energy for Fermi-Dirac statistics, we will use the same method as that used by Sondheimer and Wilson for the magnetic susceptibility of a free-electron gas.[4] We define a function $z(E)$ (related to the density of states) as the inverse Laplace transformation of the classical partition function

$$z(E)=(1/2\pi i)\int_{c-i\infty}^{c+i\infty} d\gamma\, e^{E\gamma}Z(\gamma)/\gamma^2, \tag{25}$$

where c is a positive constant chosen so that all the singularities of $Z(\gamma)$ lie to the left of the line of integration. In terms of the function $z(E)$, the free energy is given by

$$F=2\int_0^\infty dE\, z(E)\frac{\partial f_0}{\partial E}, \tag{26}$$

where f_0 is the Fermi function $[1+\exp\gamma(E-\zeta)]^{-1}$ and ζ is the Fermi energy and may be determined from the results of Sondheimer and Wilson on the magnetic susceptibility. This has been done in all the formulas following. The integral (25) is evaluated by completing the contour either to the right or left depending on which contour the integrand vanishes.

The paramagnetic term (16) presents no difficulties. For $m\neq m^*$, $Z_p(\gamma)$ has a series of simple poles along the imaginary axis with a branch point at $\gamma=0$. This is exactly the behavior of the magnetic susceptibility and following Sondheimer and Wilson the shielding constant is found to be

$$\sigma_p=\frac{4\pi N\mu_0{}^2}{V\zeta_0}\left\{1-\frac{1}{12}\left[2-\left(\frac{m}{m^*}\right)^2\right]\left(\frac{\mu_0 H}{\zeta_0}\right)^2\cdots\right.$$
$$+\frac{\pi}{\gamma}\left(\frac{1}{\mu_0 H\zeta_0}\right)^{\frac{1}{2}}\left(\frac{m}{m^*}\right)^{\frac{1}{2}}\sum_{n=1}^{\infty}$$
$$\left.\times\frac{(-)^n\sin(n\pi m^*/m)\cos(n\pi\zeta_0/\mu_0{}^*H-\pi/4)}{n^{\frac{1}{2}}\sinh(n\pi^2/\mu_0{}^*H\gamma)}\right\}, \tag{27}$$

where

$$\zeta_0=(9\pi N^2/V^2)^{\frac{1}{3}}(\pi\hbar^2/2m^*). \tag{28}$$

Clearly, the oscillatory term in (27) is a reflection of the fact that the density of states is an oscillatory function. The ratio of the amplitudes of the oscillatory term in (27) to the corresponding term in the diamagnetic susceptibility is

$$\left(\frac{\sigma_p}{\chi_d}\right)_{\text{osc}}=\frac{8\pi}{3}\left(\frac{m^*}{m}\right)\left(\frac{\mu_0{}^*H}{\zeta_0}\right)\tan\left(\frac{\pi m^*}{m}\right). \tag{29}$$

A typical value from the de Haas-van Alphen effect would be $N/V=10^{18}-10^{19}$ electrons/cc, leading to $\mu_0{}^*/\zeta_0=10^{-5}-10^{-6}$ gauss^{-1}. The other factors in (29) amount to about unity, and so, for a field of 10^4 gauss, the ratio (29) is about 10^{-2}. In an actual metal, a more exact analysis shows that the factor V^{-1} in (27) should be replaced by $|\psi(0)|^2$, where ψ refers to the wave function of an electron at the Fermi surface and is normalized in V. This may partly compensate the factor (29) if the electrons contributing to the de Haas-van Alphen effect are largely of s character. However, we will not discuss this further as a larger oscillatory term appears in the diamagnetic-shielding constant.

We now consider the diamagnetic-shielding constant arising out of (17). The steady terms are easily obtained by expanding $Z_d(\gamma)$ in powers of $\mu_0{}^*H\gamma$, and it is found that

$$\sigma_d(\text{steady})=-\frac{4\pi N\mu_0{}^{*2}}{3V\zeta_0}\times\left\{1-\frac{1}{4}\left(\frac{\mu_0{}^*H}{\zeta_0}\right)\left[\left(\frac{m^*}{m}\right)^2-\frac{29}{300}\right]\cdots\right\}. \tag{30}$$

The first term of (30) was obtained by Das and Sondheimer. We will mainly be concerned here with the oscillatory terms. The diamagnetic partition function (17) consists of two parts which we will distinguish by superscripts 1 and 2. The first part may be shown to have a series of simple poles along the imaginary axis and the oscillatory terms may be determined as above. These oscillatory terms turn out to be exactly the same order as (27) and therefore we will not consider them further. The second term in (17) may be shown to have a series of branch points along the imaginary axis at $\mu_0{}^*H\gamma=n\pi i$, $n=0\pm1\cdots$. We define

$$J(\mu_0{}^*H\gamma)=[\sinh(\mu_0{}^*H\gamma)]^{\frac{1}{2}}\times\int_0^1 ds\, A^{-\frac{1}{2}}(A-1)^{-\frac{3}{2}}\ln[A^{\frac{1}{2}}+(A-1)^{\frac{1}{2}}]. \tag{31}$$

Then, although we cannot obtain an expansion of this function about the point $\mu_0{}^*H\gamma=n\pi i$, we can, nevertheless, substitute this value in (31) to find

$$J(n\pi i)=-\tfrac{1}{2}\pi e^{\frac{1}{2}n\pi i}\int_0^1 ds[s(1-s)]^{\frac{1}{2}}|\sin n\pi s|,$$
$$=-\tfrac{1}{2}\pi e^{\frac{1}{2}n\pi i}I(n),\text{ say.} \tag{32}$$

These integrals may easily be evaluated numerically.

[$I(\infty)=\frac{1}{6}$.] In obtaining (32), use has been made of the result that for $0\leqslant s\leqslant 1$ and $z=n\pi i$

$$\sinh zs \sinh z(1-s)=|\sin n\pi s|^2 e^{in\pi}.$$

Then $Z_d^{(2)}(\gamma)$ has a series of branch points arising out of the function $[\sinh(\mu_0^*H\gamma)]^{-\frac{3}{2}}$. In order to make it single valued, we make a series of cuts in the plane from each point $n\pi i$ to $-\infty$ parallel to the real axis (see Fig. 1). For large real γ,

$$Z_d^{(2)}(\gamma)\sim\exp(|\mu_0 H\gamma|-\tfrac{3}{2}|\mu_0^*H\gamma|);$$

thus we complete the contour of (25) to the right when $E<(\frac{3}{2}|\mu_0^*H|-|\mu_0 H|)$, and hence, $z(E)$ vanishes for these values of E. For $E>(\frac{3}{2}|\mu_0^*H|-|\mu_0 H|)$, the contour is completed to the left avoiding all the branch cuts as shown in Fig. 1. As the integrand of (25) now has no poles or singularities within this contour, we only need consider the integrals along the loops encircling the branch cuts. Denoting the loop encircling the branch point $\mu_0^*H\gamma=n\pi i$ by σ_n, e.g., $ABCDE$ in Fig. 1, and putting $t=\mu_0^*H\gamma$ in (25) we have

$$z_d^{(2)}(E)=\frac{\mu_0^*H}{2\pi i}\sum_n\int_{\sigma_n}dt\times\exp(Et/\mu_0^*H)\frac{Z_d^{(2)}(t/\mu_0^*H)}{t^2}.\qquad(33)$$

Knowing the value of $Z^{(2)}$ at $t=n\pi i$ will be sufficient to obtain the most important oscillatory term. Consider the integral around $\sigma_n(n\neq 0)$ in (33) and put $t=n\pi i+x$. This integral becomes (omitting constants)

$$\exp\left[n\pi i\left(\frac{E}{\mu_0^*H}-\frac{3}{2}\right)\right]\frac{1}{2\pi i}\int_{\sigma_0}dx\times\frac{\exp(Ex/\mu_0^*H)\cosh(n\pi m^*i/m+x)J(n\pi i+x)}{(\sinh x)^{\frac{3}{2}}(n\pi i+x)}$$

$$\simeq\exp\left[n\pi i\left(\frac{E}{\mu_0^*H}-1\right)\right]\frac{\cos(n\pi m^*/m)I(n)}{2ni}\frac{1}{2\pi i}\times\int_{\sigma_0}dx\frac{\exp(Ex/\mu_0^*H)}{x^{\frac{3}{2}}}=\left(\frac{E}{\mu_0^*H}\right)^{\frac{1}{2}}\frac{(-)^nI(n)}{ni\pi^{\frac{1}{2}}}\times\cos\left(\frac{n\pi m^*}{m}\right)\exp(n\pi iE/\mu_0^*H).\qquad(34)$$

The terms omitted in (34) are of order $(\mu_0^*H/E)^{\frac{1}{2}}$. Combining (34) with the corresponding term for $-n$ gives the contribution to $z(E)$ from all those branch points with $n\neq 0$ to be

$$z_d^{(2)}(E)=-\left(\frac{m^*}{2\pi\hbar^2}\right)^{\frac{3}{2}}16\pi^{\frac{1}{2}}\mu_0^{*2}\mu_N HE^{\frac{1}{2}}\sum_{n=1}^{\infty}\frac{(-)^nI(n)}{n}\times\cos\left(\frac{n\pi m^*}{m}\right)\sin\left(\frac{n\pi E}{\mu_0^*H}\right).\qquad(35)$$

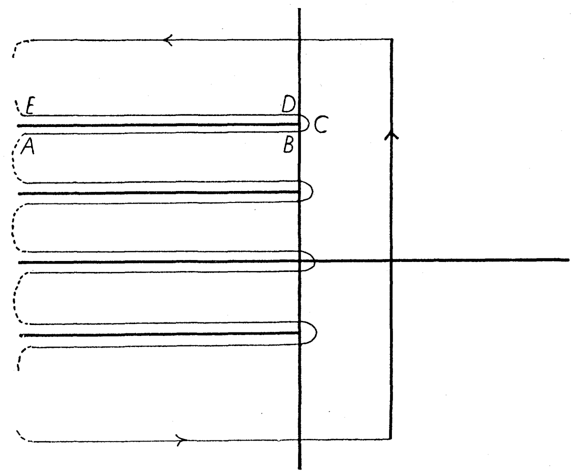

FIG. 1. Contour of integration of Eq. (33).

In order to calculate the free energy we need the integral

$$\gamma\,\mathrm{Im}\int_0^\infty dE\,E^{\frac{1}{2}}\exp(in\pi E/\mu_0^*H)\frac{e^{\gamma(E-\zeta)}}{(1+e^{\gamma(E-\zeta)})^2}.\qquad(36)$$

Put $\eta=\gamma(E-\zeta)$ and with an error of $O(e^{-\gamma\zeta})$ we can replace (36) by

$$\mathrm{Im}\exp(in\pi\zeta/\mu_0^*H)\int_{-\infty}^{\infty}d\eta\,|\zeta+\gamma^{-1}\eta|\frac{\exp(in\pi\eta/\mu_0^*H\gamma)e^\eta}{(1+e^\eta)^2}.\qquad(37)$$

This may be calculated by completing the contour in the upper half plane. Neglecting terms of order $(\gamma\zeta)^{-1}$, we find for (37) the result

$$-\frac{2\pi^2n\zeta^{\frac{1}{2}}}{\mu_0^*H\gamma}\frac{\sin(n\pi\zeta/\mu_0^*H)}{\sinh(n\pi^2/\mu_0^*H\gamma)}.\qquad(38)$$

The oscillatory terms in the diamagnetic shielding constant are determined from (38), (35), and (26) to be

$$\sigma_d(\mathrm{osc})=-\frac{12N\pi^3\mu_0^*}{V\zeta_0\gamma H}\sum_{n=1}^{\infty}\times\frac{(-)^nI(n)\cos(n\pi m^*/m)\sin(n\pi\zeta_0/\mu_0^*H)}{\sinh(n\pi^2/\mu_0^*H\gamma)}.\qquad(39)$$

The ratio of the amplitude of these terms to the corresponding terms in the diamagnetic susceptibility is (omitting factors of order unity)

$$\left(\frac{\sigma_d}{\chi_d}\right)_{\mathrm{osc}}=8\pi^2\left(\frac{\mu_0^*H}{\zeta_0}\right)^{\frac{1}{2}}I(1).$$

Owing to the extra factor of $8\pi^2$ with $H=10^4$ gauss and $(\mu_0^*/\zeta_0)=10^{-6}$ gauss^{-1}, this factor is approximately unity $[I(1)\sim 0.1]$. In order for the terms (39) to be observable, we require $\pi^2/\mu_0^* H\gamma<1$, i.e., a temperature of about 4°K and a field of about 10^4 gauss as in the de Haas-van Alphen effect. Then the amplitude of the first oscillation in (39) is

$$(12N\pi\mu_0^{*2}/V\zeta_0)I(1),$$

independent of the field and temperature. An estimation for zinc ($m^*=5\times10^{-3}$, $\mu_0^*/\zeta_0=3\times10^{-5}$)[5] gives 10^{-5} for this amplitude. Similar estimates for other metals lie in the range 10^{-4}–10^{-6}. Thus, in a favorable case, this effect may be observed as an actual shift; and in less favorable cases, it would be superimposed on the line width. The above estimates should be treated with caution. It is well known that the de Haas-van Alphen effect requires values of N/V and m^* to explain measured values which are very different from values deduced from other phenomena.[5] However, by using such measured values to make the above estimates, we would expect to obtain the correct order of magnitude.

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APPENDIX

Here we will derive Eq. (17). Substitution of (10) in (13) leads to an integral of the form

$$\int d\mathbf{r}d\mathbf{r}'\left(\frac{x'^2+y'^2-xx'-yy'}{r'^3}\right)\times\exp\{-\alpha^2[(x-x')^2+(y-y')^2]\}\times\exp[-\delta^2(z-z')^2], \quad \text{(A1)}$$

where

$$\alpha^2=\frac{m^*\mu_0^*H}{2\hbar^2}\frac{\sinh(\mu_0^*H\gamma)}{\sinh(\mu_0^*H\gamma s)\sinh[\mu_0^*H\gamma(1-s)]}, \quad \text{(A2)}$$

$$\delta^2=m^*/2\hbar^2\gamma s(1-s). \quad \text{(A3)}$$

It is convenient to integrate (A1) over the volume contained within the ellipsoid $\alpha^2x^2+\alpha^2y^2+\delta^2z^2=R^2$, although the final result is independent of the shape of the system. The scale transformation $\alpha x\rightarrow x$, $\alpha y\rightarrow y$, $\delta z\rightarrow z$ turns this ellipse into a sphere and brings (A1) into the form

$$\frac{\delta}{\alpha^3}\int d\mathbf{r}d\mathbf{r}'\left(\frac{x'^2+y'^2-xx'-yy'}{(\delta^2x'^2+\delta^2y'^2+\alpha^2z'^2)^{\frac{3}{2}}}\right)\exp[-(\mathbf{r}-\mathbf{r}')^2]. \quad \text{(A4)}$$

Keeping $\mathbf{r}'$ fixed, we integrate over all angles of $\mathbf{r}$ with respect to $\mathbf{r}'$ by choosing the axis of $\mathbf{r}$ along $\mathbf{r}'$. This gives

$$\frac{4\pi^2\delta}{\alpha^3}\int_0^\pi d\theta'\frac{\sin^3\theta'}{(\delta^2\sin^2\theta'+\alpha^2\cos^2\theta')^{\frac{3}{2}}}\int_0^R r^2dr\int_0^R r'^2dr'\times\exp(-r^2-r'^2)\left\{\frac{\sinh(2rr')}{rr'^2}+\frac{\sinh(2rr')}{2rr'^4}-\frac{\cosh(2rr')}{r'^3}\right\}. \quad \text{(A5)}$$

The first integral gives ($\alpha^2>\delta^2$)

$$\frac{2\alpha}{\delta^2(\alpha^2-\delta^2)}-\frac{2}{(\alpha^2-\delta^2)^{\frac{3}{2}}}\ln\left(\frac{\alpha+(\alpha^2-\delta^2)^{\frac{1}{2}}}{\delta}\right). \quad \text{(A6)}$$

The radial integral may be simplified by integrating the last term by parts (which cancels the first two) to give

$$\int_0^R r^2dr\exp(-r^2)\left(1-\exp(-R^2)\frac{\sinh(2rR)}{2rR}\right).$$

This is easily evaluated to give $\pi^{\frac{1}{2}}/8$ together with terms which vanish as $R\rightarrow\infty$. Together with (A6) this leads to (17).

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[5] D. Shoenberg, *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2, p. 226.