Zh. Eksperim. i Teor. Fiz. 31, 63 (1956) [Sov. Phys. JETP 4, 41 (1957)]; I. M. Lifshitz and V. G. Peschanskii, *ibid.* 35, 1251 (1958) [8, 875 (1959)].

[6] R. W. Stark and L. M. Falicov, in *Progress in Low Temperature Physics*, Vol. V, edited by C. J. Gorter (North-Holland, Amsterdam, 1967), p. 235, and enclosed references.

[7] R. W. Stark, T. G. Eck, and W. L. Gordon, Phys. Rev. 133, A443 (1964).

[8] R. W. Stark, Phys. Rev. 135, A1698 (1964).

[9] R. W. Stark and C. B. Friedberg, Phys. Rev. Letters 26, 556 (1971).

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Diamagnetic Susceptibility of Metals with Complicated Crystal Structures

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We have derived an expression for the diamagnetic susceptibility of metals with complicated crystal structures from the general expression for the diamagnetic susceptibility obtained by Misra and Roth in a pseudopotential formalism. We have used this expression to calculate the diamagnetic susceptibility of zinc, and our result agrees well with the experimental result calculated from the available data. We have also used the known parameters of bismuth to study the variation of susceptibility with the Fermi level. Our results indicate that if there were a gap over most of the original Fermi surface, we expect to have positive diamagnetism.

I. INTRODUCTION

The problem of Bloch electrons in a magnetic field has been solved by many authors[1–4] who have obtained essentially equivalent expressions for the diamagnetic susceptibility, though these are written in different forms. In its fundamental principles, there is nothing too profound in the calculation of the diamagnetic susceptibility. The action of a magnetic field upon a band can be resolved into two effects. One effect gradually transforms the parameters of that band. The other effect consists of the breaking up of the band into a series of discrete states. The bands thereby become renormalized or field dependent. The diamagnetic susceptibility is calculated from a computation of these renormalized bands. However, the resulting formalism is so enormously complicated that application to realistic band structures is a very formidable and complicated task. Because of these computational obstacles, till recently, no attempt was made to obtain even an estimate of the order of different terms in the expression for the diamagnetic susceptibility.

Recently, there have been some attempts to calculate the diamagnetic susceptibility of metals from the above formalisms by using suitable models so that they would be amenable to calculation. Ruvalds[5] has calculated the diamagnetic susceptibility in a magnetic breakdown model using the result of Wannier and Upadhyaya.[4] Fukuyama and Kubo[6] have treated the simple model of two bands produced by a weak cosine potential to analyze the interband effect appearing for a pair of bands with a small energy gap. More recently, Fukuyama and Kubo[6] and Buot and McClure[7] have employed $\vec{k}\cdot\vec{p}$ methods to calculate the diamagnetic susceptibility of bismuth. These authors conclude that a combination of spin-orbit interaction and small energy gap account for the large diamagnetism of bismuth. Buot[8] has calculated the contribution to the diamagnetism of bismuth-antimony alloys from the region of the Brillouin zone which contains the carriers and has obtained satisfactory agreement with experimental results. These last results treat the band edges very well but involve a large-$\vec{k}$ cutoff which introduces some uncertainty.

Recently, we (Misra and Roth) have obtained a tractable expression for the diamagnetic susceptibility of simple metals[9] through the use of a pseudopotential formalism and degenerate perturbation theory. Along the way we have been able to rederive the general result for the susceptibility of Bloch electrons in a relatively simple fashion. We have calculated the diamagnetic susceptibility of some simple metals and there has been good agreement with experimental results, where available. However, there is a difficulty in using our expression

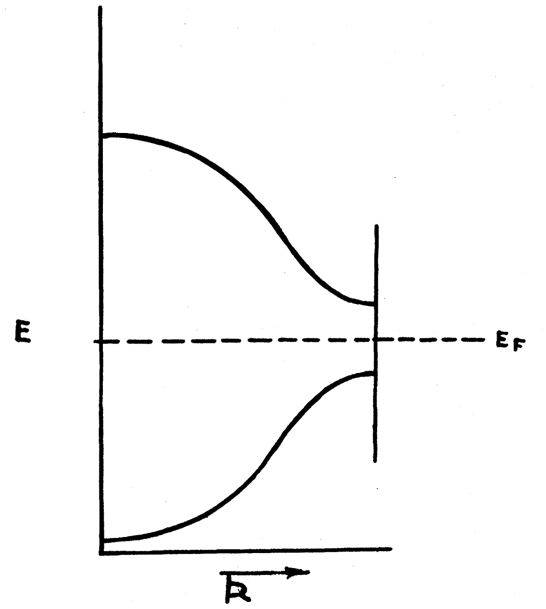

FIG. 1. Energy vs $\vec{k}$ vector in the direction of a neck in the Fermi surface.

for metals with complicated crystal structures. In order to simplify our general formula for the diamagnetic susceptibility, we have expanded the Fermi function [Eqs. (6.8) and (6.9) in I]

$$f(E)=f(E_0)+(E-E_0)f'(E_0)+\cdots \tag{1}$$

and

$$f_\zeta(E_0)=f_{\zeta_0}(E_0)+(\zeta-\zeta_0)\left.\frac{\partial f}{\partial \zeta}\right|_0+\cdots , \tag{2}$$

where E is the exact energy, ζ is the chemical potential, and E_0 and ζ_0 are the corresponding values for free electrons. These approximations are valid for simple metals but they are not valid when there is a neck in the Fermi surface. In some sense a neck is similar to the Fermi level being in an energy gap. If we look along the $\vec{k}$ vector in the direction of the neck, the energy looks as in Fig. 1. However, if we turn away from this $\vec{k}$ direction, the gap moves up above the Fermi surface. The avoidance of the above expansion thus appears to be a first step in treating more complicated band structures.

In this paper (Sec. II) we explicitly consider the case of a neck in the Fermi surface and derive an expression for the diamagnetic susceptibility from the general expression obtained in I in a way such that we avoid the approximation in Eq. (1). The contribution of the rest of the filled conduction band is also included in our calculation.

Next, in Sec. III, we show how to combine the contribution of several or many independent Bragg reflections. The main problem here is putting in the shift of the Fermi energy correctly.

The resulting expressions are valid for metals in which the pseudopotential theory is good and in which the departure from free-electron behavior is small even though the band structure is complex because of the presence of many bands. We apply the results to Zn as an example.

The present results do not apply to materials such as Bi for which the energy gap goes over most of the Brillouin zone. As mentioned above, in the case of necks there are gaps in certain $\vec{k}$ directions, but when these combine to produce a more extended gap, the Bragg reflections can hardly be called independent. It is clear that in such cases a direct evaluation of Eq. (5.36) in I is necessary, and we hope to carry this out in the future. We can, however, argue from the case of a neck that the energy gap contributes to an enhanced diamagnetism.

II. THEORY FOR A SINGLE BRAGG REFLECTION

We shall first derive an expression for the chemical potential in the pseudopotential formalism. We start with the familiar expression

$$(1/4\pi^3)\int d^3k f(E)=N , \tag{3}$$

where E is the exact energy and N is the total number of electrons per unit volume. We shall use degenerate perturbation theory to evaluate E so that we consider coupled bands. At any point on a Bragg reflection plane there are two states of the same energy which are coupled, on the line of intersection there are three states that are coupled, and where two such lines intersect, four states are coupled. For metals with complicated crystal structures, all these cases arise. However, in this paper, in order that the problem can be solved analytically, we shall consider the case of a general point on the plane so that the unperturbed eigenvalue is doubly degenerate. Also we omit spin so that the spin contribution is completely separated from the orbital part to which we focus our attention. The expression for E, the exact energy for one Bragg reflection, can be easily shown to be

$$E=\frac{1}{2}\left(\frac{k^2}{2m}+\frac{(\vec{k}+\vec{G})^2}{2m}\right)\pm\left[\frac{1}{4}\left(\frac{k^2}{2m}-\frac{(\vec{k}+\vec{G})^2}{2m}\right)^2+W_{\vec{k}\vec{G}}^2\right]^{1/2} , \tag{4}$$

where $\vec{k}$ is a wave vector, $\vec{G}$ is a reciprocal-lattice vector, m is the mass of the electron, and

$$W_{\vec{k}\vec{G}}^2 \equiv |\langle\vec{k}+\vec{G}|\,W|\vec{k}\rangle|^2 , \tag{5}$$

where W is the pseudopotential ($\hbar=1$ throughout the paper). We shall use cylindrical coordinates to

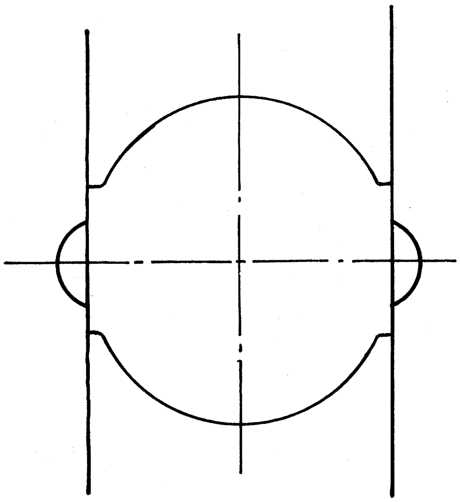

FIG. 2. Bragg planes which cut the Fermi surface.

evaluate (3). We choose $\vec{G}$ parallel to the z axis. Thus we may write

$$E = E_{xy} + E_z , \tag{6}$$

where

$$E_{xy} = (k_x^2 + k_y^2)/2m \tag{7}$$

and

$$E_z = \frac{(k_z + G)^2 + k_z^2}{4m} \pm \left(\frac{[(k_z + G)^2 - k_z^2]^2}{4m} + W^2_{\vec{k}\vec{G}} \right)^{1/2} . \tag{8}$$

So (3) may be written as

$$\frac{1}{4\pi^2} \iint dk_\rho^2 dk_z f_\zeta (E_{xy} + E_z) = N , \tag{9}$$

where the limits of k_ρ is from 0 to $[2m(\zeta - E_z)]^{1/2}$. Integrating over k_ρ, (9) becomes

$$\frac{m}{2\pi^2} \int_{E_z < \zeta} (\zeta - E_z) \, dk_z = N . \tag{10}$$

We include the case of the Bragg reflection plane cutting the Fermi surface as in Fig. 2. We must search for roots when $k_z = -\frac{1}{2}G$. We introduce dimensionless units

$$\gamma = (2/G)(\tfrac{1}{2}G + k_z) , \tag{11}$$

$$a = 8m\zeta/G^2 , \tag{12}$$

and

$$v = 4m W_{\vec{k}\vec{G}}/G^2 . \tag{13}$$

Substituting (11)–(13) in (8), we obtain

$$E_z = \frac{G^2}{4m} \left[\frac{1}{2}(1 + \gamma^2) - \gamma \left(1 + \frac{v^2}{\gamma^2}\right)^{1/2} \right] . \tag{14}$$

From (9), (11), and (14), we have

$$\frac{G^3}{16\pi^2} \int_{\gamma_-}^{\gamma_+} \left[\frac{1}{2}(a - 1 - \gamma^2) + \gamma \left(1 + \frac{v^2}{\gamma^2}\right)^{1/2} \right] d\gamma = N , \tag{15}$$

where γ_+ and γ_- are upper and lower roots of $E_z = \zeta$. These roots are obtained by solving the equation

$$\tfrac{1}{2}(a - 1 - \gamma^2) + \gamma(1 + v^2/\gamma^2)^{1/2} = 0 . \tag{16}$$

The solutions can be shown to be

$$\gamma_\pm = (1 \pm a^{1/2}) \left[1 \pm 2 \frac{(a - v^2)^{1/2} - a^{1/2}}{(1 \pm a^{1/2})^2} \right]^{1/2} . \tag{17}$$

We now integrate (15) to obtain (for both $a < 1$ and $a > 1$)

$$\frac{G^3}{32\pi^2} \left[(a-1)(\gamma_+ - \gamma_-) - \tfrac{1}{3}(\gamma_+^3 - \gamma_-^3) + \gamma_+(\gamma_+^2 + v^2)^{1/2} - |\gamma_-| (\gamma_-^2 + v^2)^{1/2} + v^2 \ln \frac{\gamma_+ + (\gamma_+^2 + v^2)^{1/2}}{\gamma_- + (\gamma_-^2 + v^2)^{1/2}} \right] = N . \tag{18}$$

It is easy to show that

$$N = \tfrac{4}{3}(G^3/32\pi^2)\, a_0^{3/2} , \tag{19}$$

where

$$a_0 = (8m/G^2) E_F \tag{20}$$

and E_F is the Fermi energy. From (18) and (19), we have

$$a_0 = \left[\frac{3}{4} \left((a-1)(\gamma_+ - \gamma_-) - \tfrac{1}{3}(\gamma_+^3 - \gamma_-^3) + \gamma_+(\gamma_+^2 + v^2)^{1/2} - |\gamma_-| (\gamma_-^2 + v^2)^{1/2} + v^2 \ln \frac{\gamma_+ + (\gamma_+^2 + v^2)^{1/2}}{\gamma_- + (\gamma_-^2 + v^2)^{1/2}} \right) \right]^{2/3} . \tag{21}$$

γ_+ and γ_- are obtained from (17) and are functions of a. We can write the right-hand side as $A(a)$ and then write (21) in the form

$$a = a_0 - [A(a) - a] . \tag{22}$$

We can now calculate a by a reiteration process. Thus the chemical potential can be evaluated to any order of accuracy.

We shall now derive an expression for the diamagnetic susceptibility. We make our starting point Eqs. (6.6) and (6.25) of I from which we have

$$\chi=\frac{h^2}{12\pi^3m^2H^2}\iiint d^3k\,f'(E)-\frac{8h_{\alpha\beta}h_{\gamma\delta}}{\pi^3H^2}G^\alpha G^\gamma\Bigg[\iiint d^3k\,\frac{W_{\vec{k}\vec{G}}^2f'(E)}{[(G^2+2\vec{k}\cdot\vec{G})^2+16m^2W_{\vec{k}\vec{G}}^2]^{3/2}}$$

$$\times\left(\frac{\delta_{\beta\delta}}{6}-\frac{k^\beta k^\delta}{[(G^2+2\vec{k}\cdot\vec{G})^2+16m^2W_{\vec{k}\vec{G}}^2]^{1/2}}\right)+m\iiint d^3k\,\frac{W_{\vec{k}\vec{G}}^2f(E)}{[(G^2+2\vec{k}\cdot\vec{G})^2+16m^2W_{\vec{k}\vec{G}}^2]^2}$$

$$\times\left(\delta_{\beta\delta}-\frac{8k^\beta k^\delta}{[(G^2+2\vec{k}\cdot\vec{G})^2+16m^2W_{\vec{k}\vec{G}}^2]^{1/2}}\right)\Bigg]\,, \qquad (23)$$

where $\vec{H}$ is the magnetic field

$$\vec{h}=e\vec{H}/2c\,, \qquad (24)$$

$$h_{\alpha\beta}=\epsilon_{\alpha\beta\gamma}h^\gamma\,, \qquad (25)$$

$\epsilon_{\alpha\beta\gamma}$ is the complete antisymmetric tensor of the third rank, and we use the Einstein summation convention. Note that we have corrected the printing errors in sign in the first and the last terms in (23). We write (23) as

$$\chi=\chi_1+\chi_2+\chi_3\,, \qquad (26)$$

where χ_1 is the first term (essentially the Landau term), and χ_2 and χ_3 are the second and third terms in the expression for susceptibility. As before, we shall use cylindrical coordinates and also use the fact that at zero temperature

$$f'(E)=-\delta(E-\zeta)\,. \qquad (27)$$

From Eqs. (11), (23), (26), and (27), we have

$$\chi_1=-\frac{\mu_B^2mG}{12\pi^2}\iint\frac{1}{2m}\,dk_\rho^2\,d\gamma\,\delta(E_{xy}+E_z-\zeta)\,, \qquad (28)$$

where μ_B is the Bohr magneton. This is easily integrated and we obtain

$$\chi_1=-\frac{\mu_B^2mG}{12\pi^2}(\gamma_+-\gamma_-)\,. \qquad (29)$$

From Eqs. (11)–(13), (23), (26), and (27), we have, after some simplification,

$$\chi_2=\frac{\mu_B^2v^2G_\perp^2G^4}{2\pi^2}\iint dk_\rho^2\,dk_z\,\frac{\delta(E-\zeta)}{[G^2\gamma(1+v^2/\gamma^2)^{1/2}]^3}$$

$$\times\left(\frac{1}{6}-\frac{k_\rho^2}{2G^2\gamma}(1+v^2/\gamma^2)^{1/2}\right). \qquad (30)$$

The integration over k_ρ yields

$$\chi_2=\frac{\mu_B^2G_\perp^2mv^2}{2\pi^2G}\int_{\gamma_-}^{\gamma_+}d\gamma\,\frac{1}{\gamma^3(1+v^2/\gamma^2)^{3/2}}$$

$$\times\left(\frac{1}{6}-\frac{4m(\zeta-E_z)}{G^2\gamma(1+v^2/\gamma^2)^{1/2}}\right). \qquad (31)$$

From Eqs. (7), (11)–(13), (23), and (26), we have

$$\chi_3=-\frac{\mu_B^2G_\perp^2m^2v^2}{2\pi^2G^3}\iint dE_{xy}\,d\gamma\,\frac{f(E)}{\gamma^4(1+v^2/\gamma^2)^2}$$

$$\times\left(1-\frac{8mE_{xy}}{G^2\gamma(1+v^2/\gamma^2)^{1/2}}\right). \qquad (32)$$

The integration over E_{xy} yields

$$\chi_3=-\frac{\mu_B^2G_\perp^2m^2v^2}{2\pi^2G^3}\int_{\gamma_-}^{\gamma_+}d\gamma\,\frac{(\zeta-E_z)}{\gamma^4(1+v^2/\gamma^2)^2}$$

$$\times\left(1-\frac{4m(\zeta-E_z)}{G^2\gamma(1+v^2/\gamma^2)^{1/2}}\right)\,. \qquad (33)$$

From (31) and (33), we have

$$\chi_2+\chi_3=\frac{\mu_B^2G_\perp^2mv^2}{2\pi^2G}\int_{\gamma_-}^{\gamma_+}d\gamma\,\frac{1}{\gamma^3(1+v^2/\gamma^2)^{3/2}}$$

$$\times\left[\frac{1}{4}\left(\frac{4m(\zeta-E_z)}{G^2\gamma(1+v^2/\gamma^2)^{1/2}}-1\right)^2-\frac{1}{12}\right]. \qquad (34)$$

This can be integrated after some further simplification. The result is

$$\chi_2+\chi_3=\frac{\mu_B^2G_\perp^2mv^2}{2\pi^2G}\,I\,, \qquad (35)$$

where

$$I=-\frac{(1-3a)}{24}\left(\frac{1}{[\gamma_++(\gamma_+^2+v^2)^{1/2}](\gamma_+^2+v^2)^{1/2}}-\frac{1}{[|\gamma_-|+(\gamma_-^2+v^2)^{1/2}](\gamma_-^2+v^2)^{1/2}}\right)$$

$$-\frac{(a-1+v^2)^2}{16}\left(\frac{1}{[\gamma_++(\gamma_+^2+v^2)^{1/2}]^2\,(\gamma_+^2+v^2)}-\frac{1}{[|\gamma_-|+(\gamma_-^2+v^2)^{1/2}]^2\,(\gamma_-^2+v^2)}\right.$$

$$-\frac{v^2}{3[\gamma_+ + (\gamma_+^2+v^2)^{1/2}]^3(\gamma_+^2+v^2)^{3/2}}+\frac{v^2}{3[|\gamma_-|+(\gamma_-^2+v^2)^{1/2}]^3(\gamma_-^2+v^2)^{3/2}}\Bigg)+\frac{1}{16}\ln\frac{\gamma_+ + (\gamma_+^2+v^2)^{1/2}}{|\gamma_-|+(\gamma_-^2+v^2)^{1/2}}\;. \tag{36}$$

From (29) and (35), we obtain

$$\chi=-\frac{\mu_B^2 mG}{12\pi^2}\left((\gamma_+-\gamma_-)-\frac{6G_\perp^2v^2}{G^2}I\right). \tag{37}$$

Our expression can be written in the alternative form

$$\chi=\chi_0\left(\frac{\gamma_+-\gamma_-}{2a_0^{1/2}}-\frac{3G_\perp^2v^2}{a_0^{1/2}G^2}I\right), \tag{38}$$

where χ_0 is the diamagnetic susceptibility of free electrons. This is the expression for the diamagnetic susceptibility of a metal.

In Fig. 3 we plot χ vs a_0, using a from Eq. (22). We note that similar results have been obtained by Ruvalds[5] and Fukuyama and Kubo.[6] Far away from the zone boundary this expression can be expanded to second order in v in which limit we have

$$\frac{\gamma_+-\gamma_-}{2a_0^{1/2}}=1-\frac{v^2}{2a_0^{1/2}a^{3/2}}\left(\frac{a^{3/2}}{a_0}\tanh^{-1}a^{1/2}-\frac{a}{1-a}\right) \tag{39}$$

and

$$I=\frac{1}{3a^{3/2}}\left(\frac{5a^2-3a^3}{8(1-a)^2}+\tfrac{3}{8}a^{3/2}\tanh^{-1}a^{1/2}\right). \tag{40}$$

From (38)–(40), we have, up to second order in v,

$$\chi=\chi_0\Bigg\{1-\frac{v^2}{2a_0^{1/2}a^{3/2}}\Bigg[\left(\frac{a^{3/2}}{a_0}\tanh^{-1}a^{1/2}-\frac{a}{1-a}\right)+\frac{2G_\perp^2}{G^2}\left(\frac{5a^2-3a^3}{8(1-a)^2}+\tfrac{3}{8}a^{3/2}\tanh^{-1}a^{1/2}\right)\Bigg]\Bigg\}, \tag{41}$$

which agrees exactly with the corresponding expression for the second order in v in I [Eq. (6.14)] and with the corrected expression of Samiolovich and Rabinovich.[10]

III. MANY INDEPENDENT BRAGG REFLECTIONS

Having obtained the result for one Bragg reflection, we now consider a more realistic case in which a number of Bragg reflections occur, some of which cut the Fermi surface. We shall assume that the different Bragg planes are independent, meaning that we neglect the crossing on the Fermi surface of two or three Bragg planes. This is based on the assumption that the pseudopotential is sufficiently small that we can treat only one Bragg plane at a time to better than second order.

In the expression for the susceptibility in Sec. II [Eqs. (38) and (17)] we had quantities in terms of the exact Fermi level which needed to be related to the unperturbed Fermi level through Eq. (22) which is solved by iteration. In the case of many Bragg reflections, however, it is not immediately clear how to take into account the change in Fermi level, which includes contributions from many reciprocal-lattice vectors.

Let us first obtain a result for the energy in the vicinity of a given Bragg reflection. The Schrödinger equation is

$$\frac{(\vec{k}+\vec{G}')^2}{2m}\psi_{\vec{G}'}+\sum_{\vec{G}''}W_{\vec{G}'\vec{G}''}\psi_{\vec{G}''}=E\psi_{\vec{G}'}\;. \tag{42}$$

Here we use the notation for the pseudopotential

$$W_{\vec{G}'\vec{G}''}=\langle\vec{k}+\vec{G}'|\,W\,|\vec{k}+\vec{G}''\rangle\,, \tag{43}$$

and $W_{\vec{G}'\vec{0}}=W_{\vec{k}\vec{G}'}$. Let us consider a region of k space in which just one reciprocal-lattice vector $\vec{G}$ (in addition to $\vec{G}=0$) is important. Then from Eq. (1) for $\vec{G}'\neq 0$, $\vec{G}$, we have

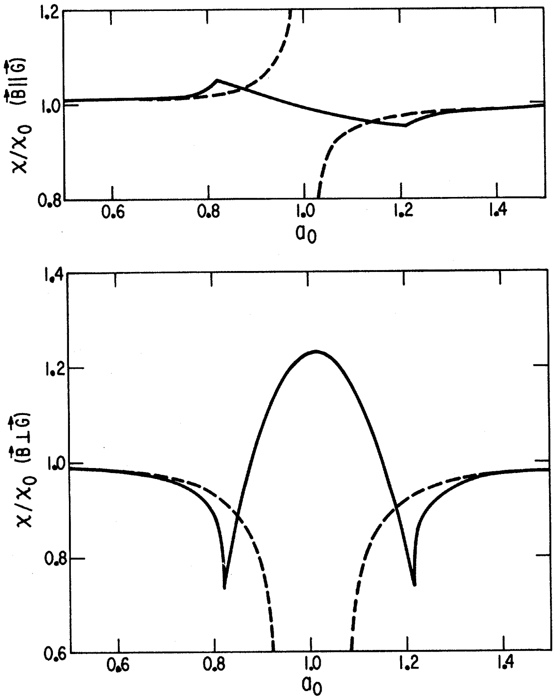

FIG. 3. Magnetic susceptibility vs a_0 for a single Bragg reflection and for the magnetic field B parallel and perpendicular to the reciprocal-lattice vector G, with $v=0.1$. Solid curves are for the present calculation and dashed curves are the corrected result of Samoilovich and Rabinovich (Ref. 10).

$$\left(E - \frac{(\vec{k}+\vec{G}')^2}{2m}\right)\psi_{\vec{G}'} \cong W_{\vec{G}'\vec{G}}\psi_{\vec{G}} + W_{\vec{G}'\vec{0}}\psi_0 . \qquad (44)$$

Substituting into the equation for $\vec{G}'=0$, $\vec{G}$, we have

$$\left(\frac{k^2}{2m} + \sum_{\vec{G}'}{}' \frac{2m\,|W_{\vec{k}\vec{G}'}|^2}{k^2-(\vec{k}+\vec{G}')^2}\right)\psi_0 + W_{\vec{k}\vec{G}}\psi_{\vec{G}} = E\psi_0 , \qquad (45)$$

$$W_{\vec{k}\vec{G}}\psi_0 + \left(\frac{(\vec{k}+\vec{G}')^2}{2m} + \sum_{\vec{G}'} \frac{2m\,|W_{\vec{G}\vec{G}'}|^2}{(\vec{k}+\vec{G})^2-(\vec{k}+\vec{G}')^2}\right)\psi_{\vec{G}} = E\psi_{\vec{G}} . \qquad (46)$$

Here we have neglected the off-diagonal second-order term in comparison with $W_{\vec{k}\vec{G}}$, and have substituted unperturbed energies for E in the second-order terms.

If we consider now the point $\vec{k}=-\frac{1}{2}\vec{G}$, in the middle of the Bragg plane, and denote by S the second-order term in Eq. (45), we have

$$S = \sum_{\vec{G}'}{}' \frac{2m\,|\langle \frac{1}{2}\vec{G}\,|W|\,-\frac{1}{2}\vec{G}+\vec{G}'\rangle|^2}{(\frac{1}{2}\vec{G})^2-(-\frac{1}{2}\vec{G}+\vec{G}')^2} . \qquad (47)$$

If we make the substitution $\vec{G}'\rightarrow\vec{G}-\vec{G}'$ and use time-inversion symmetry this is seen to be the same as the second-order expression in Eq. (46). It should therefore be a good approximation to equate the two expressions in the vicinity of the Bragg plane. This leads to the result valid near a particular Bragg plane:

$$E = E_{\vec{k}} + \sum{}' \frac{2m\,|W_{\vec{k}\vec{G}'}|^2}{k^2-(\vec{k}+\vec{G}')^2} + E_{\vec{k}\vec{G}} , \qquad (48)$$

where $E_{\vec{k}} \equiv k^2/2m$ and

$$E_{\vec{k}\vec{G}} \equiv \frac{(\vec{k}+\vec{G})^2-k^2}{4m}\left[1-\left(1+\left|\frac{4mW_{\vec{k}\vec{G}}}{(\vec{k}+\vec{G})^2-k^2}\right|^2\right)^{1/2}\right]. \qquad (49)$$

We have chosen a particular root of the secular equation as follows. We use an extended zone scheme so that the unperturbed energy is simply $E_{\vec{k}}$. Then $E_{\vec{k}\vec{G}}$ is defined to be small as long as $(\vec{k}+\vec{G})^2-k^2 \gg 4mW_{\vec{k}\vec{G}}$.

Now Eq. (49) can be generalized to give the analogous energy expression near any Bragg plane

$$E = E_{\vec{k}} + \sum\nolimits_{\vec{G}} E_{\vec{k}\vec{G}} , \qquad (50)$$

since $E_{\vec{k}\vec{G}}$ reduces to the second-order expression of Eq. (48) for $(\vec{k}+\vec{G})^2-k^2 \gg 4mW_{\vec{k}\vec{G}}$. But returning to the case of one important Bragg plane, we write this as

$$E = E_{\vec{k}} + E_{\vec{k}\vec{G}} + E'_{\vec{k}\vec{G}} , \qquad (51)$$

where

$$E'_{\vec{k}\vec{G}} = \sum\nolimits'_{\vec{G}} E_{\vec{k}\vec{G}'} .$$

To calculate the change in Fermi level let us divide $E'_{\vec{k}\vec{G}}$ into a constant term $A_{\vec{G}} = E'_{-1/2\vec{G},\vec{G}}$ and the remainder $B_{\vec{k}\vec{G}}$. Assuming initially that all Bragg planes but $\vec{G}$ are remote from the Fermi surface, we have

$$\begin{aligned} N &= \sum_{\vec{k}} f_\zeta(E_{\vec{k}} + E_{\vec{k}\vec{G}} + A_{\vec{G}} + B_{\vec{k}\vec{G}}) \\ &= \sum_{\vec{k}} f_\zeta(E_{\vec{k}} + E_{\vec{k}\vec{G}} + A_{\vec{G}}) + \sum_{\vec{k}} \frac{\partial f_\zeta(E_{\vec{k}} + E_{\vec{k}\vec{G}} + A_{\vec{G}})}{\partial E} B_{\vec{k}\vec{G}} . \end{aligned} \qquad (52)$$

Since $B_{\vec{k}\vec{G}}$ is small near the Bragg reflection let us replace the Fermi function in the second term with that for the unperturbed energy $E_{\vec{k}}$. Then

$$\begin{aligned} N = \sum_{\vec{k}} [f_{\zeta-A_{\vec{G}}}(E_{\vec{k}} + E_{\vec{k}\vec{G}}) - f_{\zeta-A_{\vec{G}}}(E_{\vec{k}})] + \sum_{\vec{k}} f_{\zeta-A_{\vec{G}}}(E_{\vec{k}}) \\ + \sum_{\vec{k}} \frac{\partial f_\zeta(E_{\vec{k}})}{\partial E} B_{\vec{k}\vec{G}} , \end{aligned} \qquad (53)$$

where we have written the first term of Eq. (52) in a different form and have added and subtracted a term. Now the first term of Eq. (53) gives the number of extra electrons due to the G'th Bragg reflection, and we notice that the effective shift in Fermi level, $\zeta - A_{\vec{G}} - \zeta_0$, for this term includes mainly the shift due to this reciprocal-lattice vector, the $A_{\vec{G}}$ approximately cancelling that owing to other reciprocal-lattice vectors. Thus it is probably a good approximation to neglect the shift and to set $\zeta - A_{\vec{G}} \cong \zeta_0$ in the first term. In the second term let us expand to first order in $\zeta - A_{\vec{G}} - \zeta_0$. Then Eq. (52) becomes

$$\begin{aligned} N - \sum_{\vec{k}} f_{\zeta_0}(E_{\vec{k}}) = 0 = \sum_{\vec{k}} [f_{\zeta_0}(E_{\vec{k}} + E_{\vec{k}\vec{G}}) - f_{\zeta_0}(E_{\vec{k}})] \\ + \sum_{\vec{k}} \frac{\partial f_{\zeta_0}(E_{\vec{k}})}{\partial E_{\vec{k}}} [E'_{\vec{k}\vec{G}} - (\zeta - \zeta_0)] , \end{aligned} \qquad (54)$$

where $A_{\vec{G}}$ now has been lumped back with $B_{\vec{k}\vec{G}}$. Equation (54) can now be solved for $\zeta - \zeta_0$.

Let us generalize this result to allow more than one Bragg plane to cut the Fermi surface:

$$\zeta - \zeta_0 = \sum_{\vec{G}} \sum_{\vec{k}} [f_{\zeta_0}(E_{\vec{k}} + E_{\vec{k}\vec{G}}) - f_{\zeta_0}(E_{\vec{k}})] \Big/ \sum_{\vec{k}} \frac{\partial f_{\zeta_0}(E_{\vec{k}})}{\partial E_{\vec{k}}} . \qquad (55)$$

This is valid for W sufficiently small such that the various approximations are valid and the $\vec{G}$'s are independent.

Turning now to the susceptibility let us use the same arguments to calculate the first term in Eq. (23) for the case of one dominant $\vec{G}$, in direct analogy to Eq. (11):

$$\sum_{\vec{k}} \frac{\partial f_\zeta(E_{\vec{k}} + E_{\vec{k}\vec{G}} + E'_{\vec{k}\vec{G}})}{\partial E}$$

$$\cong\sum_{\vec{k}}\frac{\partial f_{\zeta_0}(E_{\vec{k}})}{\partial E}+\sum_{\vec{k}}\left(\frac{\partial f_{\zeta_0}(E_{\vec{k}}+E_{\vec{k}\vec{G}})}{\partial E}-\frac{\partial f_{\zeta_0}(E_{\vec{k}})}{\partial E}\right)$$

$$+\sum_{\vec{k}}\frac{\partial^2 f_{\zeta_0}}{\partial E^2}\left[E'_{\vec{k}\vec{G}}-(\zeta-\zeta_0)\right]. \qquad (56)$$

The first term on the right-hand side is the unperturbed value, and the others correspond to the contribution from $\vec{G}$, from all other reciprocal-lattice vectors, and finally from the shift in Fermi energy. We may rewrite this in the more general form analogous to, and using, Eq. (55),

$$\sum_{\vec{k}}\frac{\partial f_{\zeta}(E_{\vec{k}}+\sum_{\vec{G}}E_{\vec{k}\vec{G}})}{\partial E}$$

$$\cong\sum_{\vec{k}}\frac{\partial f_{\zeta_0}(E_{\vec{k}})}{\partial E}+\sum_{\vec{G}}\left[\sum_{\vec{k}}\left(\frac{\partial f_{\zeta_0}(E_{\vec{k}}+E_{\vec{k}\vec{G}})}{\partial E}-\frac{\partial f_{\zeta_0}(E_{\vec{k}})}{\partial E}\right)\right.$$

$$\left.-\sum_{\vec{k}}\left[f_{\zeta_0}(E_{\vec{k}}+E_{\vec{k}\vec{G}})-f_{\zeta_0}(E_{\vec{k}})\right]\sum_{\vec{k}}\frac{\partial^2 f_{\zeta_0}}{\partial E^2}\Big/\sum_{\vec{k}}\frac{\partial f_{\zeta_0}}{\partial E}\right]. \qquad (57)$$

As far as the rest of the susceptibility in Eq. (23) is concerned, it is consistent to replace ζ by ζ_0 in it and to sum over reciprocal-lattice vectors. The final results for the extension of Eq. (38) to the case of many independent Bragg reflections is

$$\chi=\chi_0\left\{1+\sum_G\left[\frac{\gamma_+-\gamma_-}{2a_0^{1/2}}-1-\frac{3G_\perp^2v^2}{a_0^{1/2}G^2}I-\frac{1}{3}\left(\frac{N}{N_0}-1\right)\right]_G\right\}, \qquad (58)$$

where $\gamma_\pm$, v, I, and N are given by Eqs. (17), (13), (36), and (18), respectively, with a replaced by a_0 [Eq. (20)], and N_0 is given by Eq. (19).

IV. DIAMAGNETIC SUSCEPTIBILITY OF ZINC

We now apply the above results to zinc, which has the hexagonal-close-packed structure consisting of two interpenetrating simple hexagonal lattices. The lattice may be described as a Bravais lattice with a basis, the unit cell having the edges:

$$\vec{a}_1=\tfrac{1}{2}a\hat{i}-\tfrac{1}{2}\sqrt{3}\,a\hat{j},\quad \vec{a}_2=\tfrac{1}{2}a\hat{i}+\tfrac{1}{2}\sqrt{3}\,a\hat{j},\quad \vec{a}_3=c\hat{k}. \qquad (59)$$

The unit cell contains two atoms, one at the origin and the other at $\frac{1}{2}a\hat{i}+\frac{1}{6}\sqrt{3}\,a\hat{j}+\frac{1}{2}c\hat{k}$. A general reciprocal-lattice vector is

$$\vec{G}(h,k,l)=\frac{2\pi}{a}\left[(h+k)\hat{i}+\frac{1}{\sqrt{3}}(k-h)\hat{j}+\frac{a}{c}l\hat{k}\right]. \qquad (60)$$

The matrix elements of the pseudopotential can be separated as

$$\langle\vec{k}_F+\vec{G}(h,k,l)|W|\vec{k}_F\rangle=\cos\left[\tfrac{1}{6}\pi(2h+4k+3l)\right]\omega_{\vec{G}}, \qquad (61)$$

where $\omega_{\vec{G}}$ is the form factor. We have used the form factors of Animalu and Heine[11] in our calculation. We have calculated χ from Eq. (58) which we may write

$$\chi=\chi_0(1+\textstyle\sum_G D_G). \qquad (62)$$

We have evaluated the D_G's using a high-speed computer and these were summed over neighbor shells until convergence was obtained. We have used the physical parameters $a=2.6590$ Å, $c/a=1.8565$, and $k_F=1.573\times10^8$ cm^{-1} in our calculations.

In Table I the results for the diamagnetic susceptibility of zinc are tabulated. We note that there is asymmetry in the value of the diamagnetic susceptibility of zinc depending on the orientation of the field relative to the crystal axes. $(D_G)_\parallel$ and $\chi_\parallel$ are the corresponding values when the magnetic field is parallel to the hexagonal axis and $(D_G)_\perp$ and $\chi_\perp$ are the values when the magnetic field is perpendicular to the hexagonal axis. The average susceptibility χ_d is calculated from the relation

$$\chi_d=\tfrac{1}{3}\chi_\parallel+\tfrac{2}{3}\chi_\perp. \qquad (63)$$

In Table II we compare our result with the experimental result which has been obtained in an indirect way. There has been no "direct" experimental measurement of either the diamagnetic susceptibility or the spin susceptibility of zinc. So we have calculated the value of χ_d^e from the relation

$$\chi_T=\chi_i+\chi_p^*+\chi_d^e, \qquad (64)$$

where χ_T is the total magnetic susceptibility, χ_i is the ionic susceptibility, and χ_p^* is the exchange-enhanced spin susceptibility. χ_T has been experimentally determined[12] and χ_i has been calculated.[12] We have calculated χ_p^* from Silverstein's expression[13]

$$\chi_p^*=\frac{\chi_p}{1+(m/m^*-1)\chi_p/\chi_f}, \qquad (65)$$

TABLE I. Diamagnetic susceptibility of zinc (χ in 10^{-6} cgs volume units).

χ_0	$\sum_G(D_G)_\parallel$	$\sum_G(D_G)_\perp$	$\chi_\parallel$	$\chi_\perp$	χ_d
−0.3742	−0.4152	−0.3307	−0.2188	−0.2505	−0.2399

TABLE II. Comparison of χ_d with indirectly obtained experimental result χ_d^e (10^{-6} cgs volume units).

χ_T (Ref. 8)	χ_i (Ref. 8)	χ_p^*	χ_d^e	χ_d
-1.14	-1.64	0.776	-0.276	-0.240

where χ_f is the free-electron susceptibility appropriate to the density of conduction electrons in the metal, χ_p is the exchange-enhanced spin susceptibility in the free-electron approximation, and m^* is the effective mass. We have used the values $\chi_p = 1.43$[13] and $m^*/m = 0.601$[14] and we obtain $\chi_p^* = 0.776$.

We find from Table II that χ_d^e, the indirectly obtained experimental result, agrees quite well with our theoretical result. However, we note that a direct experimental measurement of the spin susceptibility would yield a more reliable value of χ_d^e.

V. VARIATION OF SUSCEPTIBILITY WITH FERMI LEVEL

In an attempt to explain the diamagnetism of bismuth, we applied our theoretical result to this case. Bismuth has A-7 (arsenic) crystal structure. The unit cell (which is a primitive cell) is rhombohedral and contains two atoms. The three primitive translation vectors can be expressed by

$$\vec{A}_1 = A_0\{\epsilon, 1, 1\}, \quad \vec{A}_2 = A_0\{1, \epsilon, 1\}, \quad \vec{A}_3 = A_0\{1, 1, \epsilon\}, \tag{66}$$

where $\{\,\}$ indicates rectangular coordinates. The parameter ϵ is related to the shear angle α by

$$\epsilon = [1 - (1 + \cos\alpha - 2\cos^2\alpha)^{1/2}]/\cos\alpha, \tag{67}$$

α being the angle between any two A_i's. The three reciprocal-lattice vectors are

$$\vec{g}_1 = g_0(-(1+\epsilon), 1, 1), \quad \vec{g}_2 = g_0(1, -(1+\epsilon), 1),$$

$$\vec{g}_3 = g_0(1, 1, -(1+\epsilon)), \tag{68}$$

and a general reciprocal-lattice vector is given by

$$\vec{G} = h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3. \tag{69}$$

The matrix elements of the pseudopotential can be separated as

$$\langle \vec{k}_F + \vec{G}(h,k,l) | W | \vec{k}_F \rangle = \cos[2\pi u(h+k+l)]\,\omega_G, \tag{70}$$

where u is the internal displacement parameter[15] and ω_G is the form factor. We have used the crystal-structure parameters of bismuth obtained by Golin[16] from a pseudopotential calculation of band structure of bismuth. We have used the form factors of Animalu and Heine[11] which are obtained in a model potential calculation.

The result we obtained for the susceptibility of bismuth was $\chi/\chi_0 = 0.6$, which is far from predicting the large diamagnetism. However, if we decreased the Fermi level by $2\frac{1}{2}\%$, χ/χ_0 increased to 2.73. This corresponds in the independent Bragg reflection model to having necks in the Fermi surface, and as we see from Fig. 3, the occurrence of a neck is connected with an enhanced diamagnetism. In some sense this is similar to the Fermi level being in a gap. So, if we were to have a gap over most of the original Fermi surface, we expect to have a positive diamagnetism.

Of course, as noted in Sec. I, the occurrence of a gap over most of the Fermi surface means that the independent-Bragg-reflection model is invalid. A direct calculation of Eq. (5.36) in I is clearly in order here. Such a calculation would complement the excellent study of the band-edge behavior by Buot[8] and Buot and McClure.[7]

VI. CONCLUSION

The principal result of this paper is the obtaining of a tractable expression for the diamagnetic susceptibility of metals with complicated crystal structures from the general expression for the diamagnetic susceptibility derived by Misra and Roth[9] in a pseudopotential formalism. This expression is valid for metals in which the pseudopotential model applies, and in which the Bragg reflections are independent. We have used this expression to calculate the diamagnetic susceptibility of zinc and our result agrees well with the indirectly obtained experimental result.

While our calculation does not apply to the case of bismuth, we have indicated, by considering a variation of the Fermi level, how the occurrence of necks gives rise to enhanced diamagnetism. We then argue that if we were to have a gap over most of the original Fermi surface, we expect to have a positive diamagnetism. Our results agree qualitatively with similar results which have been obtained recently by Ruvalds[5] and by Fukuyama and Kubo.[6]

Note added in proof. Recently, Misra and Kleinman (unpublished) have shown that there is an additional contribution to the magnetic susceptibility due to the effect of spin-orbit coupling on the orbital motion of Bloch electrons. Our result indicates that this contribution is small for zinc.

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[1] J. E. Hebborn and E. H. Sondheimer, J. Phys. Chem. Solids 13, 105 (1960).

[2] L. M. Roth, J. Phys. Chem. Solids 23, 433 (1962).

[3] E. I. Blount, Phys. Rev. 126, 1636 (1962).

[4] G. H. Wannier and U. N. Upadhyaya, Phys. Rev. 136, A803 (1964).

[5] J. Ruvalds, J. Phys. Chem. Solids 30, 305 (1969).

[6] H. Fukuyama and R. Kubo, J. Phys. Soc. Japan 27, 604 (1969); 28, 570 (1969).

[7] F. A. Buot and J. W. McClure (unpublished).

[8] F. A. Buot, J. Phys. Chem. Solids (to be published).

[9] P. K. Misra and L. M. Roth, Phys. Rev. 177, 1089 (1969) (referred to as I).

[10] A. G. Samoilovich and E. Ya Rabinovich, Fiz. Tverd. Tela 5, 778 (1963) [Sov. Phys. Solid State 5, 567 (1963)].

[11] A. O. E. Animalu and V. Heine, Phil. Mag. 12, 1249 (1965).

[12] J. A. Marcus, Phys. Rev. 76, 621 (1949).

[13] S. D. Silverstein, Phys. Rev. 130, 912 (1963).

[14] P. B. Allen, M. L. Cohen, R. V. Kasowski, and L. M. Falicov, Phys. Rev. Letters 21, 1794 (1968).

[15] L. M. Falicov and S. Golin, Phys. Rev. 137, A871 (1965).

[16] S. Golin, Phys. Rev. 166, 643 (1968).

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Pseudopotential Form Factor and Interionic Potential in Simple Metals: Many-Electron Effects*

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We construct a pseudopotential form factor and a metallic interionic potential using Shaw's nonlocal model potential and the many-electron screening due to Singwi *et al.* for eight simple metals. We have particularly examined the role of many-electron effects and found them to contribute significantly to the pseudopotential form factor in the region of $k_F < q < 2.2k_F$ and to be essential in determining a realistic interionic potential. In addition, we have studied the effects of exchange and correlation on the residual resistivity due to vacancies, the resistivity of liquid metals, the interatomic force constants, and the sound velocity. The inclusion of many-electron effects invariably improves the agreement between theory and experiment.

I. INTRODUCTION

Pseudopotential theory has proven to be a versatile and useful technique in understanding various properties of metals.[1,2] It is now possible to investigate such diverse properties as lattice dynamics, cohesive energy, optical absorption, and transport properties once an accurate pseudopotential is known for the metal. The basic starting point for investigating these properties is the pseudopotential form factor which consists of the ionic part (bare-ion pseudopotential) and the contribution from the conduction electrons resulting in the screening of the bare-ion pseudopotential. The bare-ion potential can be constructed in a semiempirical way, Ashcroft's[3] form factor is a typical example, or from first-principles considerations using results extrapolated from atomic spectroscopic data; the Heine-Abarenkov model potential[4] and the optimized model potential by Shaw[5] are good examples here. The contribution to the form factor due to the conduction electrons is generally treated in the self-consistent-field (SCF) approximation and incorporated through the use of a dielectric function either in the Hartree form or in a modified form, which includes the exchange and correlation effects (many-electron effects) among the conduction electrons. Since recent work on the interionic potential,[6,7] interatomic force constants,[7] and phonon spectra[8-10] have demonstrated within the local pseudopotential scheme the importance of many-electron effects, we wish to further investigate these effects in a nonlocal pseudopotential scheme. In Sec. II, we describe the procedure for constructing the pseudopotential form factor and the interionic potential which contain both the desired nonlocal bare-ion potential and the self-consistently determined many-electron screening. Results are presented here for eight simple metals. In addition, we have particularly examined and assessed the role of the exchange and correlation effects in influencing