Theory of Diamagnetism of Bismuth*†

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The susceptibility formula for bismuth is derived starting with the general expression for the susceptibility of Bloch electrons. By applying approximations consistent with the Lax two-band model for the energy-band structure near the symmetry point L of the Brillouin zone, the numerous terms in the susceptibility expression were condensed into a very simple form. The "induced diamagnetism" cancels both the Landau–Peierls term and the "crystalline paramagnetism," leaving a very simple and compact expression. The simple expression clearly reveals the interband origin of the large diamagnetism of bismuth and accounts for the experimental results on bismuth and bismuth-antimony alloys. The result can be expressed as the sum of a large background diamagnetism which depends on the direct-energy gap, plus carrier paramagnetism. If the Fermi level is near a band edge, the carrier paramagnetism is equal to the sum of the Landau–Peierls diamagnetism and the Pauli paramagnetism calculated using the effective g factor. For the conduction band (the contribution from valence band differs by sign) the induced diamagnetism in the general formulation for the susceptibility is made up of a paramagnetic contribution due to the second-order influence of the effective g factor in bismuth plus a diamagnetic contribution similar to the standard atomic diamagnetism using the cyclotron effective mass (with the spread of the charge distribution measured by a quantity which plays an analogous role to the Compton wavelength for free electrons). The exact expression (beyond the usual power expansion in B) of the one-band–effective-Hamiltonian function (valid near the L point) which yields the correct magnetic energy levels for the Lax model is also obtained.

I. INTRODUCTION

The standard theories of the zero-field magnetic susceptibility of solids are often mathematically tedious and complicated, and are very difficult to understand physically.[1–9] Common to all these theories is the use of the Bloch picture or the single-particle approximation of crystal electrons. The work of Roth[2] and of Wannier and Upadhyaya[3] probably gives the apparently simplest results. The formalism given by Roth includes spin-orbit coupling. An elegant treatment of zero-field magnetic susceptibility without spin-orbit coupling is given by Wannier and Upadhyaya.[3]

The general expression for the zero-field magnetic susceptibility can be written as four terms[2,3]:

$$\chi = \chi_A + \chi_{LP} + \chi_{CP} + \chi_{ID} , \qquad (1)$$

where χ_A is the ionic susceptibility multiplied by the number of atoms per unit volume in a crystal, χ_{LP} is the usual Landau–Peierls term, χ_{CP} is the crystalline paramagnetism whose origin can be traced to the source of the effective g factor in the effective-Hamiltonian function and which reduces to the Pauli term in the case of free electrons, and χ_{ID} is the induced diamagnetism whose sign can not be ascertained *a priori*.

It is quite well known that the application of the general formalism of zero-field magnetic susceptibility to metals can be a very complicated and formidable task (bismuth is no exception). So far the formulation has been applied only to a few simple models.[10,11] The difficulty lies in the existence of a vast number of seemingly unrelated terms whose relative magnitude are very hard to assess *a priori*. It turns out that with the use of a more practical model of the energy-band structure (EBS) of bismuth, one can actually use the general formalism for χ to obtain a very simple result. The same simple result can now be obtained by several other methods. Our interest in the use of the general formalism of the zero-field magnetic susceptibility in this paper lies in the way the numerous terms group together to yield a very compact and physically meaningful simple result. We obtain expression for and relative magnitudes of the various terms in Eq. (1), and also shed some light on their physical meaning.

The susceptibility can also be calculated by a direct sum over the Landau levels. The EBS model for bismuth is mathematically the same as for the H point of graphite, and the susceptibility result[12] is the same as in the present work. Recently Fukuyama and Kubo[13] have also calculated the magnetic susceptibility of bismuth by a different method using the same model of the EBS used in this paper. We show in Appendix B that the leading term of their result is the same as ours. Finally, the new formulation by Fukuyama[14] can be applied to the EBS model to give the same simple result. None of these alternate methods gives expressions for the individual terms in Eq. (1).

II. $\vec{k}\cdot\vec{p}$ MODEL OF EBS NEAR L POINT

It has for some time been realized that the diamagnetism of bismuth and its alloys has an interband origin.[1,15–19] We are therefore mainly interested in the region of the Brillouin zone (BZ) which has a small energy gap. We employ the $\vec{k}\cdot\vec{p}$ model of the EBS near the L point of the BZ. In what follows we will use the atomic units: $e=\hbar=m=1$, and the unit of energy is 1 hartree = 27.2 eV.

The "full" $\vec{k}\cdot\vec{p}$ Hamiltonian matrix is usually written[20] as

$$\mathcal{H}=\begin{array}{c} \begin{matrix} L_5 & L_6 & L_7 & L_8 \end{matrix} \\ \begin{pmatrix} K_1+\Delta & 0 & t & u^* \\ 0 & K_1+\Delta & -u & t^* \\ t^* & -u^* & K_0-\Delta & 0 \\ u & t & 0 & K_0-\Delta \end{pmatrix} \end{array}, \tag{2}$$

where we have indicated the symmetry types of the corresponding band-edge wave functions and $\Delta=\frac{1}{2}E_g$, where E_g is the direct band gap, $K_1=\frac{1}{2}k^2+R_1$, $K_0=\frac{1}{2}k^2+R_0$, where R_1 and R_0 are corrections, quadratic in $\vec{k}$, coming from bands other than the valence and conduction bands at L, and t and u are $\vec{k}\cdot\vec{p}$ matrix elements (or, more properly, $\vec{k}\cdot\vec{\pi}$ as the effect of spin-orbit coupling is included). Energies are measured from the center of the band gap. It is important to realize that the phases of u and t can be chosen independently while keeping the form of the $\vec{k}\cdot\vec{p}$ Hamiltonian matrix. We have

$$u=\langle L_8|\pi_y|L_5\rangle k_y+\langle L_8|\pi_z|L_5\rangle k_z = q_2k_y+q_3k_z\,, \tag{3}$$

$$t=\langle L_8|\pi_x|L_6\rangle k_x\,. \tag{4}$$

The coordinate axes employed are the binary (along Σ symmetry line), bisectrix (on the σ plane), and trigonal (along Λ symmetry line) crystal directions (bbt system).

By full $\vec{k}\cdot\vec{p}$ Hamiltonian we mean that the quadratic terms on the diagonal are included. We shall use the Lax model,[21] which neglects the quadratic terms.[22] An intermediate case (neglect of R_0 and R_1, but retention of the free-electron kinetic energy $\frac{1}{2}k^2$) was investigated by Fukuyama and Kubo,[13] but *a priori* both types of terms are of the same magnitude. The experimentally established effective masses[23] show that neglect of the quadratic terms is a good approximation except in the y (bisectrix) direction, where they make a 20% correction to the effective mass. The eigenvalues of the resulting $\vec{k}\cdot\vec{p}$ Hamiltonian matrix are

$$E=\pm(\Delta^2+|t|^2+|u|^2)^{1/2}\,, \tag{5}$$

the + and − values of E being doubly degenerate. The Fermi surface is ellipsoidal in shape and is slightly tilted ($\sim 6°$) about the binary axis, there being a cross term in k_yk_z coming from $|u|^2$. Referred to the principal axes x', y', z' of the electron ellipsoid, the relation $\mathrm{Re}(q_2'q_3')=0$ holds.[24] We will choose the phases of u' and t' such that

$$q_1'=Q_1\,,\quad q_2'=-iQ_2\,,\quad q_3'=Q_3\,, \tag{6}$$

where Q_1, Q_2, and Q_3 are all real. We thus have

$$\mathcal{H}'=\begin{pmatrix} \Delta & 0 & Q_1k_x & Q_3k_z+iQ_2k_y \\ 0 & \Delta & -Q_3k_z+iQ_2k_y & Q_1k_x \\ Q_1k_x & -Q_3k_z-iQ_2k_y & -\Delta & 0 \\ Q_3k_z-iQ_2k_y & Q_1k_x & 0 & -\Delta \end{pmatrix} \tag{7}$$

in the principal axes of the electron ellipsoid.

The $\vec{k}\cdot\vec{p}$ Hamiltonian matrix is of such a form that one can easily do three things: (a) One can readily solve the magnetic energy levels by the method of Luttinger and Kohn[25] when the magnetic field is in the x direction. The resulting magnetic energy levels[21] are the same as at point H in graphite,[12] and one can therefore conclude that χ for the simplified Lax two-band model can be obtained by integration along the k direction parallel to the magnetic field of the expression established for the H point in graphite.

(b) If we let $Q_1k_x=\xi$, $Q_2k_y=\eta$, and $Q_3k_z=\zeta$ then one can easily show[24] that a cyclical rearrangement of ξ, ζ, η is affected by the unitary transformation U and U^{-1}, where

$$U=\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 & 0 & 0 \\ i & i & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & -i & i \end{pmatrix}. \tag{8}$$

(c) One can reduce the 4×4 matrix to diagonal block form of two 2×2 matrices, one being the Hermitian conjugate of the other. If we cyclically rearrange ξ, ζ, η to η, ξ, ζ then the transformation

$$T=\begin{pmatrix}\alpha_+ I & -\alpha_- I\\ \alpha_- I & \alpha_+ I\end{pmatrix}\ ,\quad I=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\ , \tag{9}$$

where $\alpha_\pm=\{\frac{1}{2}[1\pm\Delta/(\Delta^2+\eta^2)^{1/2}]\}^{1/2}$, diagonalizes the matrix with respect to η with $\epsilon=(\eta^2+\Delta^2)^{1/2}$ occurring in the diagonal matrix elements. This becomes, on rearranging the order of rows and columns,

$$H=\begin{array}{c}\begin{matrix}L_5 & L_8 & L_6 & L_7\end{matrix}\\ \begin{pmatrix}\epsilon & \rho & 0 & 0\\ \rho^* & -\epsilon & 0 & 0\\ 0 & 0 & \epsilon & -\rho^*\\ 0 & 0 & -\rho & -\epsilon\end{pmatrix}\end{array}\ , \tag{10}$$

where $\rho=Q_1 k_x+iQ_3 k_z$. On changing sign of the fourth basis function, we obtain the desired result of (c). For future reference let us write the eigenfunction of the upper 2×2 block in Eq. (10), which we shall denote by H_1 as

$$\begin{aligned}L_c(k)&=aL_c+b^*L_v\ ,\\ L_v(k)&=aL_v-bL_c\ ,\end{aligned} \tag{11}$$

where L_c and L_v are the periodic parts of the Bloch function belonging to the conduction and valence bands, respectively, at point L, $a=[(E+\epsilon)/(2E)]^{1/2}$, $b=\rho/[2E(E+\epsilon)]^{1/2}$.

III. MAGNETIC SUSCEPTIBILITY OF BLOCH ELECTRONS NEAR L POINT

The magnetic susceptibility of Bloch electrons in bismuth, where spin-orbit coupling is important and should be included in all stages of the calculation can, in principle, be described fully by the formalism given by Roth.[2] The elegant formalism given by Wannier and Upadhyaya[3] is for spinless electrons. Both formalisms are essentially similar and involved the calculation of the trace of an operator function of the effective Hamiltonian that occurs in the expansion of the free energy. Their treatment is based on the single-band effective Hamiltonian which is expanded in powers of the magnetic field strength. The magnetic susceptibility depends on the integral over $\vec{k}$ space of quantities involving the single-band functions $W^0_\alpha(\vec{k})$, $W^{(1)}_\alpha(\vec{k})$ and $W^{(2)}_\alpha(\vec{k})$. $W^0_\alpha(\vec{k})$ is the energy-band function in the absence of the magnetic field. Since an integral is involved the susceptibility can be calculated even if band degeneracies exist, provided that the integral converges at the singularities.[26]

The EBS model considered here enabled us to calculate the susceptibility coming from the region of the symmetry point L, denoted as χ_L, which is the main contribution.[24,27] The largest value of χ_L comes when the magnetic field is in the 2 direction (small-cyclotron-mass direction) so that χ^{22}_L is the dominant contribution[27] to $\chi_\perp$, the susceptibility with the magnetic field perpendicular to the trigonal axis. The 2 direction is also the direction of the magnetic field where the simplified ($k^2/2$ neglected) Lax two-band model for the EBS is a good approximation for describing the motion perpendicular to the magnetic field. One can neglect $\vec{\mu}_0\cdot\vec{B}$ in the effective Hamiltonian in this direction, the experimental g factor being of the order of 100 times that of a free electron.[23] The formulas for χ^{11}_L and χ^{33}_L can be obtained from χ^{22}_L by cyclic permutation of the the Q_i's.

The susceptibility expression of Roth can be written as a group of terms proportional to the first and second powers of $\vec{\mu}_0\cdot\vec{B}/B$ plus an expression similar to that of Wannier and Upadhyaya with $\vec{p}$ replaced by $\vec{\pi}$, differing only in the taking of traces due to the mixing of spin states in the wave function.[24] As mentioned above, the $\vec{\mu}_0\cdot\vec{B}$ terms can be neglected in the present case. Our division of Roth's expression is more useful than that proposed by Misra and Kleinman,[28] who included with the $\vec{\mu}_0\cdot\vec{B}$ terms a term which is not always zero in the absence of spin-orbit coupling,[29] and which is large in the present case. Furthermore, using the simplified Lax two-band model for calculating χ with $\vec{\mu}_0\cdot\vec{B}$ neglected in Roth's expression will yield the same results as using the eigenvalues and eigenfunctions of H_1, the upper 2×2 block in Eq. (10) in the Wannier–Upadhyaya expression for χ with $\vec{p}$ replaced by $\vec{\pi}$ to include spin-orbit coupling. We emphasize that the effect of spin-orbit coupling is still present by replacing $\vec{p}$ by $\vec{\pi}$ in the Wannier–Upadhyaya expression for χ. In our case the whole problem of electrons with spin-orbit coupling is mathematically reduced to that of spinless electron but with $\vec{p}$ replaced by $\vec{\pi}$, resulting in a considerable saving of computational labor.

Following Wannier and Upadhyaya[3] we have

$$\chi=-\frac{1}{48\pi^3}\sum_\alpha\int d\vec{k}\left[\frac{\partial^2 W^0_\alpha}{\partial k_x^2}\frac{\partial^2 W^0_\alpha}{\partial k_y^2}-\left(\frac{\partial^2 W^0_\alpha}{\partial k_x\,\partial k_y}\right)^2\right]\frac{\partial f(W^0_\alpha)}{\partial W^0_\alpha}-\frac{1}{(2\pi)^3}\sum_\alpha\int d\vec{k}\,[W^{(1)}_\alpha(\vec{k})]^2\frac{\partial f(W^0_\alpha)}{\partial W^0_\alpha}$$

$$-\frac{1}{(2\pi)^3}\sum_\alpha\int d\vec{k}\,2\,W^{(2)}_\alpha(\vec{k})f(W^0_\alpha)\ , \tag{12}$$

where the first, second, and third terms are, respectively, the χ_{LP}, χ_{CP}, and χ_{ID} of Eq. (1), and $W_\alpha^{(1)}(\vec{k})$, $W_\alpha^{(2)}(\vec{k})$ appear in the expansion of the field-dependent $W_\alpha(\vec{k})$, which is often referred to as the renormalized energy-band function.

We choose to work in the Landau gauge,[24] as there are fewer matrix elements to be evaluated than in the symmetric gauge. Since we are concerned with the small-cyclotron-mass direction of the magnetic field, we shall take the operator (which operates on the periodic part of the Bloch function) equality:

$$\vec{\pi}_s = \vec{\pi}_p ,$$

where $\vec{\pi}_p$ is the velocity operator in parametrizing the EBS near the L point and $\vec{\pi}_s$ is the velocity operator in the susceptibility expression. Strictly speaking, $\vec{\pi}_s = \vec{\pi}_p + \vec{k}'$, where $\vec{k}'$ is measured from L. The above equality approximation is consistent with the neglect of $\vec{k}^2/2$ term in $\mathcal{H}$.

Examination of the terms in χ_{ID} leads to the neglect of the terms similar to the atomic diamagnetism (using the bare-electron mass), consistent with the above approximations. The remaining terms in χ_{ID} are all important and actually combine to produce a simpler expression. We can write the six remaining terms in χ_{ID} as

$$\chi_{ID}^{22} = \frac{1}{2\pi^3 c^2}\int d\vec{k} \sum_{s\neq q} \frac{1}{W_s^0 - W_q^0}\left|\left\langle s\left|\pi_z X - \frac{\partial W_q^0}{\partial k_x} Z\right|q\right\rangle\right|^2 f(W_q^0) - \frac{1}{4\pi^3 c^2}\int d\vec{k}\langle q|Z\pi_z X + X\pi_z Z|q\rangle \frac{\partial f(W_q^0)}{\partial W_q^0}\frac{\partial W_q^0}{\partial k_x}$$

$$- \frac{1}{2\pi^3 c^2}\int d\vec{k}\,\frac{\partial W_q^0}{\partial k_x}\frac{\partial}{\partial k_x}\langle q|Z^2|q\rangle f(W_q^0) - \frac{1}{4\pi^3 c^2}\int d\vec{k}\,\frac{\partial W_q^0}{\partial k_x^2}\langle q|Z^2|q\rangle f(W_q^0)$$

$$- \frac{1}{16\pi^3 c^2}\int dk\,\frac{\partial^4 W_q^0}{\partial k_x^2 \partial k_z^2} f(W_q^0) - \frac{1}{2\pi^3 c^2}\int d\vec{k}\, W_q^{(1)}\frac{\partial}{\partial k_x}\langle q|Z|q\rangle f(W_q^0) , \quad (13)$$

where the operators X and Z are the well-known Adam's coordinate operators and in Eq. (13) operate only on adjacent wave functions (periodic part of Bloch function), i.e., if operating to the left $X = -i\partial/\partial k_x$, and if operating to the right $X = i\partial/\partial k_x$. The above expression for χ_{ID}^{22} will be evaluated only for the valence and conduction bands. We give an example of evaluating the matrix elements using the eigenvalues and eigenfunctions of H_1. Thus, for example, in the second term of Eq. (13)

$$\langle L_c(k)|Z\pi_z X + X\pi_z Z|L_c(k)\rangle = 2\,\mathrm{Re}\, iQ_3(a_z b_x - a_x b_z)$$

$$= \frac{Q_3^2 Q_1}{2}\epsilon\left[I^2 R\left(\frac{1}{e^2E^4} + \frac{1}{e^4E^2}\right) - \frac{R}{e^2E^2}\right], \quad (14)$$

where $e^2 = E(E+\epsilon)$, $R = Q_1 k_x$, and $I = Q_3 k_z$. The subscripts on a and b indicate differentiation with respect to the appropriate components of $\vec{k}$.

The quantity $W_q^{(1)}$ which appears in χ_{ID} and χ_{CP} is the effective magnetic moment of the Bloch electron.[3] When evaluated for the conduction band using the 2×2 matrix H_1, we find

$$W_q^{(1)} = \frac{1}{2}\frac{Q_3 Q_1}{cE} . \quad (15)$$

Thus $\frac{1}{2} g_{eff}\mu_B = \frac{1}{2} Q_3 Q_1/cE$ and hence $1/m_s = Q_3 Q_1/E = \frac{1}{2} g_{eff}$, where m_s is the spin mass. On the other hand, the cyclotron effective mass is defined by $m_c = (1/2\pi)(\partial A/\partial E)$, where A is the cross-sectional area, perpendicular to the small cyclotron-effective-mass direction, of the constant-energy surface in $\vec{k}$ space. We obtain the well-known result[30] of the two-band model: $m_s = m_c$. We have also shown that χ_{CP} in Eq. (12) is indeed due to the influence of the effective g factor, as mentioned in Sec. I. Using the experimentally determined band parameters for bismuth, we find g_{eff} at the Fermi surface, which is well within experimentally reported values[23] of the g factor in the small-cyclotron-mass direction of the magnetic field.

In carrying out the integration in $\vec{k}$ space, we make the change of variables:

$$\int d\vec{k} = (Q_1 Q_2 Q_3)^{-1}\int_0^{2\pi}\int_\epsilon^\infty\int_{-Z}^{Z} d\eta\, E\, dE\, d\phi , \quad (16)$$

where $Z = Q_2 K$, K is the limit of the validity of the $\vec{k}\cdot\vec{p}$ method, and $\eta = Q_2 k_y$. We have for the conduction band

$$\chi_{ID}^{22} = -\frac{1}{2\pi^3 c^2}(Q_1 Q_2 Q_3)^{-1}\int_{-Z}^{Z} d\eta\int_\epsilon^\infty E\, dE\, S , \quad (17)$$

where S is the sum of six terms corresponding to the six terms in Eq. (13), given in Appendix A. Performing the above-indicated integration and condensing, we end up with the contribution of the conduction band,

$$\chi_{ID}^{22} = \frac{Q_3 Q_1}{Q_2}\frac{1}{2\pi^2 c^2}\int_{-Z}^{Z} d\eta\left[\frac{f(\epsilon)}{6\epsilon}\right.$$

$$+\int_{\epsilon}^{\infty}\left(\frac{1}{4E}-\frac{1}{12}\frac{\epsilon^2}{E^3}\right)\frac{\partial f}{\partial E}\,dE\Bigg]. \quad (18)$$

When one evaluates the remaining two terms in χ, namely, χ_{LP} and χ_{CP} for the conduction band, one has

$$\chi_{LP}^{22}=\frac{1}{24\pi^2c^2}\left(\frac{Q_3Q_1}{Q_2}\right)\int_{-Z}^{Z}d\eta\int_{\epsilon}^{\infty}\frac{\epsilon^2}{E^3}\frac{\partial f}{\partial E}\,dE\,, \quad (19)$$

$$\chi_{CP}^{22}=-\frac{1}{8\pi^2c^2}\left(\frac{Q_3Q_1}{Q_2}\right)\int_{-Z}^{Z}d\eta\int_{\epsilon}^{\infty}\frac{1}{E}\frac{\partial f}{\partial E}\,dE\,. \quad (20)$$

Therefore, for the conduction band

$$\chi_L^{22}=\frac{1}{12\pi^2c^2}\left(\frac{Q_3Q_1}{Q_2}\right)\int_{-Z}^{Z}d\eta\,\frac{f(\epsilon)}{\epsilon}\,. \quad (21)$$

By the same procedure leading to Eq. (21), a similar result is obtained for the valence band with ϵ replaced by $-\epsilon$, and therefore the total χ_L^{22} can be written as

$$\chi_L^{22}=(6\pi^2c^2)^{-1}\left(\frac{Q_3Q_1}{Q_2}\right)\int_{0}^{Z}d\eta\,\frac{[f(\epsilon)-f(-\epsilon)]}{\epsilon}\,. \quad (22)$$

It is remarkable that all of the numerous terms have combined together to give such a simple result for the total susceptibility.

One observes that the contribution of the conduction electrons to χ is paramagnetic and that of the valence electrons is diamagnetic. By writing $f(\epsilon)-f(-\epsilon)=-1+[f(\epsilon)+1-f(-\epsilon)]$ we can split the expression for χ_L^{22} into a large background diamagnetism $\chi_{L,G}^{22}$, independent of the Fermi level and temperature, and $\chi_{L,C}^{22}$, which gives the paramagnetism of the carriers and thus depends on the Fermi level and temperature. $\chi_{L,G}^{22}$ and $\chi_{L,C}^{22}$ both depend on the energy gap E_g.

When the Fermi level lies in the forbidden gap and the temperature is low, χ_{CP}^{22}, χ_{LP}^{22}, and $\chi_{L,C}^{22}$ are all zero and thus

$$\chi_{ID}^{22}=\chi_{L,G}^{22}\,.$$

When the Fermi level is near the band edge at low temperature, then several simple relations hold[24]:

$$\chi_{LP}^{22}+\chi_{CP}^{22}=\chi_{L,C}^{22}\,, \quad (23)$$

$$\chi_{ID}^{22}=\chi_{L,G}^{22}\,, \quad (24)$$

$$\chi_{LP}^{22}=-\tfrac{1}{3}\chi_{CP}^{22}\,. \quad (25)$$

The value of χ_{CP} is equal to the Pauli paramagnetism using the effective g factor, so that (25) also agrees with the Cohen–Blount two-band result.[30] (Similar relations hold for the other two principal directions of the magnetic field by simple cyclical rearrangement of the Q_i's.)

When the Fermi level is not in or near the forbidden gap, or when the temperature is not low enough, none of the relations (23)–(25) is valid. Except when the Fermi level is in the forbidden gap at low temperature, each of the terms in Eq. (1) is important. Moreover $\chi_{L,C}^{22}$ is not given by the sum of χ_{LP}^{22} and χ_{CP}^{22} calculated separately except when the Fermi level is near the band edge at low temperature. In Sec. IV we shall attempt to go deeper into the physical understanding of the problem by closely reexamining the terms that made up χ_{ID}. We will show that χ_{ID} can be written as

$$\chi_{ID}=\chi_g+\chi_{sp}\,, \quad (26)$$

where χ_g is due to the second-order effect of the g factor in bismuth and χ_{sp} arises from the inherent spread or minimum spread of a one-band wave packet in bismuth. This will be discussed within the context of the renormalized energy-band function first annunciated by Wannier and Fredkin.[31]

At absolute zero temperature we have a very simple analytic expression for χ_L^{22}:

$$\chi_L^{22}=(6\pi^2c^2)^{-1}\,\frac{Q_3Q_1}{Q_2}\left[\sinh^{-1}\left(\frac{Z}{\Delta}\right)-\sinh^{-1}\left(\frac{\eta_{\min}}{\Delta}\right)\right], \quad (27)$$

where

$$\eta_{\min}=(E_F^2-\Delta^2)^{1/2} \quad \text{for} \quad |E_F|\geq\Delta$$

$$=0 \quad \text{for} \quad -\Delta\leq E_F<\Delta\,.$$

IV. RENORMALIZED EBS NEAR L POINT

Wannier and Fredkin[31] have shown quite generally that the effect of a uniform magnetic field on Bloch electrons can be thought of as a two-stage process. First, the magnetic field renormalizes the energy band (as a function of the wave vector $\vec{k}$ and of the magnetic field strength B) and second, the energy spectrum is transformed from a band type to a level type.

We apply this concept here and shall show the explicit form of the renormalized energy-band functions, since they add to our physical understanding of the problem above and beyond our understanding in the specialized situation when the Fermi level is near the band edge at very low temperatures. We will show that χ_{ID} in Eq. (18) can be written as a sum of two more familiar and physically meaningful terms. This is a very important result since in the general formalism χ_{ID} consists of numerous terms and several authors have tried to attach physical meaning to these terms. Within the EBS model considered here, our result shows that numerous other terms are intermediary in obtaining the terms that are more familiar and can be assigned definite physical

meanings.

By partial integration with respect to E of Eq. (18) and using Eq. (16), χ_{ID}^{22} may be written as

$$\chi_{\mathrm{ID}}^{22}=-\frac{2}{(2\pi)^3}\sum_{\alpha}\int d\vec{\mathrm{k}}\ \left(\frac{Q_3 Q_1}{c}\right)^2\left(-\frac{1}{8E^3}+\frac{\epsilon^2}{8E^5}\right)f(E)\ . \tag{28}$$

$W_{\alpha}^{(2)}(\vec{\mathrm{k}})$ in Eq. (12) can thus be written as

$$W_{\alpha}^{(2)}(\vec{\mathrm{k}})=\beta\left(\frac{Q_3 Q_1}{c}\right)^2\left(-\frac{1}{8E^3}+\frac{\epsilon^2}{8E^5}\right), \tag{29}$$

where

$$\beta=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}.$$

Equation (29) accounts for all the four bands at the point L; i.e., in the matrix β the first rows refer to the conduction bands and the last two rows to the valence bands. From Eq. (15) and the corresponding expression for $W_{\alpha}^{(1)}(\vec{\mathrm{k}})$ using the lower 2×2 block in Eq. (10), we can finally write the renormalized energy-band function (with units restored) as

$$W_{\alpha}(\vec{\mathrm{k}})=\beta\left[E+e\hbar\left(\frac{Q_3 Q_1}{c}\right)\frac{\vec{\sigma}\cdot\vec{\mathrm{B}}}{2E}-\left(\frac{Q_3 Q_1}{c}\right)^2(e\hbar)^2\frac{(\vec{\sigma}\cdot\vec{\mathrm{B}})^2}{8E^3}+\left(\frac{Q_3 Q_1}{c}\right)^2(e\hbar)^2\frac{\epsilon^2}{8}\frac{B^2}{E^5}\cdots\right], \tag{30}$$

where $\vec{\sigma}$ is the usual Pauli matrix. $W_{\alpha}(\vec{\mathrm{k}})$ has all the required inversion and time-reversal symmetries. The first three terms in Eq. (30) are the second-order expansion of $\beta[E^2+e\hbar(Q_3 Q_1/c)\times\vec{\sigma}\cdot\vec{\mathrm{B}}]^{1/2}$ so that the second and third terms represent the influence of the effective g factor in bismuth. It is very interesting to note that the magnetic energy levels are just the eigenvalues obtained from the effective Hamiltonian derived from $\beta[E^2+e\hbar(Q_3 Q_1/c)\vec{\sigma}\cdot\vec{\mathrm{B}}]^{1/2}$ by replacement of $\vec{\mathrm{k}}$ by $\vec{\mathrm{k}}+(e/\hbar c)\vec{\mathrm{A}}[i(\partial/\partial\vec{\mathrm{k}})]$.

For the conduction band the last term in Eq. (30) can also be given an appropriate physical meaning. It arises from an induced moment similar to the standard atomic diamagnetism. This can easily be seen if one equates the induced moment due to the spread [last term of Eq. (30)] to the induced magnetic moment due to a distribution of charge. We have

$$\frac{(e\hbar Q_3 Q_1)^2\epsilon^2 B}{4c^2E^5}=\frac{e^2\langle r^2\rangle B}{4m_c c^2}\ , \tag{31}$$

where the left-hand side is the derivative with respect to B of the spread term in Eq. (30), the right-hand side is the induced magnetic moment due to a distribution of charge (using the cyclotron effective mass), and $\langle r^2\rangle$ is the effective spread of the distribution normal to the magnetic field. Equation (31) essentially defines $\langle r^2\rangle$ which is

$$\langle r^2\rangle=\left(\frac{\hbar}{m_c(Q_3 Q_1)^{1/2}(E/\epsilon)}\right)^2, \tag{32}$$

and at the band edge this reduces to

$$\langle r^2\rangle=\left(\frac{\hbar}{m_c(Q_3 Q_1)^{1/2}}\right)^2. \tag{33}$$

The interpretation is reasonable, as we can show that $\langle r^2\rangle$ is related to the spread of a wave packet. The quantity within the large parentheses of Eq. (33) plays a role analogous to the Compton wavelength for the free electrons. The expression for $\langle r^2\rangle$ has the same form as the square of the Compton wavelength for free electrons with c replaced by $(Q_3 Q_1)^{1/2}$ and m replaced by m_c. One of the authors has recently shown that the electron's spread equal to its Compton wavelength is responsible for the diamagnetic contribution to the susceptibility of a relativistic Dirac electron gas,[32] which arises in the same manner as given here.

We now show the relation of $\langle r^2\rangle$ defined by Eq. (32) to

$$(\langle X^2\rangle+\langle Z^2\rangle),$$

where

$$\vec{\mathrm{R}}=\vec{\mathrm{X}}+\vec{\mathrm{Y}}+\vec{\mathrm{Z}}$$

is the well-known Adam's coordinate operator used in Sec. III. The quantity $\langle X^2\rangle+\langle Z^2\rangle$ is the minimum spread of a one-band wave packet and its average over the BZ is related to the spread of the Wannier function.[33] By averaging over all directions perpendicular to the magnetic field (replacing Q_3^2 and Q_1^2 by $Q_3 Q_1$ in the matrix element of $\langle X^2\rangle$ and $\langle Z^2\rangle$) we have

$$2(\langle X^2\rangle+\langle Z^2\rangle)=\frac{\hbar^2 Q_3 Q_1\epsilon^2}{2E^4}+\frac{Q_3 Q_1\hbar^2}{e^2}\ , \tag{34}$$

where $e=[E(E+\epsilon)]^{1/2}$. The first term is of the form of Eq. (32) for $\langle r^2\rangle$ except for the factor $\frac{1}{2}$. At the band edge Eq. (34) gives exactly the $\langle r^2\rangle$ of Eq. (33). Equation (34) evaluated at the band edge is consistent with Blount's[33] result: $\langle\vec{\mathrm{R}}^2\rangle$ in Dirac theory is $\frac{3}{4}(\hbar/mc)^2$ for an electron at rest. Thus one expects $2(\langle X^2\rangle+\langle Z^2\rangle)$ to play the role of $(\hbar/mc)^2$, the square of the Compton wavelength. Therefore the contribution to χ_{sp} from electrons near the band edge is given by a pseudoatomic term using the cyclotron mass and with $\langle r^2\rangle$ the minimum spread of the one-band wave packet. Unfortunately, the structure of Eq. (34) does not allow such a simple interpretation for arbitrary energy in the valence band, which is the source of the large background diamagnetism. However, these

considerations may provide a clue to more complete and satisfactory physical interpretation.

Using the established band parameters[27] for bismuth, we find at the band edge $\langle r^2\rangle^{1/2} \sim 1000$ Å when the magnetic field is in the small-cyclotron-mass direction. This is in satisfactory agreement with Blount's order-of-magnitude estimate for the minimum spread of the one-band wave packet in bismuth.

V. DISCUSSION

We have derived the expression for $\chi_\perp$ in bismuth. The derivation is based on the Wolff[22] or simplified Lax[21] two-band model for the EBS near the L point. This is the natural model to use for $\chi_\perp$ since $\chi_\perp$ is essentially proportional to χ_L^{22}. The inclusion of the quadratic terms that occur in the diagonal element of the Hamiltonian matrix for a two-band model would make the calculation of χ_L^{22} from the general formalism for χ less tractable; however, if one just retains the k_y^2 dependence, there would be only slight modification in the expression already obtained for χ_L^{22}; i.e., one simply replaces Δ by $\Delta + \frac{1}{2}k_y^2$. This would also make integration over the whole $\vec{k}$ space convergent. Fukuyama and Kubo calculated the effect of the $\frac{1}{2}k^2$ term, but not R_0 and R_1. Another way in which one can go around the problems is to ignore the quadratic terms and treat the cutoff K as a parameter. This is what was actually done[27] in fitting the susceptibility data of Wehrli.[34] The cutoff K has been shown[24] not to exceed the linear dimension of the BZ. Indeed, the simple formula given for $\chi_\perp$ was able to explain quite satisfactorily the measured values of $\chi_\perp$ over the considerable range of bismuth-rich $Bi_{1-x}Sb_x$ alloys, using the experimentally known energy-band parameters for these alloys.[27]

The second important result of this paper is, we believe, a significant step towards a better understanding of χ_{ID}. This is the most complicated part of χ in the general formalism, and even its sign alone cannot be determined *a priori*. In Eq. (28) χ_{ID} is shown to be composed of two physically meaningful and familiar terms. As it now stands, none of the terms written for χ_{ID} in the general formalism individually gives any one of the two physically meaningful terms. We have also looked for combinations of some of the terms in the general formalism of χ_{ID} to yield either χ_g or χ_{sp}, but were unable to find these combinations. Thus it is concluded that none of the terms in χ_{ID} written in the literature is useful, and the way they are written mixes χ_g and χ_{sp} over all these terms. However, at the band edge the $W_{sp}^{(2)}(\vec{k})$ and $W_g^{(2)}(\vec{k})$ are given by the fourth and last terms of Eq. (13), respectively.

We have indicated in Sec. IV of the paper that the pseudoatomic term in χ due to the spread is closely related to the minimum spread of the one-band wave packet in bismuth. Thus we may interpret the pseudoatomic terms as due to the inherent spread of Bloch electrons in the bismuth crystal. This interpretation is only valid for the conduction electrons and does not hold for valence electrons because of the change of sign of the last term of Eq. (30). However, for deficit of electrons or presence of holes, the same interpretation applies for holes.

It would be very interesting if terms in the general formalism of χ_{ID} could similarly be cast into a sum of two terms of the same physical meanings. Although the new formalism of Fukuyama[14] more readily gives the expression for the total susceptibility for real bands than the older formalism, the older formalism still has the virtue of exposing the physically meaningful terms that contribute to χ. Thus much work is still needed in this direction.

Finally, the large diamagnetism of bismuth is only incidentally related to the spin-orbit coupling. Exactly the same form of Hamiltonian as Eq. (10) applies at the H point of graphite (with the spin-orbit effects neglected) and also produces a large diamagnetism.[12]

APPENDIX A: TERMS MAKING UP χ_{ID}

In Eq. (17) S is the sum of six terms which result after integration with respect to ϕ. They are

$$\mathrm{I} = (Q_3 Q_1)^2 \pi \left(-\frac{1}{16}\frac{\epsilon}{E^4} + \frac{5}{32}\frac{\epsilon^2}{E^5} + \frac{1}{32E^3} + \frac{1}{8e^2E} - \frac{1}{8}\frac{\epsilon^4}{E^7} - \frac{1}{8}\frac{\epsilon}{e^2E^2}\right) f(E), \quad \text{(A1)}$$

$$\mathrm{II} = \tfrac{1}{4}(Q_3 Q_1)^2 \pi \left(-\frac{1}{2}\frac{\epsilon}{E^3} + \frac{1}{4}\frac{\epsilon^2}{E^4} + \frac{1}{4}\frac{\epsilon^4}{E^6}\right)\frac{\partial f(E)}{\partial E}, \quad \text{(A2)}$$

$$\mathrm{III} = \tfrac{1}{4}(Q_3 Q_1)^2 \pi \left(\frac{12}{8}\frac{\epsilon}{E^4} - \frac{12}{8}\frac{\epsilon^2}{E^5} - \frac{2}{e^2E} + \frac{\epsilon^4}{E^7}\right) f(E), \quad \text{(A3)}$$

$$\mathrm{IV} = \tfrac{1}{8}(Q_3 Q_1)^2 \pi \left(\frac{1}{2e^2E} + \frac{3}{2}\frac{\epsilon^2}{e^2E^3} + \frac{1}{4}\frac{\epsilon^4}{E^7} + \frac{3}{4}\frac{\epsilon^2}{E^5}\right) f(E), \quad \text{(A4)}$$

$$\mathrm{V} = \tfrac{1}{8}(Q_3 Q_1)^2 \pi \left(\frac{1}{4E^3} + \frac{3}{2}\frac{\epsilon^2}{E^5} - \frac{15}{4}\frac{\epsilon^4}{E^7}\right) f(E), \quad \text{(A5)}$$

$$\mathrm{VI} = -\tfrac{1}{4}(Q_3 Q_1)^2 \pi \frac{\epsilon}{E^4} f(E), \quad \text{(A6)}$$

where

$$\epsilon = [\eta^2 + (E_g/2)^2]^{1/2}$$

and

$$e = [E(E+\epsilon)]^{1/2}.$$

The relative contributions of these terms to the background susceptibility are -0.45, 0.0, 1.41, -0.70, 0.0, and 0.75, respectively.

APPENDIX B: COMPARISON WITH FUKUYAMA AND KUBO

Fukuyama and Kubo[13] calculated for the same energy-band model (neglecting R_0 and R_1 but both with and without the $\frac{1}{2}k^2$ terms) by a different method, and for $T=0\,^\circ\mathrm{K}$ only. We can generalize their result to finite temperature using the prescription

$$\chi(E_F, T) = -\int_{-\infty}^{\infty} dE\, \chi(E, 0)\, \frac{\partial f(E-E_F)}{\partial E} \quad . \tag{B1}$$

In our notation, their equation (3.27) for the leading term in the diamagnetism is

$$\chi = (6\pi^2 c^2)^{-1}\, \frac{Q_3 Q_1}{Q_2} \int_0^Z d\eta\, \frac{\eta^4 [f(\epsilon) - f(-\epsilon)]}{\epsilon^5} \quad . \tag{B2}$$

Two partial integrations yield

$$\chi = (6\pi^2 c^2)^{-1}\, \frac{Q_3 Q_1}{Q_2} \Bigg[\int_0^Z d\eta\, \frac{f(\epsilon) - f(-\epsilon)}{\epsilon} + \int_0^Z d\eta \left(\frac{\eta}{\epsilon}\right)\left(1+\frac{\eta^2}{3\epsilon^2}\right) \frac{\partial}{\partial \eta}\, [f(\epsilon) - f(-\epsilon)] - \left(\frac{Z}{\epsilon_g}\right)\left(1+\frac{Z^2}{3\epsilon_g^2}\right) [f(\epsilon_g) - f(-\epsilon_g)] \Bigg] \quad , \tag{B3}$$

where $\epsilon_g = [Z^2 + (E_g/2)^2]^{1/2}$. The first term is the same as our result. The last term is equal to $\frac{4}{3}$ when $Z \gg E_g$, and the middle term goes monotonically from 0 to $-\frac{4}{3}$ as E_F goes from 0 to $\pm\epsilon_g$ at low temperature. Thus, the maximum deviation from our result is $\frac{4}{3}$, which occurs when the leading term is largest. When the Fermi level is in the forbidden gap at low temperature, the leading term is $\sinh^{-1}(2Z/E_g)$, which is approximately 4.8 for our estimate of the cutoff, and approximately 4.4 for Fukuyama and Kubo's estimate. Thus, the leading terms in the two calculations agree, but their result for the same model differs from ours in an important way. Calculations using Fukuyama's new formula or summing over the Landau levels give exactly the same result as ours. The discrepancy is probably due to the fact that the truncation of the exact Hamiltonian to a 4×4 matrix occurs at different stages in the different calculations.

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Group-Theoretical Selection Rules in Inelastic Neutron Scattering within the Rigid-Molecule Model

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The model-independent technique of Elliott and Thorpe (ET) is extended to apply to a class of models in which molecular units undergo translational vibrations with respect to each other and also librations, but in which the internal vibronics of the molecules are neglected. Within the model we find that the ET "structure function" $F^{(\gamma)}(\vec{k})$, associated with irreducible representation γ and momentum transfer $\vec{k}$, can be written in the form $F^{(\gamma)}(\vec{k}) = F^{(\gamma)}(\vec{k}\,|\,R) + F^{(\gamma)}(\vec{k}\,|\,\theta)$, where R and θ signify translational and rotational oscillations. Moreover, the translational part is identical to that of ET except that the atomic scattering lengths a_n which appear in their result are to be replaced by $\vec{k}$-dependent molecular form factors $a_n(\vec{k}')$. $F^{(\gamma)}(\vec{k}\,|\,\theta)$ contains a vector form factor equal to $i\nabla_{\vec{k}} \cdot a_n(\vec{k}')$, where $\vec{k}'$ is related to $\vec{k}$ via a rotation. Mathematically, their result is contained in ours as a special case. Physically, we indicate how to use both procedures in concert, thereby aiding in the identification of γ as well as in separating the internal from external vibrations and among the latter, the translational and rotational parts thereof. At the Brillouin-zone boundary we employ the so-called multiplier representations, thereby achieving a simplification both of our results and theirs. By significantly reducing the number of phonon modes to be considered in complex molecular crystals, we have likewise increased the diagnostic power of this method which requires no detailed knowledge of force constants. It is hoped that our results will receive wide application in the identification of phonons in such crystals.

I. INTRODUCTION AND QUALITATIVE CONCLUSIONS

Several years ago Elliott and Thorpe[1] (ET) introduced an elegant *model-independent* technique to aid in identifying phonon branches group theoretically[2] in inelastic neutron scattering experiments. Despite its potential power, their method has been applied rather sparingly,[3] one reason being perhaps that for sufficiently complex crystals the number of modes is so large that other more or less model-dependent assumptions must be introduced *a posteriori* to help resolve possible ambiguities in the assignments. (Another reason, of course, lies in the fact that only recently have molecular crystals come under intensive experimental study.) It is our purpose here to narrow the field of possibilities considerably while retaining as much as possible the generality of their approach. We do so by extending their analysis to apply to the well-known rigid-molecule model within which the internal degrees of freedom of each molecular unit are neglected.[4] Within this model or, better, *class* of models, our procedure is completely general in that details regarding force constants, etc., are left wholly unspecified, as in the original ET work.

As will be seen, the extension of their analysis to the rigid-molecule model involves the resolution of several points of principle, notably, ascertaining the correct transformation properties of the polarization "vectors" $\xi_\lambda^{\vec{\alpha}j}(\vec{\rho}_n\,|\,\theta)$ appearing in the normal-mode expansion of the (moment-of-inertia weighted) angular displacements about the principal axes of inertia in equilibrium. Neither the $\xi_\lambda^{\vec{\alpha}j}(\vec{\rho}_n\,|\,\theta)$ nor the weighted nor unweighted angular displacements mentioned above have simple transformation properties such as possessed by vector or axial-vector fields. Rather, one must revert to a more general set of coordinates which qualify