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On the Diamagnetism of the Conduction Electrons in the Alkali Metals

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(3. V. 62)

Summary. The field independent diamagnetic susceptibility of the conduction electrons in the alkali metals has been calculated. The method for determining the energy levels of Bloch electrons in a magnetic field, recently proposed by Y. YAFET, has been used. Special attention is paid to magnetic field induced band transitions. In the case of lithium an *s-p* band model is used, while sodium is represented by a *p-s-p* band model. The *s* bands are considered to be parabolic in both cases. The band interaction is included to all orders. Although a reasonable description of the susceptibility is obtained in this way, higher bands play an important role. KJELDAAS and KOHN in an earlier calculation considered all bands, but the band interaction up to fourth order only. It is shown that the band interaction of higher order cannot be neglected.

Zusammenfassung. Es wurde die feldunabhängige diamagnetische Suszeptibilität der Leitungselektronen in den Alkalimetallen berechnet. Zur Bestimmung der Energie-Niveaux der Bloch-Elektronen in einem Magnetfeld wurde die kürzlich von Y. YAFET vorgeschlagene Methode verwendet; spezielle Beachtung wurde den durch ein Magnetfeld induzierten Bandübergängen geschenkt. Für Lithium wurde ein *s-p*-Bänder-Modell benützt, während Natrium durch ein *p-s-p*-Bänder-Modell dargestellt wird; in beiden Fällen werden die *s*-Bänder parabolisch angenommen. Innerhalb dieser Voraussetzungen wird die Bandwechselwirkung exakt berücksichtigt. Obwohl man auf diese Weise eine zweckmässige Darstellung der Suszeptibilität erhält, müsste sie noch durch Hinzunahme weiterer Bänder ergänzt werden. KJELDAAS und KOHN behandeln in einer früheren Rechnung alle Bänder. Sie berücksichtigen die Bandwechselwirkung jedoch nur bis zur vierten Ordnung. Es wird gezeigt, dass die höheren Ordnungen der Bandwechselwirkung nicht vernachlässigt werden dürfen.

1. Introduction

Despite many attempts to explain the magnetic susceptibility of the alkali metals theoretically, there still remains a discrepancy between theory and experiment[1]). If we assume that the conduction electrons and

the core electrons can be treated separately and if we moreover take into account the fact that the spin orbit coupling in the alkali metals is very small[2]), the total susceptibility can be written as a sum of three terms.

$$\chi = \chi_c + \chi_s + \chi_d \,. \tag{1.1}$$

Here χ_c is the core susceptibility and is given by the familiar Langevin formula[3]). Since the spin susceptibility χ_s, as calculated by PINES[4]) agrees well with the experiments by SLICHTER[5]), we are led to the conclusion that the discrepancy is due to a lack of understanding of χ_d, the diamagnetism of the conduction electrons.

Since the fundamental paper of LANDAU[6]) on the diamagnetism of a free electron gas, much work has been done to solve this problem for electrons moving in a crystal lattice. A first step in this direction was made by PEIERLS[7]), who proved the following important theorem. The exact Hamilton function

$$X = \frac{\left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A}\right)^2}{2\,m} + V(\boldsymbol{r}) \tag{1.2}$$

where $V(\boldsymbol{r})$ is the periodical potential, is approximately equivalent to the hamiltonian, that one gets by replacing $\boldsymbol{k}$ in

$$E(\boldsymbol{k}) = E_n^H(\boldsymbol{k}) + H^2\, e(\boldsymbol{k}) \tag{1.3}$$

by an operator $\boldsymbol{K}$, satisfying the commutation relation

$$K_x\, K_y - K_y\, K_x = \frac{i\,e}{\hbar\, c}\, H_z \,. \tag{1.4}$$

Here $E_n^H(\boldsymbol{k})$ is a function with the same dependence on the wave vector $\boldsymbol{k}$ as the eigenstates $E_n(\boldsymbol{k})$ of the hamiltonian without magnetic field. However, $E_n^H(\boldsymbol{k})$ may still depend weakly on the magnetic field. The second term in (1.3) is the level shift due to the magnetic field H[8]). PEIERLS himself worked out his theorem in the tight binding limit, but as has been proved by HARPER[9]), the theorem is more generally valid. It should be emphasized that the mixing by the magnetic field of wave functions belonging to different bands has been neglected in this procedure. For that reason the band index n still occurs in (1.3). The theorem is also not applicable to degenerate bands.

By means of the density matrix technique PEIERLS was able to derive the susceptibility resulting from (1.3). He gets three terms, one of which (χ_1, in PEIERLS' notation) has no unique sign and no easy physical interpretation. The second (χ_2) is the analogue of the atomic diamagnetism, whereas the third (χ_3) is a generalization of the original Landau formula.

Special cases of this theorem have been obtained by LUTTINGER[10]) and later by LUTTINGER and KOHN[11]).

These authors develop $E_n(\boldsymbol{k})$ into a power series in $\boldsymbol{k}$, up to second order terms and substitute for $\boldsymbol{k}$ the operator $\boldsymbol{p} - (e/c)\,\boldsymbol{A}$. The susceptibility obtained in this way is just the LANDAU susceptibility with the free electron mass replaced by the zero field effective mass. They also discussed the effect of spin orbit coupling. LUTTINGER[12]) generalized this theory to degenerate bands, so it is applicable to semiconductors with large band widths, for which the effective mass concept is particularly appropriate.

An extension of the Luttinger-Kohn theory was given by KJELDAAS and KOHN[13]) who develop $E_n(\boldsymbol{k})$ up to fourth order terms. The effective hamiltonian then consists of two parts. A completely symmetrized term, $E_n(\boldsymbol{K})$ to fourth order in $\boldsymbol{K}$ (with $\boldsymbol{K} = \boldsymbol{p} - (e/c)\,\boldsymbol{A}$), plus a remainder $R(\boldsymbol{K})$, which comes from the noncommutivity of the components of $\boldsymbol{K}$. $E_n(\boldsymbol{K})$ results in a special form of PEIERLS' χ_3, whereas the contribution from $R(\boldsymbol{K})$ agrees with χ_2 in the tight binding approximation.

Recently, Y. YAFET[14]) proposed a new method for determining the energy levels of Bloch electrons in a magnetic field. This method is an improvement over the LUTTINGER, KOHN, KJELDAAS versions in that it is in principle valid for all $\boldsymbol{k}$ and allows for magnetic field induced band transitions to all orders. The energy levels of the electrons in different bands are obtained by solving a set of homogeneous linear algebraic equations, instead of a system of coupled differential equations. In order to be able to derive analytical expressions for the energy levels it is necessary to limit the number of bands. It is the purpose of this paper to discuss the effect of band interaction on the susceptibility in the case of the alkali metals with the aid of this technique.

There exists another class of treatments, which do not calculate the energy levels explicitly, but which use the density matrix formalism[15]) [16]) [17]). Although the results are in principle exact (except that spin orbit coupling is neglected and non degenerate bands are assumed throughout), the final formulae for the susceptibility are so complex that no physical interpretation or numerical application is possible.

Finally we want to mention a letter by BLATT[1]) who suggests that a touching of the Fermi surface and the border of the first Brillouin zone is responsible for the observed anomalies in the alkali metals. However, this question is still unsettled[18]) and we shall not discuss it further.

In section 2 we give a description of the Yafet method. In sections 3 and 4 the energy levels within an *s-p* band model (in the case of Li) and within a *p-s-p* band model (in the case of Na) are obtained. Here it is assumed that the bands are parabolic. In section 5 the corresponding susceptibilities are derived. In section 6 a discussion of the results is given.

2. Description of Yafet's method

In this section we shall give an account of Yafet's method for determining the energy levels of Bloch electrons in a magnetic field. We shall, however, only mention those features, which will actually be used in later sections.

Let X_0 and X be the Hamilton functions of an electron in the periodic potential without and with magnetic field respectively. The eigenfunctions of X_0 are the Bloch functions $\psi_{n\,\boldsymbol{k}}$ and the corresponding eigenvalues $E_n(\boldsymbol{k})$, where n is the band index and $\boldsymbol{k}$ the wave vector running from zero to the border of the first Brillouin zone.

The functions $\psi_{n\,\boldsymbol{k}}$ are written as

$$\psi_{n\,\boldsymbol{k}} = u_{n\,\boldsymbol{k}}\, e^{i\,\boldsymbol{k}\cdot\boldsymbol{r}} \tag{2.1}$$

where $u_{n\,\boldsymbol{k}}$ is a function with lattice periodicity.

If we choose the magnetic field in the z-direction and if we introduce for the vector potential the special gauge

$$A_x = 0\,, \quad A_y = -\,H_z\,x\,, \quad A_z = 0 \tag{2.2}$$

the Hamilton function with magnetic field becomes

$$X = X_0 + \frac{s}{m}\,x\,p_y + \frac{s^2}{2\,m}\,x^2 \tag{2.3}$$

with $s = e\,H_z/c$.

In order to find the wave function ψ with the magnetic field present we have to solve the Schrödinger equation

$$X\,\psi = E\,\psi\,. \tag{2.4}$$

For that purpose LUTTINGER and KOHN introduced a set of functions

$$\chi_{n\,\boldsymbol{k}} = u_{n\,0}\, e^{i\,\boldsymbol{k}\cdot\boldsymbol{r}} \tag{2.5}$$

in which ψ is to be expanded. This set is complete and orthonormal if the $\psi_{n\,\boldsymbol{k}}$ are. Expanding

$$\psi = \sum_{n'} \int d\boldsymbol{k}'\, A_{n'}(\boldsymbol{k}')\, \chi_{n\,\boldsymbol{k}'} \tag{2.6}$$

and inserting this in (2.4) we get a set of equations for the $A_n(\boldsymbol{k})$, which read:

$$\sum_{n'} \int d\boldsymbol{k}'\, \langle n\,\boldsymbol{k}\,|\,X\,|\,n'\,\boldsymbol{k}'\rangle\, A_{n'}(\boldsymbol{k}') = E\,A_n(\boldsymbol{k})\,. \tag{2.7}$$

Here

$$\left.\begin{aligned}\langle n\,\boldsymbol{k}\,|\,X\,|\,n'\,\boldsymbol{k}'\rangle = &\left[\left(E_n(0)+\frac{\hbar^2 k^2}{2\,m}\right)\delta_{n\,n'}+\frac{\hbar\,k_\alpha}{m}\,p^\alpha_{n\,n'}\right]\delta\,(\boldsymbol{k}'-\boldsymbol{k})\\ &+\frac{s}{m}\,(\hbar\,k_y\,\delta_{n\,n'}+p^y_{n\,n'})\,i\,\frac{\partial}{\partial k_x}\,\delta\,(\boldsymbol{k}'-\boldsymbol{k})\\ &-\frac{s^2}{2\,m}\,\frac{\partial^2\delta\,(\boldsymbol{k}'-\boldsymbol{k})}{\partial k_x^2}\,\delta_{n\,n'}\end{aligned}\right\}\quad(2.8)$$

is the hamiltonian in the Luttinger-Kohn representation[11]). At this point LUTTINGER and KOHN make this hamiltonian subject to a canonical transformation in order to remove interband elements of first order in $\boldsymbol{k}$. Afterwards they neglect interband terms of the order k^2 but keep the intraband terms of this order. In this way these authors are led to the following equivalence theorem. In order to find an approximate hamiltonian for an electron moving in a periodic potential in the presence of a magnetic field one has to develop $E_n(\boldsymbol{k})$ into a power series of $\boldsymbol{k}$ up to second order terms and replace $\hbar\,\boldsymbol{k}$ by the operator $(\boldsymbol{p}-(e/c)\,\boldsymbol{A})$. Here $E_n(\boldsymbol{k})$ should be a non degenerate band. KJELDAAS and KOHN[13]) go a step further and apply another canonical transformation to remove interband elements of order k^2. Now interband elements of fourth order in $\boldsymbol{k}$ are neglected whereas intraband terms of this order are kept. By making a sufficient number of canonical transformations to decouple bands, one could get a very good one band approximation, but soon the formulae become not very transparent. Moreover, this procedure does not work so well in case the bands under consideration are degenerate.

YAFET[14]), however, found a method to replace the set of coupled differential equations (2.7) (2.8) by a set of coupled homogeneous algebraic equations.

We now introduce the following operators

$$\bar{k}_x=\hbar\,k_x\,,\qquad \bar{k}_y=\hbar\,k_y+i\,s\,\frac{\partial}{\partial k_x}\,,\qquad \bar{k}_z=\hbar\,k_z\,.\tag{2.9}$$

With the aid of these operators and with $|\,\boldsymbol{k}\rangle=e^{i\,\boldsymbol{k}\cdot\boldsymbol{r}}$ (2.8) can be written

$$\left.\begin{aligned}\langle n\,\boldsymbol{k}\,|\,X\,|\,n\,\boldsymbol{k}'\rangle = E_n(0)\,\delta_{n\,n'}\,\delta\,(\boldsymbol{k}'-\boldsymbol{k})+\frac{p^\alpha_{n\,n'}}{m}\langle\boldsymbol{k}\,|\,\bar{k}_\alpha\,|\,\boldsymbol{k}'\rangle\\ +\frac{1}{2\,m}\,\delta_{n\,n'}\,\langle\boldsymbol{k}\,|\,\bar{k}^2_\alpha\,|\,\boldsymbol{k}'\rangle\,.\end{aligned}\right\}\quad(2.10)$$

Since (2.10) contains only derivatives with respect to k_x it is clear that solutions of (2.7), (2.10) are of the form:

$$A_n(\boldsymbol{k})\sim\delta\,(k'_y-k_y)\,\delta\,(k'_z-k_z)\,F_{n,\,f,\,k'_y,\,k'_z}(k_x)\tag{2.11}$$

where $F_{n,f,k'_y,k'_z}(k_x)$ is a function of k_x only. It may still depend parametrically on n, k'_y, k'_z and f. Here f denotes the degree of freedom of k_x.

By substituting (2.11) into (2.7) and (2.10) we find for the equations for $F(k_x)$

$$\left(E_n(0) + \frac{1}{2m}\bar{k}^2 - E\right) F_n(k_x) + \frac{1}{m}\sum_{n' \neq n} p^{\alpha}_{n\,n'}\,\bar{k}_\alpha\,F_{n'}(k_x) = 0\,. \tag{2.12}$$

The indices f, k'_y and k'_z of $F(k_x)$ have been dropped and use has been made of the fact that $p^{\alpha}_{n\,n} = 0$.

For $F_n(k_x)$ we make the Ansatz

$$F_n(k_x) = e^{i\hbar k_y k_x/s}\,G_n(k_x) \tag{2.13}$$

where $G_n(k_x)$ is again a function of k_x only and which still contains the parameters f, k'_y and k'_z.

By means of this transformation the variable k_y is removed from (2.12) as can be easily verified. Consequently the energy levels do not depend on k_y. After carrying out the transformation (2.13) the equation for $G_n(k_x)$ can be written as

$$\left.\begin{aligned}&\left\{E_n(0) + \frac{1}{2m}\left(\hbar^2 k_x^2 + \hbar^2 k_z^2 - s^2\frac{\partial^2}{\partial k_x^2}\right) - E\right\} G_n(k_x)\\ &\quad + \frac{1}{m}\sum_{n' \neq n}\left(p^{+}_{n\,n'}\,\bar{k}_- + p^{-}_{n\,n'}\,\bar{k}_+ + p^{z}_{n\,n'}\,k_z\right) G_{n'}(k_x) = 0\end{aligned}\right\} \tag{2.14}$$

with
$$p^{\pm}_{n\,n'} = \frac{1}{2}\left(p^{x}_{n\,n'} \pm i\,p^{y}_{n\,n'}\right)$$

and
$$\bar{k}_\pm = \hbar\,k_x \mp s\frac{\partial}{\partial k_x}\,.$$

YAFET made the observation that an approximate solution for can be found if one puts

$$u_{n\,0} = R_b(r)\,Y^m_l(\varphi,\theta) = R_b(r)\,e^{i m\varphi}\,p^m_l(\varphi,\theta) \tag{2.15}$$

where $R_b(r)$ is a radial function for the band b and $Y^m_l(\varphi,\theta)$ a spherical harmonic for angular momentum l and a component of angular momentum m in the direction of the magnetic field. The band n is now characterized by the three indices b, l, m. The approximation (2.15) contains implicitly the assumption that the energy bands, at least as far as the filled portions are concerned, are spherical. This should be a good approximation for the s bands of the alkali metals. What has also been neglected by taking (2.15) is lattice broadening, i.e. the fact that when the energy band is not spherical the Landau levels are broadened into a narrow band[19][20]. This should only be of importance at the corners of the Brillouin zones, and can presumably be neglected in the alkali metals.

With (2.15) the matrix elements $p^{\pm}_{n\,n'}$ and $p^{z}_{n\,n'}$ obey the important selection rule, that $p^{\pm}_{n\,n'}$ may only be different from zero if $m = m' \pm 1$ and that $p^{z}_{n\,n'}$ vanishes unless $m = m'$.

Next we notice that the reduced operators $a^{\pm} = \bar{k}_{\pm}/\sqrt{2\,s\,\hbar}$ satisfy the commutation relation

$$(a^{-}, a^{+}) = 1 \tag{2.16}$$

which is just the harmonic oscillator commutator.

Therefore the eigenvalues of the operator $a^{+}\,a^{-}$ are integers and the corresponding eigenfunctions the harmonic oscillator wave functions φ_i. Further a^{+} acting on φ_i increases i by unity whereas a^{-} diminishes i by unity.

Using these properties and the selection rules for $p^{\pm}_{n\,n'}$ and $p^{z}_{n\,n'}$ we find that solutions of (2.14) are given by

$$\left.\begin{aligned} G_{n,\,k_z}(k_x) &= C_b^{l,\,m}(k_z, j, s)\,\varphi_{j-m}\left(\frac{k_x}{\sqrt{2\,s\,\hbar}}\right), \qquad j \geqslant m\,, \\ &= 0 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad j < m \end{aligned}\right\} \tag{2.17}$$

where j is an integer and $C_b^{l,\,m}(k_z, j, s)$ are constants which indicate the mixture of Landau wave functions φ_{j-m} in different bands. The set of coupled algebraic equations for these constants is immediately obtained

$$\left.\begin{aligned} &\left(E_n(0) + \frac{1}{2\,m}\,\alpha^m - E\right) C_n^{l,\,m} + \frac{1}{m}\sum_{n' \neq n} \\ &\times \left(p^{+}_{n\,n'}\,\beta^{m-1}\,C_{n'}^{l';\,m-1} + p^{-}_{n\,n'}\,\gamma^{m+1}\,C_{n'}^{l';\,m+1} + p^{z}_{n\,n'}\,\delta^m\,C_{n'}^{l';\,m}\right) = 0 \end{aligned}\right\} \tag{2.18}$$

where the summation over m has already been carried out. The coefficients α^m, β^m, γ^m and δ^m follow from the well known harmonic oscillator matrix elements.

$$\left.\begin{aligned} \alpha^m &= (\varphi_{j-m}, \bar{k}^2\,\varphi_{j-m}) = \hbar^2\,k_z^2 + s\,\hbar\,(2\,j + 1 - 2\,m)\,, \\ \beta^m &= (\varphi_{j-m-1}, \bar{k}_{-}\,\varphi_{j-m}) = \sqrt{2\,s\,\hbar}\,\sqrt{j - m}\,, \\ \gamma^m &= (\varphi_{j-m+1}, \bar{k}_{+}\,\varphi_{j-m}) = \sqrt{2\,s\,\hbar}\,\sqrt{j - m + 1}\,, \\ \delta^m &= (\varphi_{j-m}, \bar{k}_z, \varphi_{j-m}) = \hbar\,k_z\,. \end{aligned}\right\} \tag{2.19}$$

The equations (2.18) give rise to a secular determinant from which the eigenvalues E are to be determined.

How this is actually done, will be shown in the next sections for a few special cases.

3. Energy levels in an *s*-*p* band model

We consider an s band and a higher lying p band. Both bands are assumed to have their energy extrema at $\boldsymbol{k} = 0$ and these extrema are Δ energy units apart. This model should be representative of lithium, because here the $1\,s$ band does not couple with the $2\,s$ conduction band through the matrix elements $p^{\pm}_{n\,n'}$ and $p^{z}_{n\,n'}$, and the higher lying $3\,s$ band is energetically far away.

We now want to calculate the energy levels in the conduction band in the presence of a magnetic field taking into account the interaction with the p band. For that purpose we need the following property of the matrix elements $p^{\pm}_{n\,n'}$ and $p^{z}_{n\,n'}$. If we write $p^{\pm}_{n\,n'} = p^{\pm}_{b,\,l,\,m,\,b',\,l',\,m'}$ and using the symmetry operation $\varphi \to -\varphi$ one can show, that

$$p^{\pm}_{b,\,l,\,m,\,b',\,l',\,m'} = p^{\mp}_{b,\,l,\,-m,\,b',\,l',\,-m'} \tag{3.1}$$

and

$$(p^{\pm}_{n\,n'})^* = p^{\pm}_{n'\,n}; \quad (p^{z}_{n\,n'})^* = p^{z}_{n'\,n} \tag{3.2}$$

where the star means complex conjugate.

Consequently the only matrix elements occurring in (2.18) are

$$p^{+}_{b,\,0,\,0,\,b',\,1,\,-1} = p^{-}_{b,\,0,\,0,\,b',\,1,\,1} = p^{+}_{b',\,1,\,1,\,b,\,0,\,0} = p^{-}_{b',\,1,\,-1,\,b,\,0,\,0} = p^{+}$$

and

$$p^{z}_{b,\,0,\,0,\,b',\,1,\,0} = p^{z}_{b',\,1,\,0,\,b,\,0,\,0} = p^{z}$$

where b refers to the s band and b' to the p band. There are no transitions within the p band, because for such transitions the angular momentum l does not change.

The number of equations (2.18) for the $C_b^{l,\,m}$ reduces to four. The corresponding secular determinant is

$$\begin{vmatrix} \lambda & \frac{1}{m}\,p^{+}\gamma^{0} & \frac{1}{m}\,p^{+}\beta^{0} & \frac{1}{m}\,p^{z}\,\delta^{0} \\ \frac{1}{m}\,p^{+}\gamma^{0} & \lambda + \Delta + \frac{s\,\hbar}{m} & 0 & 0 \\ \frac{1}{m}\,p^{+}\beta^{0} & 0 & \lambda + \Delta - \frac{s\,\hbar}{m} & 0 \\ \frac{1}{m}\,p^{z}\,\delta^{0} & 0 & 0 & \lambda + \Delta \end{vmatrix} = 0 \tag{3.3}$$

where $\lambda = E_b(0) + (1/2\,m)\,\alpha^0 - E$. From (2.19) it follows that $\beta^{-1} = \gamma^0$ and $\beta^0 = \gamma'$, which fact has been used in (3.3). It should be emphasized

that in (3.3) the quantum number $j \geqslant 1$. For $j = 0$ we have another set of equations with secular determinant

$$\begin{vmatrix} \lambda & \frac{1}{m} p^+ \gamma^0 & \frac{1}{m} p^z \delta^0 \\ \frac{1}{m} p^+ \gamma^0 & \lambda + \Delta + \frac{s\hbar}{m} & 0 \\ \frac{1}{m} p^z \delta^0 & 0 & \lambda + \Delta \end{vmatrix} = 0 . \tag{3.4}$$

Before solving the equations (3.3) and (3.4) it is useful to write down the secular determinant in the absence of a magnetic field. The matrix elements of the Hamilton function between Luttinger-Kohn states are now $\langle n\, \boldsymbol{k} \,|\, X_0 \,|\, n'\, \boldsymbol{k}' \rangle$. Solutions of (2.7) have then the form

$$A_n(\boldsymbol{k}) \sim \delta\,(k'_x - k_x)\, \delta\,(k'_y - k_y)\, \delta\,(k'_z - k_z)\, C_{n,\, k'_x,\, k'_y,\, k'_z} \tag{3.5}$$

while the equations for the constants $C_{n,\, k'_x,\, k'_y,\, k'_z}$ are

$$\left.\begin{aligned} &\left(E_b(0) + \frac{\hbar^2}{2\,m} k^2 - E\right) C_n + \frac{\hbar}{m} \sum_{n' \neq n} \\ &\qquad\qquad \times \left(p^+_{n\,n'}\, k_- + p^-_{n\,n'}\, k_+ + p^z_{n\,n'}\, k_z\right) C_{n'} = 0 \end{aligned}\right\} \tag{3.6}$$

where $k_\pm = k_x \pm i\, k_y$.

The secular determinant which follows from (3.6) can be obtained by replacing in (3.3) β^0 and γ^0 by $\hbar\, k_-$ and $\hbar\, k_+$ respectively and dropping the term $s\hbar/m$ from the diagonal elements. The eigenvalue λ now has the meaning $\lambda = E_b(0) + (\hbar^2/2\,m)\, k^2 - E$. The fourth order equation for this λ becomes

$$(\lambda + \Delta)^2 \left\{\lambda^2 + \lambda\,\Delta - \frac{2(p^+)^2\, \hbar^2\, k_-\, k_+ + (p^z)^2\, \hbar^2\, k_z^2}{m^2}\right\} = 0 . \tag{3.7}$$

One can prove, using explicit expressions for the spherical harmonics Y^0_0, Y^{-1}_1, Y^0_1, Y^1_1 and writing $(p_x + i\, p_y)$ in polar coordinates that $2(p^+)^2 = (p^z)^2 = p^2$. Therefore (3.7) can be written

$$(\lambda + \Delta)^2 \left\{\lambda^2 + \lambda\,\Delta - \frac{p^2\, \hbar^2\, k_z^2}{m^2}\right\} = 0 . \tag{3.8}$$

The energy levels of the s band are obtained from (3.8) by solving the quadratic equation for λ and taking the highest value of λ.

$$\left.\begin{aligned} E &= E_b(0) + \frac{\hbar^2}{2\,m} k^2 - \lambda \\ &= E_b(0) + \frac{\hbar^2}{2\,m} k^2 + \frac{\Delta}{2} - \frac{\Delta}{2} \sqrt{1 + \frac{4\,\hbar^2\, k^2\, p^2}{m^2\, \Delta^2}} \end{aligned}\right\} \tag{3.9}$$

which for small k (parabolic approximation) takes the form

$$E = E_b(0) + \frac{\hbar^2}{2\,m} k^2 - \frac{\hbar^2 p^2}{m^2 \Delta} k^2 = E_b(0) + \frac{\hbar^2}{2\,m^*} k^2 \tag{3.10}$$

with the reciprocal effective mass

$$\frac{1}{m^*} = \frac{1}{m} - \frac{2\,p^2}{m^2 \Delta}. \tag{3.11}$$

The fourth order equation for λ, with the magnetic field present is

$$\left.\begin{aligned} &(\lambda + \Delta)^2 \left\{\lambda^2 + \lambda \Delta - \frac{p^2 (\hbar^2 k_z^2 + s\,\hbar\,(2\,j+1))}{m^2}\right\} \\ &\qquad + \frac{s^2 \hbar^2}{m^2} \left\{\frac{p^2}{m} (\lambda + \Delta) + \frac{p^2 \hbar^2 k_z^2}{m^2} - \lambda\,(\lambda + \Delta)\right\} = 0 \end{aligned}\right\} \tag{3.12}$$

which is the analogue of (3.8).

We develop λ in a power series in s. For the temperature independent susceptibility we need λ only up to second order in s. With

$$\lambda = A + C\,s + B\,s^2 \tag{3.13}$$

in analogy with (3.10) A satisfies the equation

$$A^2 + A\,\Delta - \frac{\{\hbar^2 k_z^2 + s\,\hbar\,(2\,j+1)\}\,p^2}{m^2} = 0\,. \tag{3.14}$$

By substituting (3.13) into (3.12) we find immediately that $C = 0$ for the s band. Thus we are left with $\lambda = A + B\,s^2$. The equation for B is then

$$\left.\begin{aligned} &B\,(A + B\,s^2 + \Delta)^2\,(2\,A + B\,s^2 + \Delta) \\ &\frac{\hbar^2}{m^2} \left\{\frac{p^2}{m} (A + B\,s^2 + \Delta) + \frac{p^2 \hbar^2 k_z^2}{m^2} - (A + B\,s^2)\,(A + B\,s^2 + \Delta)\right\} = 0\,. \end{aligned}\right\} \tag{3.15}$$

Since the s independent part of B is required in (3.13) we get for B from (3.15)

$$B\left(k_z, j + \frac{1}{2}\right) = -\frac{\frac{\hbar^2}{m^2} \left\{\frac{p^2}{m} (A + \Delta) + \frac{p^2 \hbar^2 k_z^2}{m^2} - (A + \Delta)\,A\right\}}{(A + \Delta)^2\,(2\,A + \Delta)}. \tag{3.16}$$

If we again make the parabolic approximation, i.e.

$$A = \frac{\hbar^2 k_z^2 + s\,\hbar\,(2\,j+1)}{2\,\mu} \tag{3.17}$$

where $1/\mu = 1/m - 1/m^*$, the final expression for the energy levels of the s band in the presence of the magnetic field is

$$\left.\begin{aligned} &E\left(k_z, j + \frac{1}{2}\right) \\ &= E_b(0) + \frac{\hbar^2 k_z^2 + s\,\hbar\,(2\,j+1)}{2\,m^*} - B\left(k_z, j + \frac{1}{2}\right) s^2\,, \quad j \geqslant 1\,. \end{aligned}\right\} \tag{3.18}$$

In much the same way one can find the zero point energy ($j = 0$) from (3.4)

$$E(k_z) = E_b(0) + \frac{\hbar^2 k_z^2 + s\,\hbar}{2\,m^*} - B'(k_z)\,s\,, \quad j = 0 \tag{3.19}$$

where

$$B'(k_z) = -\frac{\frac{\hbar}{m}\left\{A'\,(A' + \Delta) - \frac{p^2\,\hbar^2\,k_z^2}{m^2}\right\}}{(A' + \Delta)\,(2\,A' + \Delta)}\,. \tag{3.20}$$

Here A' is the same as in (3.18), with $j = 0$.

If j is so large that α^m, β^m and γ^m in (2.19) can be written as

$$\left.\begin{aligned} \alpha^m &= \hbar^2\,k_z^2 + s\,\hbar\,2\,j\,, \\ \beta^m &= \sqrt{2\,s\,\hbar}\,\sqrt{j}\,, \\ \gamma^m &= \sqrt{2\,s\,\hbar}\,\sqrt{j} \end{aligned}\right\} \tag{3.21}$$

the energy levels which follow from (3.3) are

$$E = E_b(0) + \frac{\hbar^2\,k_z^2 + s\,\hbar\,2\,j}{2\,m^*} \tag{3.22}$$

so that the total energy is

$$E = E_b(0) + \frac{\hbar^2\,k_z^2 + s\,\hbar\,(2\,j + 1)}{2\,m^*} - B'\,s\,. \tag{3.23}$$

In section 5 it will be shown that $-B'\,s$ does not contribute to the susceptibility. Therefore (3.23) gives the susceptibility which one would have expected in a one band approximation. Using a semi classical picture, large j means that the Landau orbits are large compared to the lattice spacing d i.e. $\sqrt{\hbar\,c/e\,H} \gg d$. This condition for the applicability of the one band approximation has already been obtained by ZIL'BERMAN on intuitive grounds[21]).

4. Energy levels in a *p-s-p* band model

A model of this type may be representative of the conduction band in sodium. There is still a lower lying s band which couples strongly with the lowest p band. This p band could give a contribution to the susceptibility which however, we shall not calculate. For full bands the non parabolicity plays an essential role. The Luttinger-Kohn representation will not give reliable results in such cases, unless a sufficiently large number of bands is included. There are indications that the contribution of the lowest p band is rather small. These will be explained in section 6. We denote the upper p band with index p and the lower with index q. The conduction

band gets the index 0. The equation of seventh order for the case of zero magnetic field is

$$\left.\begin{aligned}&(\lambda+\Delta_p)^2\,(\lambda-\Delta_q)^2\\ \times\Big\{&\lambda\,(\lambda+\Delta_p)\,(\lambda-\Delta_q)-\frac{\hbar^2\,k^2\,p^2}{m^2}\,(\lambda-\Delta_q)-\frac{\hbar^2\,k^2\,q^2}{m^2}\,(\lambda+\Delta_p)\Big\}=0\end{aligned}\right\}\tag{4.1}$$

where $\Delta_p = E_p(0) - E_0(0)$ and $\Delta_q = -E_q(0) + E_0(0)$.

The energy levels of the s band in the parabolic approximation are readily obtained

$$E = E_0(0) + \frac{\hbar^2}{2\,m^*}\,k^2 \tag{4.2}$$

with

$$\frac{1}{m^*} = \frac{1}{m} - \frac{2}{m^2}\left(\frac{p^2}{\Delta_p} - \frac{q^2}{\Delta_q}\right).$$

Analogous to (4.1) the secular equation with the magnetic field present can be written

$$\left.\begin{aligned}&(\lambda+\Delta_p)^2\,(\lambda-\Delta_q)^2\Big\{\lambda\,(\lambda+\Delta_p)\,(\lambda-\Delta_q)\\ &\qquad-\frac{p^2\,(\hbar^2\,k_z^2+s\,\hbar\,(2\,j+1))}{m^2}\,(\lambda-\Delta_q)\\ &\qquad-\frac{q^2\,(\hbar^2\,k_z^2+s\,\hbar\,(2\,j+1))}{m^2}\,(\lambda+\Delta_p)\Big\}\\ &-\frac{s^2\,\hbar^2}{m^2}\,(\lambda+\Delta_p)^3\,(\lambda-\Delta_q)\,\lambda-\frac{s^2\,\hbar^2}{m^2}\,(\lambda-\Delta_q)^3\,(\lambda+\Delta_p)\,\lambda\\ &+\frac{s^2\,\hbar^2}{m^2}\left\{\frac{p^2}{m}\,(\lambda+\Delta_p)+\frac{p^2\,\hbar^2\,k_z^2}{m^2}\right\}(\lambda-\Delta_q)^3\\ &+\frac{s^2\,\hbar^2}{m^2}\left\{\frac{q^2}{m}\,(\lambda-\Delta_q)+\frac{q^2\,\hbar^2\,k_z^2}{m^2}\right\}(\lambda+\Delta_p)^3\\ &+\frac{s^2\,\hbar^2}{m^2}\{\hbar^2\,k_z^2+s\,\hbar\,(2\,j+1)\}\,\frac{p^2}{m^2}\,(\lambda+\Delta_p)^2\,(\lambda-\Delta_q)\\ &+\frac{s^2\,\hbar^2}{m^2}\{\hbar^2\,k_z^2+s\,\hbar\,(2\,j+1)\}\,\frac{q^2}{m^2}\,(\lambda-\Delta_q)^2\,(\lambda+\Delta_p)\\ &+\frac{s^4\,\hbar^4}{m^2}\,\lambda\,(\lambda+\Delta_p)\,(\lambda-\Delta_q)\\ &-\frac{s^4\,\hbar^4}{m^4}\left\{\frac{p^2}{m}\,(\lambda+\Delta_p)+\frac{p^2\,\hbar^2\,k_z^2}{m^2}\right\}(\lambda-\Delta_q)\\ &-\frac{s^4\,\hbar^4}{m^4}\left\{\frac{q^2}{m}\,(\lambda-\Delta_q)+\frac{q^2\,\hbar^2\,k_z^2}{m^2}\right\}(\lambda+\Delta_p)=0\,.\end{aligned}\right\}\tag{4.3}$$

Putting again $\lambda = A + C\,s + B\,s^2$ where A satisfies the equation

$$\left.\begin{aligned} A\,(A+\Delta_p)\,(A-\Delta_q) - \frac{p^2\,(\hbar^2\,k_z^2 + s\,\hbar\,(2\,j+1))}{m^2}\,(A-\Delta_q) \\ - \frac{q^2\,(\hbar^2\,k_z^2 + s\,\hbar\,(2\,j+1))}{m^2}\,(A+\Delta_p) = 0 \end{aligned}\right\} \quad (4.4)$$

one finds that C for the conduction band is zero.

In the parabolic approximation

$$A = \frac{\hbar^2\,k_z^2 + s\,\hbar\,(2\,j+1)}{2\,\mu} \quad (4.5)$$

with $1/\mu = 1/m - 1/m^*$, $1/m^*$ being defined by (4.2).

For B we obtain by substituting $\lambda = A + B\,s^2$ in (4.3)

$$\left.\begin{aligned} B\left(k_z, j+\frac{1}{2}\right) = \frac{\hbar^2}{m^2}\Big[&(A+\Delta_p)^3\,(A-\Delta_q)\,A + (A-\Delta_q)^3\,(A+\Delta_p)\,A \\ &- \left\{\frac{p^2}{m}\,(A+\Delta_p) + \frac{p^2\,\hbar^2\,k_z^2}{m^2}\right\}(A-\Delta_q)^3 \\ &- \left\{\frac{q^2}{m}\,(A-\Delta_q) + \frac{q^2\,\hbar^2\,k_z^2}{m^2}\right\}(A+\Delta_p)^3 \\ &- \left\{\frac{p^2}{m^2}\,2\,\mu\,A\,(A+\Delta_p)^2\,(A-\Delta_q)\right\} \\ &- \left\{\frac{q^2}{m^2}\,2\,\mu\,A\,(A-\Delta_q)^2\,(A+\Delta_p)\right\}\Big]\,. \end{aligned}\right\} \quad (4.6)$$

$$(A+\Delta_p)^{-2}\,(A-\Delta_q)^{-2}\Big\{A\,(A+\Delta_p) + A\,(A-\Delta_q) + (A-\Delta_q)\,(A+\Delta_p) - \frac{2\,\mu\,A}{m^2}\,(p^2+q^2)\Big\}^{-1}.$$

The energy levels of the conduction band are finally

$$\left.\begin{aligned} E\left((k_z, j+\frac{1}{2}\right) = E_0(0) + \frac{\hbar^2\,k_z^2 + s\,\hbar\,(2\,j+1)}{2\,m^*} \\ - B\left(k_z, j+\frac{1}{2}\right)s^2\,, \quad j \geqslant 1\,. \end{aligned}\right\} \quad (4.7)$$

The secular equation for $j = 0$ leads to the zero point energy of the conduction band

$$E(k_z) = E_0(0) + \frac{\hbar^2\,k_z^2 + s\,\hbar}{2\,m^*} - B'(k_z)\,s \quad (4.8)$$

with

$$\left.\begin{aligned} B'(k_z) = \frac{\hbar}{m}\Big[&A'(A'+\Delta_p)^2(A'-\Delta_q) + A'(A'-\Delta_q)^2(A'+\Delta_p) \\ &- \frac{p^2}{m^2}(A'+\Delta_p)(A'-\Delta_q)\,2\mu A' \\ &- \frac{q^2}{m^2}(A'+\Delta_p)(A'-\Delta_q)\,2\mu A' \\ &- \frac{p^2}{m^2}\hbar^2 k_z^2 (A'-\Delta_q)^2 - \frac{q^2}{m^2}\hbar^2 k_z^2 (A'+\Delta_p)^2\Big]. \end{aligned}\right\} \tag{4.9}$$

$$(A'+\Delta_p)^{-1}(A'-\Delta_q)^{-1}\Big\{A'(A'+\Delta_p) + A'(A'-\Delta_q) + (A'+\Delta_p)(A'-\Delta_q) - \frac{2\mu A'}{m^2}(p^2+q^2)\Big\}^{-1}.$$

where

$$A' = \frac{\hbar^2 k_z^2 + s\hbar}{2\mu} \tag{4.10}$$

in the parabolic approximation.

For large j one gets again the familiar expression for the energy levels in the one band approximation.

5. Susceptibility

The energy levels E, as calculated in the two preceding sections, determine the free energy F[22]).

$$\left.\begin{aligned} F = N\zeta &- \frac{2eH}{ch^2} k_B T \sum_{j=0}^{\infty} \int_{-\infty}^{+\infty} dk_z \ln\left[1 + e^{[\zeta - E(k_z, j+(1/2))]/k_B T}\right] \\ &+ \frac{2eH}{ch^2} k_B T \int_{-\infty}^{+\infty} dk_z \ln\left[1 + e^{[\zeta - E(k_z, 0)]/k_B T}\right] \\ &- \frac{2eH}{ch^2} k_B T \int_{-\infty}^{+\infty} dk_z \ln\left[1 + e^{[\zeta - E(k_z)]/k_B T}\right]. \end{aligned}\right\} \tag{5.1}$$

N is the number of conduction electrons per unit volume.

ζ is the Fermi energy.

We calculate F up to second order in H, so that the magnetic field independent susceptibility is

$$\chi = -\frac{1}{H}\frac{\partial F}{\partial H}. \tag{5.2}$$

s-p model. By means of Euler's formula the sum in (5.1) can be transformed into

$$-\frac{2\,e\,H}{c\,h^2}\,k_B\,T\int_0^{\infty} dx\int_{-\infty}^{+\infty} dk_z \ln\left[1+e^{[\zeta-E(k_z,\varkappa)]/k_B T}\right] \tag{5.3a}$$

$$+\frac{e\,H}{12\,c\,h^2}\int_{-\infty}^{+\infty} dk_z\,\frac{\left\{\dfrac{dE(k_z,\varkappa)}{d\varkappa}\right\}_{\varkappa=0}}{1+e^{-[\zeta-E(k_z,0)]/k_B T}}\,. \tag{5.3b}$$

We evaluate first the double integral in (5.3a).

It is convenient to introduce new variables

$$y=\frac{\hbar^2 k^2}{2\,m^*\,k_B\,T}\,,\qquad z=\frac{s\,\hbar}{m^*\,k_B\,T}\,\varkappa\,. \tag{5.4}$$

With (3.18), (3.16) and (3.17) the double integral then becomes

$$\left.\begin{aligned}-\frac{2\,\pi}{h^3}\,(2\,m^*)^{3/2}\,(k_B\,T)^{5/2}\int_0^{\infty} y^{-1/2}\,dy\int_0^{\infty} dz\\ \times\ln\left[1+e^{[\tilde{\zeta}-y-z-R\,H^2 f(y,z)]}\right].\end{aligned}\right\} \tag{5.5}$$

Here $f(y, z)$ is

$$\frac{m}{2\,\mu}\,\frac{\tilde{\Delta}\,(y+z+\tilde{\Delta})+\tilde{\Delta}y-(y+z+\tilde{\Delta})\,(y+z)}{(y+z+\tilde{\Delta})^2\,(2\,y+2\,z+\tilde{\Delta})} \tag{5.6}$$

and

$$\tilde{\zeta}=\frac{\zeta}{k_B\,T}\,,\qquad \tilde{\Delta}=\frac{\mu\,\Delta}{m^*\,k_B\,T}\,,\qquad R=\frac{e^2\,\hbar^2\,\mu}{m^2\,c^2\,m^*\,k_B^2\,T^2}\,. \tag{5.7}$$

We develop (5.5) into a power series of H^2. For the susceptibility we need only the first order term, which is

$$\frac{2\,\pi}{h^3}\,(2\,m^*)^{3/2}\,(k_B\,T)^{5/2}\,R\,H^2\int_0^{\infty} y^{-1/2}\,dy\int_0^{\infty} dz\,\frac{f(y,z)}{1+e^{-[\tilde{\zeta}-y-z]}}\,. \tag{5.8}$$

Since we are only interested in the temperature independent susceptibility, (5.8) can be written as

$$\frac{2\,\pi}{h^3}\,(2\,m^*)^{3/2}\,(k_B\,T)^{5/2}\,R\,H^2\int_0^{\tilde{\zeta}} y^{-1/2}\,dy\int_0^{\tilde{\zeta}-y} dz\,f(y,z)\,. \tag{5.9}$$

From now on the integration is elementary, and will not be shown here. With (5.2) we find that the contribution to the susceptibility from (5.3a) is

$$\left.\begin{aligned}\chi_{a1} = &- |\chi_L|\, 24 \frac{\mu m^*}{m^2} \left(\frac{\mu \Delta}{m^* \zeta}\right)^{1/2} \\ &\times \left[\frac{1}{3}\left(\frac{m^* \zeta}{\mu \Delta}\right)^{3/2} \frac{1}{1 + \dfrac{m^* \zeta}{\mu \Delta}} - \left(\frac{m}{\mu} + \frac{1}{3}\right) \frac{1}{\sqrt{2}}\right. \\ &\times \operatorname{arc\,tan}\left(\frac{2\, m^* \zeta}{\mu \Delta}\right)^{1/2} + \left(\frac{m}{\mu} + \frac{5}{3}\right) \operatorname{arc\,tan}\left(\frac{m^* \zeta}{\mu \Delta}\right)^{1/2} \\ &\left. - \frac{4}{3}\left(\frac{m^* \zeta}{\mu \Delta}\right)^{1/2}\right]\end{aligned}\right\} \tag{5.10}$$

where

$$\chi_L = - \frac{(2\, m^*)^{3/2}\, e^2}{24\, \pi^2\, \hbar\, m^{*2}\, c^2}\, \zeta^{1/2}$$

is the Landau susceptibility with the effective mass m^*. The contribution from (5.3b) has been calculated in the same way, and is

$$\chi_{b1} = - |\chi_L| \,. \tag{5.11}$$

It can be shown, following a similar method of integration, that the contributions of the second and third term in (5.1) cancel, so that the total susceptibility is

$$\chi_1 = \chi_{a1} + \chi_{b1} \,. \tag{5.12}$$

If χ_{a1} is developed in a power series of ζ/Δ, the first two terms are

$$\left.\begin{aligned}\chi_{a1} = &\, |\chi_L|\, 8 \frac{\zeta}{\Delta} \frac{m^*}{m} \left(1 - \frac{m^*}{m}\right) \\ &+ |\chi_L| \frac{72}{5} \left(\frac{\zeta}{\Delta}\right)^2 \frac{m^*}{m} \left(\frac{m^*}{m} - 1\right) \left(\frac{13}{9} \frac{m^*}{m} - 1\right) + \ldots\end{aligned}\right\} \tag{5.13}$$

p-s-p model. To make the integration somewhat easier, we assume that $m = m^*$, which means $p^2/\Delta_p = q^2/\Delta_q$ (see (4.2)).

From (4.5) it then follows that $A = 0$, so that (4.6) becomes

$$\begin{aligned}B\left(k_z, j + \frac{1}{2}\right) = - \Big[&\frac{\hbar^2}{m^2} \left(\frac{p^2}{m} \Delta_p \Delta_q^3 + \frac{p^2}{m} \Delta_q^2 \Delta_p^2\right) \\ &+ \frac{p^2}{m^2} s\, \hbar\, \Delta_q \left(\Delta_p^2 - \Delta_q^2\right) (2\, j + 1)\Big] \,. \\ \Delta_p^{-2} \Delta_q^{-2} &\left\{\Delta_p \Delta_q + \frac{p^2 + q^2}{m^2} \left(\hbar^2 k_z^2 + s\, \hbar\, (2\, j + 1)\right)\right\}^{-1}\end{aligned} \tag{5.14}$$

and a corresponding expression for $B'(k_z)$.

Again the contributions to the susceptibility of the second and third term in (5.1) cancel, while (5.3b) gives

$$\chi_{b2} = - |\chi_L| \,. \tag{5.15}$$

Here, χ_L is the Landau susceptibility now containing the free electron mass m.

The integral (5.3a) can be written in the form (5.9), where $R f$ is now

$$\left.\begin{aligned}\frac{e^2 \hbar^2}{m^2 c^2 k_B T} \frac{p^2}{m} \frac{\Delta_p + \Delta_q}{\Delta_p^2 \Delta_q^2} \left\{\Delta_q + 2 k_B T \frac{\Delta_p - \Delta_q}{\Delta_p} z\right\} \\ \times \left\{1 + \frac{2 (p^2 + q^2) k_B T}{m \Delta_p \Delta_q} (y + z)\right\}^{-1}.\end{aligned}\right\} \tag{5.16}$$

After carrying out the integration we find for the total susceptibility of the s band $\chi_2 = \chi_{a\,2} + \chi_{b\,2}$, where

$$\left.\begin{aligned}\chi_{a\,2} = - |\chi_L| \, 24 \left\{1 - \frac{1}{(\Sigma \zeta)^{1/2}} \arctan (\Sigma \zeta)^{1/2}\right\} - |\chi_L| \, 32 \\ \times \frac{\Delta_p - \Delta_q}{\Sigma \Delta_p \Delta_q} \left\{- 1 + \frac{1}{3} \Sigma \zeta + \frac{1}{(\Sigma \zeta)^{1/2}} \arctan (\Sigma \zeta)^{1/2}\right\}.\end{aligned}\right\} \tag{5.17}$$

The symbol Σ has the meaning

$$\Sigma = \frac{2 (p^2 + q^2)}{m \Delta_p \Delta_q}. \tag{5.18}$$

Developing $\chi_{a\,2}$ into a power series of ζ, we get for the first two terms

$$\chi_{a\,2} = - |\chi_L| \, 8 \Sigma \zeta + |\chi_L| \frac{24}{5} (\Sigma \zeta)^2 - |\chi_L| \frac{32}{5} \frac{\Delta_p - \Delta_q}{\Sigma \Delta_p \Delta_q} (\Sigma \zeta)^2. \tag{5.19}$$

6. Discussion of results

In this section we give a numerical estimate of the above calculated susceptibilities. Further we discuss the tight binding and weak coupling limit respectively. And finally we compare our calculations more carefully with those of KJELDAAS and KOHN.

s-p model, numerical estimate. In section 3 we mentioned that this model should be representative of lithium. We now look to what extent this hypothesis is fulfilled. A reasonable value for the effective mass in lithium lies between 1.40 m and 1.80 m. The Fermi energy consequently varies from 3.37 eV to 2.62 eV. The energy gap Δ is not known and we assume it lies somewhere between 3 eV and 10 eV. With these values we

Table 1

The relative susceptibility $\chi_1/|\chi_L|$ as a function of the interband distance Δ for two values of the effective mass m^*

Δ in eV	$\chi_1/\lvert\chi_L\rvert$ $(m^*/m = 1.4)$	$\chi_1/\lvert\chi_L\rvert$ $(m^*/m = 1.8)$
3	−0.39	−0.09
3.5	−0.85	−0.82
4	−1.16	−1.28
5	−1.50	−1.86
7	−1.75	−2.26
9	−1.76	−2.39

have computed Table 1 for $\chi_1/|\chi_L|$. Here χ_1 is defined by (5.10). From Table 1 we see that the total suceptibility χ_1 in the case $m^* = 1.4$ m lies between $-0.39\,|\chi_L|$ and $-1.76\,|\chi_L|$. For $m^* = 1.8$ m it lies between $-0.09\,|\chi_L|$ and $-2.39\,|\chi_L|$.

Experimentally $\chi_{1\,exp} = (-0.7 \pm 0.75)\,|\chi_L|$. The best value for Δ which fits the experiment is therefore between 3 eV and 4 eV in the case $m^* = 1.4$ m as well as for $m^* = 1.8$ m. As the experimental value is not accurate, these results are not very conclusive.

Tight binding. To get a little more insight, we consider the tight binding limit. If m^* tends to infinity, the total susceptibility becomes

$$\chi_1 = \lim_{m^* \to \infty} |\chi_L|\, 8 \frac{\zeta}{\Delta} \frac{m^*}{m} \left(1 - \frac{m^*}{m}\right) = -N \frac{e^2 \hbar^2}{m c^2} \frac{1}{\Delta}. \tag{6.1}$$

Here N is the number of electrons per unit volume. Since in this limit $2\,p^2/m\,\Delta = 1$, the susceptibility can also be written

$$\chi_1 = -N \frac{e^2 \hbar^2}{m c^2} \frac{2\, p^z_{b\,b'}\, p^z_{b'\,b}}{\Delta_{b\,b'}\, \Delta_{b\,b'}} = -N \frac{2\,e}{m\,c^2} z_{b\,b'}\, z_{b'\,b}\,. \tag{6.2}$$

Here we have used the relation

$$-i\,\hbar\, p^z_{b\,b'} = m\,\Delta_{b\,b'}\, z_{b\,b'} \tag{6.3}$$

which follows from the commutative properties of p and z with the Hamilton function. $z_{b\,b'}$ is the matrix element of the z coordinate between the s band and the p band. The atomic diamagnetism is given by

$$\chi_{atomic} = -N \frac{e}{6\,m\,c^2} (r^2)_{b\,b} \tag{6.4}$$

which should be compared with (6.2). To give an idea we evaluate (6.2) and (6.4) for hydrogen like $2s$ and $2p$ wave functions with effective charge Z. This gives

$$\chi_1 = -N \frac{e}{6\,m\,c^2} \frac{18}{7} (r^2)_{b\,b} \tag{6.5}$$

where $(r^2)_{b\,b} = 42\,(a_0/Z)^2$. Here a_0 is the Bohr radius.

This is too large by a factor 18/7 compared to (6.4). Although the use of hydrogen wave functions may not be justified, this suggests that our model is not complete, and higher bands are likely to contribute to the susceptibility.

Weak coupling. In the weak coupling limit ($m^* \to m$) the free electron susceptibility is obtained correctly.

Comparison with the treatment of Kjeldaas and Kohn. The treatment of KJELDAAS and KOHN consists in the successive application of canonical transformations. Each of these gives rise to a further term in a power series expansion of the susceptibility as a function of ζ.

$$\chi = -|\chi_L|\,\{1 + \alpha\,\zeta + \beta\,\zeta^2 + \ldots\}\,.$$

KJELDAAS and KOHN evaluate α, which contains interband effects as well as corrections from the non parabolicity. Using the expansion (5.13) of our result (5.10) a comparison of the two treatments is possible in several respects.

a) First of all we shall examine the validity of the parabolic approximation, which we have made. For that purpose it is necessary to apply the Kjeldaas-Kohn treatment to the *s-p* model. Formula (3.9) of reference 13 evaluated for this restricted number of bands gives

$$\chi_1 = -\,|\chi_L|\left\{1 + 8\frac{\zeta}{\Delta}\frac{m^*}{m}\left(\frac{m^*}{m} - 1\right) - \frac{2}{3}\frac{\zeta}{\Delta}\left(\frac{m^*}{m} - 1\right)^2\right\} \tag{6.6}$$

where the effective mass m^* is defined in (3.11).

Comparing this formula with the first order term of our expansion (5.13) we see that there is an additive correction due to the non parabolicity. Since numerically, it amounts to 5 per cent at most, the parabolic approximation appears to be justified.

Table 2
The relative susceptibility up to the first order term in ζ

Δ in eV	$\chi_1/\lvert\chi_L\rvert$ $(m^*/m = 1.4)$	$\chi_1/\lvert\chi_L\rvert$ $(m^*/m = 1.8)$
3	−6.03	−11.06
9	−2.68	− 4.35

b) To see the importance of higher order terms in ζ we compare our full result (5.10) with the first order term in (5.13). Comparing values in Table II with those in Table I we find that higher terms give an considerable paramagnetic contribution to the susceptibility. This suggests that KJELDAAS' and KOHN's treatment is incomplete.

c) The influence of higher bands finally becomes evident by comparing our first order term (Table II) with the full KJELDAAS, KOHN result $\chi = -\,|\chi_L|\, c_0\, k_0^2 = +\,0.63\,|\chi_L|$ (with $m^*/m = 1.4$; see ref. [13]). The significant difference implies that higher bands play an active role.

p-s-p model. Here things are a little more complicated, because the deeper lying $2\,p$ band might contribute to the susceptibility. However we believe its contribution is small. To explain this we use the very general formulae for the susceptibility obtained by HEBBORN and SONDHEIMER[17]). The terms containing the factor $\partial f_0(E_m)/\partial E_m$ ($f_0(E_m)$ is the distribution function) are zero, because this p band is completely filled. The term containing the factor $\partial E_m/\partial k_2$ (E_m is the energy band) should be small because the p electrons are tightly bound. The only term we need to consider is

$$-\,2\frac{\hbar^2}{m}\int \sum_{n \neq m} \frac{1}{E_n - E_m}\left| k_1\, Y_{n\,m} - \int \frac{\partial u_n^*}{\partial x}\frac{\partial u_m}{\partial k_2}\, d\tau_0 \right|^2 d\boldsymbol{k}\,. \qquad \text{(see ref. 17)}$$

This term is zero in the weak coupling limit, and reduces to the atomic diamagnetism in the tight binding approximation. Since the atomic diamagnetism is small, and if we assume that interpolation is allowed, it follows that the contribution of the p band might indeed be small.

A numerical application of the formula (5.19) is not very conclusive because χ_2 depends on the ratio Δ_p/Δ_q. The experimental value of the susceptibility is $\chi_{exp} = (-0.27 \pm 0.40)\,|\chi_L|$. Since $\chi_{2b} = -|\chi_L|$ a paramagnetism is needed. For $\Delta_p = \Delta_q$ the correction to the Landau term has the wrong sign. It is again evident that higher order terms in ζ give appreciable contributions.

Since in this model we only considered the case $m^* = m$, the tight binding limit cannot be studied here.

It should be noted that also in this model in the weak coupling limit ($\Delta \to \infty$) the free electron susceptibility is obtained.

7. Conclusion

There exist now two approaches to the problem of the diamagnetism of Bloch electrons which have actually been applied to a simple metal, like lithium. The merits of the two methods are displayed in Table 3.

In each of the three comparisons the more complete model is listed to the left. Its susceptibility is in each case more paramagnetic. This is in agreement with the general trend that experimental values for the susceptibility are too paramagnetic if compared with trivial theories.

The main conclusion of this work is that interband effects give important contributions to the susceptibility. At present no numerically reliable theory has been developed. A straight forward extension of the Kjeldaas-Kohn treatment is cumbersome. On the other hand an improve-

Table 3

Comparison of our with KJELDAAS' and KOHN's treatment

Comparison of the models		Difference in ζ	Conclusion
Kjeldaas-Kohn model restricted to s-p bands	s-p model linear in ζ	small	parabolic approximation justified
Complete s-p model	s-p model linear in ζ	appreciable	higher terms in ζ important
Complete Kjeldaas-Kohn model	s-p model linear in ζ	appreciable	higher bands important

ment of our model seems hopeful in view of the following fact. The Luttinger-Kohn representation starts with bands containing free electrons. However p electrons behave so differently, that their energy spectrum is even inverted. Therefore a model for which the highest and lowest bands are s bands or d bands would be more satisfactory. In the case of lithium this is an s-p-s band model, while for sodium an s-p-s-p-d-s band model would serve.

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