

Zero-Field Susceptibility of Bloch Electrons*

G. H. WANNIER AND U. N. UPADHYAYA

University of Oregon, Eugene, Oregon

(Received 1 June 1964)

An expression for the zero-field magnetic susceptibility arising from electrons in a simple Bloch band is derived. Uncoupled field-dependent bands developed earlier are employed in the derivation. The expression thus obtained is amenable to very simple physical interpretation. Namely, it consists of three terms: the Landau-Peierls term, crystalline paramagnetism, and induced diamagnetism. Reduction of this result to parameters defined for field-free bands shows the equivalence of this result to those derived by earlier workers.

1. INTRODUCTION

THE zero-field magnetic susceptibility arising from electrons in Bloch bands has been computed repeatedly in the past.¹⁻⁶ There is little difficulty of principle in its calculation. What is required is an expression for the fermion partition function

$$\mathcal{F} = - (1/\beta) \sum_i \ln \{ 1 + \exp[-\beta(E_i - \eta)] \} \quad (1)$$

for the electrons under consideration. The expression must be in powers of H and good to square terms. The susceptibility χ then results from this expression by the operation

$$\chi = \lim_{H \rightarrow 0} - (1/\Omega) (\partial^2 \mathcal{F} / \partial H^2). \quad (2)$$

The definition of χ thus seems to presuppose that \mathcal{F} can be expanded in powers of H . In a strict sense this is almost certainly not true. But expansion is usually possible in a formal or asymptotic sense if some side effects are neglected. The resulting expression for χ is then likely to have approximate validity.

Thus, computation of (2) looks like a fairly straightforward job involving second-order perturbation theory. The reason why the problem nevertheless still retains the attention of physicists is that this apparently simple computation leads to an extremely long and involved result. To complicate matters still further, this result can be put in many apparently different, but actually equivalent, forms.

In the following we approach this old problem with the help of a new formalism. Wannier and Fredkin^{7,8} have shown that the action of the magnetic field upon a band can be resolved into two effects. One effect gradually transforms the parameters (wave functions,

energies, etc.) of that band. The other effect consists in the breaking up of the band into a series of discrete states. References 7 and 8 show that the second effect is described fully by the formalism first postulated by Onsager,⁹ provided the first effect is not ignored. The bands thereby become renormalized or field-dependent. We believe that these renormalized bands provide a great computational advantage in many problems, and we are recomputing the magnetic susceptibility to show up the resultant simplifications in this particular instance.

The core of the new derivation occupies Sec. 2, and the result at the end of that section is actually terminal from the point of view of the new formalism. The susceptibility arising from electrons in a band consists of just three terms if the band is simple and the electrons may be assumed spinless. The terms refer to conceptually very simple quantities characteristic of the band. In Sec. 3 the result is analyzed. The physical significance and structure of the three terms is worked out. They are given in tensorial form and in terms of quantities defined for the field-free band. Calculations incidental to this task are omitted; they are available elsewhere.¹⁰

An Appendix is added which shows the equivalence of our result with that of Hebborn and Sondheimer.³

2. DERIVATION OF THE SUSCEPTIBILITY

The starting point of the derivation is preferably Eq. (14) Ref. 7, or Eq. (53), Ref. 8, which reads

$$\mathcal{H} A_q(\mathbf{x}; \boldsymbol{\rho}) = \sum_{\boldsymbol{\rho}'} \exp[\frac{1}{2} i \mathbf{H} \cdot \boldsymbol{\rho} \times \boldsymbol{\rho}'] w_q(\boldsymbol{\rho} - \boldsymbol{\rho}') A_q(\mathbf{x}; \boldsymbol{\rho}'). \quad (3)$$

\mathcal{H} is a one-electron Hamiltonian containing a magnetic field; $A_q(\mathbf{x}; \boldsymbol{\rho})$ are Wannier functions associated with the band q , modified by a Peierls phase factor; $w_q(\boldsymbol{\rho})$ is the $\boldsymbol{\rho}$ th Fourier component of the energy-band function $W_q(\mathbf{k})$. Both w_q and A_q are field-dependent over and beyond the Peierls phase factor. The reason is that these quantities have undergone renormalization

* This work was supported by the U. S. Office of Naval Research.

¹ R. Peierls, *Z. Physik* **80**, 763 (1933).

² E. N. Adams, *Phys. Rev.* **89**, 633 (1953).

³ J. E. Hebborn and E. H. Sondheimer, *Phys. Chem. Solids* **13**, 105 (1960). Hereafter referred to as HS.

⁴ C. P. Enz, *Helv. Phys. Acta* **33**, 89 (1960).

⁵ L. M. Roth, *Phys. Chem. Solids* **23**, 433 (1962).

⁶ E. I. Blount, *Phys. Rev.* **126**, 1636 (1962).

⁷ G. H. Wannier and D. R. Fredkin, *Phys. Rev.* **125**, 1910 (1962). In the following quoted as I. Equation (15) of that paper is quoted as (I,15).

⁸ G. H. Wannier, *Rev. Mod. Phys.* **34**, 645 (1962).

⁹ L. Onsager, *Phil. Mag.* **43**, 1006 (1952).

¹⁰ G. H. Wannier and U. N. Upadhyaya, Contract NONR 2771(05) Technical Report No. 3 (unpublished). Copies of the report are available at the Physics Department, University of Oregon, Eugene, Oregon.

as functions of the field so as to make the Hamiltonian free of coupling terms. Finally, there is in Eq. (3) the exponential factor containing the field. Although the exponent of this term is extremely small (of the order 10^{-5}), it produces the change in the energy spectrum from the band type to the level type. Without it, the matrix problem (3) would be cyclic; with it, the problem is of the Onsager type. We can see this easily by some slight reasoning on (3). First, change the summation index

$$\mathfrak{H}A_q(\mathbf{x}; \boldsymbol{\varrho}) = \sum_{\boldsymbol{\varrho}' } w_q(\boldsymbol{\varrho}') \exp[-\frac{1}{2}i\mathbf{H} \cdot \boldsymbol{\varrho} \times \boldsymbol{\varrho}'] A_q(\mathbf{x}; \boldsymbol{\varrho} - \boldsymbol{\varrho}').$$

The argument of A_q on the right now appears as a shift expressible by a symbolic exponential of exponent $-\boldsymbol{\varrho}' \cdot \partial / \partial \boldsymbol{\varrho}$. This exponent commutes with the exponent already present so that the exponentials can be simply united. This yields

$$\mathfrak{H}A_q(\mathbf{x}; \boldsymbol{\varrho}) = \sum_{\boldsymbol{\varrho}' } w_q(\boldsymbol{\varrho}') \exp\left[i\left(\frac{\partial}{\partial \boldsymbol{\varrho}} - \frac{1}{2}\mathbf{H} \times \boldsymbol{\varrho}\right) \cdot \boldsymbol{\varrho}'\right] A_q(\mathbf{x}; \boldsymbol{\varrho}'). \quad (4)$$

The expression in the square bracket is an operator function of the vector operator \mathbf{K} represented by the round bracket. This vector obeys the commutation rule (I,19) with reversed sign. This sign reversal simply arises because we operate here on the wave functions themselves, while (I,19) refers to operation on a supposed multiplier function.

Calculation of the magnetic susceptibility is a statistical problem which involves the computation of traces of powers and more complicated functions of the Hamiltonian. For this purpose, linear independence of the functions $A_q(\mathbf{x}; \boldsymbol{\varrho})$ is essential. It is a not an entirely trivial requirement. Functions like $A_q(\mathbf{x}; \boldsymbol{\varrho})$ can be constructed using the states belonging to a single energy level only; if this is done, a one-dimensionally infinite set results with the remainder being linear functions of that set. To have the functions $A_q(\mathbf{x}; \boldsymbol{\varrho})$ linearly independent, they must be formed from a *full* band. *A priori* construction of such a band at finite field is still somewhat of a problem. Fortunately, the present task is one which must be handled in powers of the field anyway and in this context a full band poses no difficulties.

To evaluate our traces, we use the inversion of the Fourier series (I,7) for $W_q(\mathbf{k})$, writing the integral in the discrete notation for convenience

$$w_q(\boldsymbol{\varrho}) = (1/N) \sum_{\mathbf{k}} W_q(\mathbf{k}) \exp(-i\mathbf{k} \cdot \boldsymbol{\varrho}). \quad (5)$$

Here N is the number of primitive cells in the Born-von

Karman volume, and the summation over \mathbf{k} goes over N equidistant points in the first Brillouin zone. We then get immediately from (3)

$$\begin{aligned} \text{Tr}(\mathfrak{H}\mathcal{C}) &= \sum_{\rho} \text{coefficient of } A_q(\mathbf{x}; \boldsymbol{\varrho}) \text{ on the right of (3)} \\ &= \sum_{\rho} w_q(0) = Nw_q(0) \end{aligned}$$

or with (5)

$$\text{Tr}(\mathfrak{H}\mathcal{C}) = \sum_{\mathbf{k}} W_q(\mathbf{k}). \quad (6)$$

Now we iterate (3) once and get

$$\begin{aligned} \mathfrak{H}^2 A_q(\mathbf{x}; \boldsymbol{\varrho}) &= \sum_{\boldsymbol{\varrho}', \boldsymbol{\varrho}''} \exp[\frac{1}{2}i\mathbf{H} \cdot (\boldsymbol{\varrho} \times \boldsymbol{\varrho}' + \boldsymbol{\varrho}' \times \boldsymbol{\varrho}'')] \\ &\quad \times w_q(\boldsymbol{\varrho} - \boldsymbol{\varrho}') w_q(\boldsymbol{\varrho}' - \boldsymbol{\varrho}'') A_q(\mathbf{x}; \boldsymbol{\varrho}''). \end{aligned} \quad (7)$$

Again, we get the trace of \mathfrak{H}^2 by collecting coefficients of $A_q(\mathbf{x}; \boldsymbol{\varrho})$ on the right. This yields

$$\begin{aligned} \text{Tr}(\mathfrak{H}^2 \mathcal{C}) &= \sum_{\rho, \rho'} w_q(\boldsymbol{\varrho} - \boldsymbol{\varrho}') w_q(\boldsymbol{\varrho}' - \boldsymbol{\varrho}) = N \sum_{\rho} w_q(\boldsymbol{\varrho}) w_q(-\boldsymbol{\varrho}) \\ &= \frac{1}{N} \sum_{\rho, \mathbf{k}, \mathbf{k}'} \exp[i(\mathbf{k} - \mathbf{k}') \cdot \boldsymbol{\varrho}] W_q(\mathbf{k}) W_q(\mathbf{k}'). \end{aligned}$$

Finally, because the summation over $\boldsymbol{\varrho}$ yields $N\delta_{\mathbf{k}, \mathbf{k}'}$, we get

$$\text{Tr}(\mathfrak{H}^2 \mathcal{C}) = \sum_{\mathbf{k}} [W_q(\mathbf{k})]^2. \quad (8)$$

The first nontrivial calculation arises for the trace of \mathfrak{H}^3 . Proceeding as previously, we get

$$\begin{aligned} \text{Tr}(\mathfrak{H}^3 \mathcal{C}) &= \sum_{\rho, \rho', \rho''} \exp[\frac{1}{2}i\mathbf{H} \cdot (\boldsymbol{\varrho} \times \boldsymbol{\varrho}' + \boldsymbol{\varrho}' \times \boldsymbol{\varrho}'' + \boldsymbol{\varrho}'' \times \boldsymbol{\varrho})] \\ &\quad \times w_q(\boldsymbol{\varrho} - \boldsymbol{\varrho}') w_q(\boldsymbol{\varrho}' - \boldsymbol{\varrho}'') w_q(\boldsymbol{\varrho}'' - \boldsymbol{\varrho}). \end{aligned}$$

We simplify the expression by the substitutions

$$\begin{aligned} \boldsymbol{\varrho}' &= \mathbf{r}' + \boldsymbol{\varrho}, \\ \boldsymbol{\varrho}'' &= \mathbf{r}'' + \boldsymbol{\varrho}. \end{aligned}$$

This transformation makes $\boldsymbol{\varrho}$ drop out of the equation and yields

$$\begin{aligned} \text{Tr}(\mathfrak{H}^3 \mathcal{C}) &= N \sum_{\mathbf{r}', \mathbf{r}''} \exp[\frac{1}{2}i\mathbf{H} \cdot \mathbf{r}' \times \mathbf{r}''] \\ &\quad \times w_q(-\mathbf{r}') w_q(\mathbf{r}' - \mathbf{r}'') w_q(\mathbf{r}''). \end{aligned}$$

Complete evaluation of this expression is not needed in this context. We want the result only to square terms in H . Using (5) at the same time, we write the expression in the form

$$\begin{aligned} \text{Tr}(\mathfrak{H}^3 \mathcal{C}) &= (1/N^2) \sum_{\mathbf{k}, \mathbf{k}', \mathbf{k}''} \sum_{\mathbf{r}', \mathbf{r}''} [1 + \frac{1}{2}iH(r_x' r_y'' - r_y' r_x'') - \frac{1}{8}H^2(r_x' r_y'' - r_y' r_x'')^2 + O(H^3)] \\ &\quad \times e^{i[\mathbf{r}' \cdot (\mathbf{k} - \mathbf{k}') + \mathbf{r}'' \cdot (\mathbf{k}' - \mathbf{k}'')]} W_q(\mathbf{k}) W_q(\mathbf{k}') W_q(\mathbf{k}''). \end{aligned}$$

Here H is taken to be along the z axis of a rectangular x, y, z coordinate system. The next step is to interpret the multipliers \mathbf{r}' and \mathbf{r}'' as derivatives of the exponential with respect to \mathbf{k} and \mathbf{k}'' and to integrate by parts on those two variables. The integrated-out parts vanish because all terms are periodic in reciprocal space. We get, therefore,

$$\begin{aligned} \text{Tr}(\mathcal{H}\mathcal{C}^3) &= \frac{1}{N^2} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{k}''} \sum_{\mathbf{r}', \mathbf{r}''} \exp i[\mathbf{r}' \cdot (\mathbf{k} - \mathbf{k}') + \mathbf{r}'' \cdot (\mathbf{k}' - \mathbf{k}'')] \\ &\times \left[1 + \frac{1}{2} iH \left(\frac{\partial^2}{\partial k_x \partial k_y} - \frac{\partial^2}{\partial k_y \partial k_x} \right) - \frac{1}{8} H^2 \left(\frac{\partial^4}{\partial k_x^2 \partial k_y'^2} + \frac{\partial^4}{\partial k_x''^2 \partial k_y^2} - 2 \frac{\partial^4}{\partial k_x \partial k_y \partial k_x'' \partial k_y''} \right) \right] W_i(\mathbf{k}) W_q(\mathbf{k}') W_q(\mathbf{k}''). \end{aligned}$$

Summation over \mathbf{r}' and \mathbf{r}'' is now possible and yields $N^2 \delta_{\mathbf{k}, \mathbf{k}'} \delta_{\mathbf{k}', \mathbf{k}''}$. Thus all \mathbf{k} vectors come out to be equal. This result also annuls the linear term in H which contains now a cross product of a vector with itself. We are left with the constant and quadratic term which equal

$$\text{Tr}(\mathcal{H}\mathcal{C}^3) = \sum_{\mathbf{k}} [W_q(\mathbf{k})]^3 - \frac{1}{4} H^2 \sum_{\mathbf{k}} W_q(\mathbf{k}) \left[\frac{\partial^2 W_q}{\partial k_x^2} \frac{\partial^2 W_q}{\partial k_y^2} - \left(\frac{\partial^2 W_q}{\partial k_x \partial k_y} \right)^2 \right] + O(H^3). \quad (9)$$

The trace of $\mathcal{H}\mathcal{C}^3$ is typical of the general case. Employing essentially the same procedure, we find for the trace of the n 'th power

$$\text{Tr}(\mathcal{H}\mathcal{C}^n) = \sum_{\mathbf{k}} [W(\mathbf{k})]^n - \frac{1}{24} n(n-1) H^2 \sum_{\mathbf{k}} [W(\mathbf{k})]^{n-2} \left[\frac{\partial^2 W}{\partial k_x^2} \frac{\partial^2 W}{\partial k_y^2} - \left(\frac{\partial^2 W}{\partial k_x \partial k_y} \right)^2 \right] + O(H^3). \quad (10)$$

Having found the trace of any power of $\mathcal{H}\mathcal{C}$, we can find the trace of any function of $\mathcal{H}\mathcal{C}$ by McLaurin's theorem

$$\text{Tr}[F(\mathcal{H}\mathcal{C})] = \sum_{n=0}^{\infty} \frac{1}{n!} -F^{(n)}(0) \text{Tr}(\mathcal{H}\mathcal{C}^n);$$

and thus with (10)

$$\text{Tr}[F(\mathcal{H}\mathcal{C})] = \sum_{\mathbf{k}} F[W(\mathbf{k})] - \frac{1}{24} H^2 \sum_{\mathbf{k}} \frac{d^2 F[W(\mathbf{k})]}{dW^2} \left[\frac{\partial^2 W}{\partial k_x^2} \frac{\partial^2 W}{\partial k_y^2} - \left(\frac{\partial^2 W}{\partial k_x \partial k_y} \right)^2 \right] + O(H^3). \quad (11)$$

Since the calculation given here is purely orbital, we must add an extra factor 2 for spin when applying (11) to (1). We find then

$$F = - (2/\beta) \sum_{\mathbf{k}} \ln(1 + e^{-\beta(W-\eta)}) - \frac{1}{12} H^2 \sum_{\mathbf{k}} \frac{df(W-\eta)}{dW} \left[\frac{\partial^2 W}{\partial k_x^2} \frac{\partial^2 W}{\partial k_y^2} - \left(\frac{\partial^2 W}{\partial k_x \partial k_y} \right)^2 \right] + O(H^3), \quad (12)$$

where $f(E)$ is the Fermi distribution function

$$f(E) = 1/(e^{\beta E} + 1). \quad (13)$$

To get the susceptibility, we must isolate the term in (12) which is quadratic in H , treating η as constant. This is immediately done for the second term which has an explicit factor H^2 . In that term we simply replace the field dependent W by its field-independent limit. In the first term, on the other hand, we must insert

$$W(\mathbf{k}) = W^{(0)}(\mathbf{k}) + HW^{(1)}(\mathbf{k}) + H^2 W^{(2)}(\mathbf{k}) \quad (14)$$

and expand in powers of H . We find

$$\begin{aligned} F &= - (2/\beta) \sum_{\mathbf{k}} \ln[1 + \exp -\beta(W^{(0)}(\mathbf{k}) - \eta)] + 2H \sum_{\mathbf{k}} W^{(1)}(\mathbf{k}) f(W^{(0)} - \eta) \\ &+ 2H^2 \sum_{\mathbf{k}} W^{(2)}(\mathbf{k}) f(W^{(0)} - \eta) + \frac{1}{2} [W^{(1)}(\mathbf{k})]^2 \frac{df(W^{(0)} - \eta)}{dW^{(0)}} - \frac{1}{24} \left[\frac{\partial^2 W^{(0)}}{\partial k_x^2} \frac{\partial^2 W^{(0)}}{\partial k_y^2} - \left(\frac{\partial^2 W^{(0)}}{\partial k_x \partial k_y} \right)^2 \right] \frac{df(W^{(0)} - \eta)}{dW^{(0)}}. \end{aligned} \quad (15)$$

Finally, Eq. (2) yields for the susceptibility

$$\chi = -\frac{4}{\Omega} \sum_{\mathbf{k}} \left[W^{(2)}(\mathbf{k}) f + \frac{1}{2} (W^{(1)})^2 \frac{df}{dW^{(0)}} - \frac{1}{24} \left\{ \frac{\partial^2 W^{(0)}}{\partial k_x^2} \frac{\partial^2 W^{(0)}}{\partial k_y^2} - \left(\frac{\partial^2 W^{(0)}}{\partial k_x \partial k_y} \right)^2 \right\} \frac{df}{dW^{(0)}} \right] \quad (16a)$$

or, in the form of an integral over the first Brillouin zone, and with dimensions restored,

$$\chi = -\frac{1}{2\pi^3} \int d\mathbf{k} \left[W^{(2)}(\mathbf{k}) f(W^{(0)} - \eta) + \frac{1}{2} (W^{(1)}(\mathbf{k}))^2 \frac{df(W^{(0)} - \eta)}{dW^{(0)}} - \frac{1}{24} \frac{e^2}{\hbar^2 c^2} \left\{ \frac{\partial^2 W^{(0)}}{\partial k_x^2} \frac{\partial^2 W^{(0)}}{\partial k_y^2} - \left(\frac{\partial^2 W^{(0)}}{\partial k_x \partial k_y} \right)^2 \right\} \frac{df(W^{(0)} - \eta)}{dW^{(0)}} \right]. \quad (16b)$$

Formula (16) has already been published as Eq. (101) of Ref. 5. The derivation given there is, however, very much more involved than the one presented here.

3. DISCUSSION

It is our belief that the three terms in Eq. (16) represent physically distinguishable contributions to the susceptibility. This belief is supported by the fact, proved in Ref. 10, that all three terms are separately gauge invariant. A proof is also found there that the third term and the sum of the first two terms are independent of the phase employed for the unperturbed Bloch functions. This seems to speak against the idea that the first two terms have separate physical meaning. However, we feel that a result need not be phase independent to be physically meaningful. The work of Gibson¹¹ and Kohn¹² has shown that there is a *natural phase* for Bloch functions. In this phase, the corresponding Wannier function is exponentially convergent in space, and the lattice vector operator¹³ is most closely related to true position. We shall work with this natural phase in later parts of this paper.

Among the three terms the third is the most easily understood. It represents the so-called Landau-Peierls diamagnetism. The Landau-Peierls susceptibility reads, with the dimensions restored,

$$\chi_{\text{L.P.}} = \frac{1}{48\pi^3} \frac{e^2}{\hbar^2 c^2} \int d\mathbf{k} \left[\frac{\partial^2 W^0}{\partial k_x^2} \frac{\partial^2 W^0}{\partial k_y^2} - \left(\frac{\partial^2 W^0}{\partial k_x \partial k_y} \right)^2 \right] \frac{df(W^0 - \eta)}{dW^0} \quad (17)$$

or, in tensor form,

$$\chi_{\text{L.P.}}^{\nu\mu} = \frac{1}{96\pi^3} \frac{e^2}{\hbar^2 c^2} \int d\mathbf{k} \frac{\epsilon_{\nu\alpha\beta} \epsilon_{\mu\sigma\tau}}{\partial k_\alpha \partial k_\sigma \partial k_\beta \partial k_\tau} \frac{\partial^2 W^0}{\partial k_\alpha \partial k_\sigma} \frac{\partial^2 W^0}{\partial k_\beta \partial k_\tau} \frac{df(W^0 - \eta)}{dW^0}, \quad (18)$$

where $\epsilon_{\nu\alpha\beta}$ is the totally antisymmetric unit tensor. The Landau-Peierls susceptibility is a gauge- and phase-invariant contribution. It is the only term present if the electrons are free. Our computation clearly separates it from all other terms in the susceptibility as arising from the breakup of the band continuum into discrete states. We must therefore anticipate that the De Haas-van Alphen effect will primarily arise because the derivation of Sec. 2 has to be modified for finite magnetic field. It is quite likely that such a

modification will make little or no difference in the first two terms of Eq. (16).

The second term in (16) is always positive and associated with the square of $W^{(1)}(\mathbf{k})$. It is seen from (14) that $W^{(1)}$ enters into the energy like a magnetic moment. The term in (16) which it gives rise to is the paramagnetic susceptibility due to that moment; indeed it has the usual paramagnetic form $N\mu^2/kT$. It may at first sight seem strange that the present calculation gives rise to any paramagnetism at all since we assumed neither orbital nor spin degeneracy. However, closer examination shows that there is another cause for paramagnetism, which is often overlooked, namely a crystalline medium with an intrinsic "handedness." The paramagnetic term in (16) arises from this handedness. We shall show this by proving that $W^{(1)}$ vanishes in a crystal having inversion symmetry. We shall also make it plausible that this "crystalline paramagnetism" is a physically identifiable phenomenon by proving that $W^{(1)}(\mathbf{k})$ is real and odd in \mathbf{k} , as one would expect from its interpretation as a magnetic moment. These features are not entirely trivial; for $W^{(1)}(\mathbf{k})$ is after all, not directly a physical entity, but only an intermediary in operational calculations.

In terms of quantities defined for the field-free band, $W^{(1)}$ turns out to be¹⁰

$$W_q^{(1)}(\mathbf{k}) = \frac{1}{2} \langle q | \left(p_x + \frac{\partial W_q^{(0)}}{\partial k_x} \right) Y - \left(p_y + \frac{\partial W_q^{(0)}}{\partial k_y} \right) X | q \rangle. \quad (19)$$

Here, q is the band index, X and Y the Adams operators.^{14,15} Their definition is given in Eq. (29) below. Equation (14) shows $W_q^{(1)}$ to be the co-factor of H in an invariant. It is therefore an axial vector and can be expressed in tensor form. Its components W^ν are

$$W^\nu = \frac{e}{2mc} \epsilon_{\nu\alpha\beta} \langle q | \left(p_\alpha + \frac{m}{\hbar} \frac{\partial W_q^{(0)}}{\partial k_\alpha} \right) X_\beta | q \rangle. \quad (20)$$

Similarly, the contribution of the crystalline paramagnetism to the susceptibility can be written in tensorial form. We find

$$\chi_{\text{cp}}^{\nu\mu} = -\frac{1}{16\pi^3} \frac{e^2}{m^2 c^2} \int d\mathbf{k} \frac{\epsilon_{\nu\alpha\beta} \epsilon_{\mu\sigma\tau}}{\partial k_\alpha \partial k_\sigma \partial k_\beta \partial k_\tau} \langle q | \left(p_\alpha + \frac{m}{\hbar} \frac{\partial W_q^{(0)}}{\partial k_\alpha} \right) X_\beta | q \rangle \times \langle q | \left(p_\sigma + \frac{m}{\hbar} \frac{\partial W_q^{(0)}}{\partial k_\sigma} \right) X_\tau | q \rangle \frac{df(W_q^{(0)} - \eta)}{dW_q^{(0)}}. \quad (21)$$

¹¹ J. B. Gibson, Bull. Am. Phys. Soc. **3**, 146 (1958).

¹² W. Kohn, Phys. Rev. **115**, 809 (1959).

¹³ G. H. Wannier, Phys. Rev. **117**, 432 (1960).

¹⁴ E. N. Adams, J. Chem. Phys. **21**, 2013 (1953).

¹⁵ J. N. Luttinger, Phys. Rev. **95**, 1154 (1954).

Further analysis of $W_q^{(1)}$ brings in the point discussed earlier, namely, that there exists a "natural" phase for Bloch functions. We are discussing here a simple band with a spinless electron. In such a band, the states \mathbf{k} and $-\mathbf{k}$ are linked by time reversal, and have among other things equal energy $W_q^{(0)}$. This symmetry can be obscured artificially by the introduction of a \mathbf{k} -dependent phase factor for the wave function. Physically incomprehensible results for $W_q^{(1)}$ could thereby be obtained. In the following we do not allow such phase factors. The wave functions of \mathbf{k} and $-\mathbf{k}$ are then linked by the identity

$$b_s^{0*}(\mathbf{x}; \mathbf{k}) = b_s^0(\mathbf{x}; -\mathbf{k}). \quad (22)$$

If we apply this to the definition (29) of the Adams operators, we get

$$\langle s, -\mathbf{k} | X | q, -\mathbf{k} \rangle = \langle q, \mathbf{k} | X | s, \mathbf{k} \rangle, \quad (23a)$$

which implies, in particular, that

$$X_q(-\mathbf{k}) = X_q(\mathbf{k}), \quad (23b)$$

where we set

$$\langle q | X | q \rangle = X_q. \quad (23c)$$

Reduction of (19) to matrix elements of the Adams operator is possible by reduction of the operator \mathbf{p} . The appropriate relation is obtained by differentiating the Schrödinger equation just once with respect to \mathbf{k} . It yields

$$(\mathcal{E} - W_q^0) \mathbf{X} b_q^0 = -i[\mathbf{p} - (\partial W_q^0 / \partial \mathbf{k})] b_q^0 \quad (24a)$$

and hence

$$\langle s | \mathbf{p} - (\partial W_q^0 / \partial \mathbf{k}) | q \rangle = i(W_s^0 - W_q^0) \langle s | \mathbf{X} | q \rangle. \quad (24b)$$

Application of (24) to (19) yields

$$W_q^{(1)}(\mathbf{k}) = (\partial W_q^0 / \partial k_x) Y_q - (\partial W_q^0 / \partial k_y) X_q - i \sum_s (W_s^0 - W_q^0) \{ \langle q | X | s \rangle \langle s | Y | q \rangle - \langle q | Y | s \rangle \langle s | X | q \rangle \}. \quad (25)$$

It is now relatively easy to reason on $W^{(1)}$. First, we have

$$W_q^{(1)}(\mathbf{k}) = W_q^{(1)}(\mathbf{k})^* = \text{real}. \quad (26)$$

This is true because all three terms in (25) are real; for the third, it follows from the fact that the curly bracket is purely imaginary. Second, we see from (25) that

$$W_q^{(1)}(-\mathbf{k}) = -W_q^{(1)}(\mathbf{k}). \quad (27)$$

Again it is true because it applies to each of the three terms in (25). In the first two terms the expectation values of the Adams operators are even by (23b), and the derivatives of the energy are odd. In the third term the energies are even, and the curly bracket, by (23a), is odd.

It is not, in general, the purpose of this paper to examine the susceptibility in crystals of various types of symmetry. However, a very much better understand-

ing of $W_q^{(1)}$ results if we realize that

$$W_q^{(1)} = 0 \text{ in a crystal with inversion symmetry.} \quad (28)$$

This is again most easily checked with the help of Eq. (25). If a crystal has inversion symmetry, the wave function (22) can be realized in still a third way, namely, by taking the wave function of negative argument. Since the square of this operation is the identity we must have

$$b_s^0(-\mathbf{x}; \mathbf{k}) = \pm b_s^0(\mathbf{x}; -\mathbf{k}). \quad (22a)$$

The sign of this relation cannot be generally determined; it depends on whether the totally periodic function $b_s^0(\mathbf{x}, \mathbf{0})$ is even or odd with respect to the inversion center. From continuity reasons it follows then that the sign is characteristic for the entire band of band index s . Now let us investigate first the behavior of the diagonal elements X_q under inversion. By definition we have

$$X_q = i \int u_q^*(\mathbf{x}; \mathbf{k}) \frac{\partial u_q(\mathbf{x}; \mathbf{k})}{\partial k_x} d\tau. \quad (29)$$

If we apply inversion to the variables of integration in this expression, then by (29) and (22) each function is replaced by the conjugate complex times ± 1 . It follows that the factor for the integral as a whole is $+1$:

$$X_q = i \int u_q(\mathbf{x}, \mathbf{k}) \frac{\partial u_q^*(\mathbf{x}; \mathbf{k})}{\partial k_x} d\tau,$$

or, with an integration by parts

$$X_q = -i \int u_q^*(\mathbf{x}; \mathbf{k}) \frac{\partial u_q(\mathbf{x}; \mathbf{k})}{\partial k_x} d\tau,$$

which means that

$$\mathbf{X}_q = 0. \quad (30a)$$

If the same reasoning is applied to off-diagonal elements of the Adams operator we get

$$\langle s | \mathbf{X} | q \rangle = \mp \langle q | \mathbf{X} | s \rangle, \quad (30b)$$

with the sign typical of the index pair q, s . From this it follows that

$$\langle q | X | s \rangle \langle s | Y | q \rangle - \langle q | Y | s \rangle \langle s | X | q \rangle = 0. \quad (30c)$$

The identities (30) render the expression (25) equal to zero.

The first term in (16) deals with the induced moment for the electron system, that is, diamagnetism in the sense of classical physics. The term contains the Fermi distribution function rather than its derivative; in other words, all electrons, not only those at the surface of the Fermi sea, acquire an induced moment. We know from the case of atoms that this moment is opposed to the field. When we pass to the case of a

band we find this contribution lost in a number of other terms whose sign cannot generally be predicted.

$W_q^{(2)}$ can be given a variety of equivalent forms when expressed in terms of parameters of the field-free band. The shortest form reads

$$\begin{aligned}
W_q^{(2)} = & - \sum_{s \neq q} \frac{1}{W_s^0 - W_q^0} \left| \langle s | p_x Y - \frac{\partial W_q^0}{\partial k_y} X | q \rangle \right|^2 - \frac{1}{2} \frac{\partial}{\partial k_y} \langle q | X p_x Y + Y p_x X | q \rangle + \frac{\partial W_q^0}{\partial k_y} \frac{\partial}{\partial k_y} \langle q | X^2 | q \rangle \\
& + \frac{1}{2} \langle q | Y^2 | q \rangle + \frac{1}{2} \frac{\partial^2 W_q^0}{\partial k_y^2} \langle q | X^2 | q \rangle + \frac{1}{8} \frac{\partial^4 W_q^0}{\partial k_x^2 \partial k_y^2} + W_q^{(1)} \frac{\partial X_q}{\partial k_y} + \frac{1}{4} \frac{\partial W_q^0}{\partial k_x} \frac{\partial}{\partial k_y} \langle q | XY + YX | q \rangle \\
& - \frac{1}{4} \frac{\partial W_q^0}{\partial k_y} \frac{\partial}{\partial k_x} \langle q | XY + YX | q \rangle. \quad (31)
\end{aligned}$$

This form is most directly related to the Landau gauge, but can also be derived from the symmetric gauge, if desired.¹⁰ The shortest form which is obviously real and symmetric in x and y reads

$$\begin{aligned}
W_q^{(2)} = & - \frac{1}{4} \sum_{s \neq q} \frac{1}{W_s^0 - W_q^0} \left| \langle s | \left(p_x + \frac{\partial W_q^0}{\partial k_x} \right) Y - \left(p_y + \frac{\partial W_q^0}{\partial k_y} \right) X | q \rangle \right|^2 + \frac{1}{4} \frac{\partial}{\partial k_y} \langle q | X \left(p_y + \frac{\partial W_q^0}{\partial k_y} \right) X | q \rangle \\
& + \frac{1}{4} \frac{\partial}{\partial k_x} \langle q | Y \left(p_x + \frac{\partial W_q^0}{\partial k_x} \right) Y | q \rangle - \frac{1}{8} \frac{\partial}{\partial k_y} \langle q | X \left(p_x + \frac{\partial W_q^0}{\partial k_x} \right) Y + Y \left(p_x + \frac{\partial W_q^0}{\partial k_x} \right) X | q \rangle \\
& - \frac{1}{8} \frac{\partial}{\partial k_x} \langle q | Y \left(p_y + \frac{\partial W_q^0}{\partial k_y} \right) X + X \left(p_y + \frac{\partial W_q^0}{\partial k_y} \right) Y | q \rangle + \frac{1}{8} \left(1 - \frac{\partial^2 W_q^0}{\partial k_x^2} \right) \langle q | Y^2 | q \rangle + \frac{1}{8} \left(1 - \frac{\partial^2 W_q^0}{\partial k_y^2} \right) \langle q | X^2 | q \rangle \\
& + \frac{1}{8} \frac{\partial^2 W_q^0}{\partial k_x \partial k_y} \langle q | XY + YX | q \rangle + \frac{1}{2} W_q^{(1)} \left(\frac{\partial X_q}{\partial k_y} - \frac{\partial Y_q}{\partial k_x} \right). \quad (32)
\end{aligned}$$

The atomic diamagnetism in the Y^2 and X^2 terms is clearly lost in a welter of other contributions whose nature is not clearly understood. It is possible to show, however, that the expression (32) is even in \mathbf{k} .¹⁰ This suggests, together with the earlier results that, generally,

$$W_q(-\mathbf{k}, -\mathbf{H}) = W_q(\mathbf{k}, \mathbf{H}) = \text{real}, \quad (33)$$

in agreement with the principle of time reversal. This result is not proved at the present time. Equation (32) is also easily put in tensor form. The contribution of induced diamagnetism to the susceptibility comes out to be, with dimensions restored,

$$\begin{aligned}
\chi_{\text{id}}^{\nu\mu} = & \frac{1}{2\pi^3} \int d\mathbf{k} f(W_q^0 - \eta) \epsilon_{\nu\alpha\beta} \epsilon_{\mu\sigma\tau} \\
& \times \left[\frac{e^2}{4m^2 c^2} \sum_{s \neq q} \frac{1}{W_s^0 - W_q^0} \langle q | X_\beta \left(p_\alpha + \frac{m}{\hbar} \frac{\partial W_q^0}{\partial k_\alpha} \right) | s \rangle \langle s | \left(p_\sigma + \frac{m}{\hbar} \frac{\partial W_q^0}{\partial k_\beta} \right) X_\tau | q \rangle \right. \\
& \left. - \frac{e^2}{8m\hbar c^2} \frac{\partial}{\partial k_\alpha} \langle q | X_\beta \left(p_\sigma + \frac{m}{\hbar} \frac{\partial W_q^0}{\partial k_\sigma} \right) X_\tau + X_\tau \left(p_\sigma + \frac{m}{\hbar} \frac{\partial W_q^0}{\partial k_\sigma} \right) X_\beta | q \rangle - \frac{e^2}{8m c^2} \left\{ \delta_{\sigma\alpha} - \frac{m}{\hbar^2} \frac{\partial^2 W_q^0}{\partial k_\alpha \partial k_\sigma} \right\} \langle q | X_\beta X_\tau | q \rangle \right] \\
& - \frac{1}{2\pi^2} \int d\mathbf{k} f(W_q^0 - \eta) \frac{e}{2\hbar c} W^{\nu} \epsilon_{\mu\sigma\tau} \frac{\partial}{\partial k_\tau} \langle q | X_\sigma | q \rangle. \quad (34)
\end{aligned}$$

The calculations which lead to (19), (31), and (32) are quite lengthy and have been suppressed in this publication. The work is available in the form of a report as stated in Ref. 10.

APPENDIX

We now show the equivalence of our result with that of Hebborn and Sondheimer (HS). This is most easily carried out by deriving our result from their expression. Although the expression for χ is gauge-independent, the

form for χ in Landau gauge is most convenient for the present purpose. The term χ_1 of HS can be recognized in our expression as consisting of Landau-Peierls terms and the contribution to χ from the term involving the fourth derivative of the energy with respect to components of the wave vector appearing in the expression (31) for $W_q^{(2)}$. The latter, after integration by parts once with respect to x and y components of k , yields the terms involving the third derivative of the energy occurring in χ_1 . The expression for $W_q^{(1)}$ in Landau gauge can be written as¹⁰

$$W_q^{(1)} = \langle q | p_x Y - \frac{\partial W_q^0}{\partial k_y} X | q \rangle - \frac{i}{2} \frac{\partial^2 W_q^0}{\partial k_x \partial k_y}. \quad (a)$$

In terms of notation used by HS for W_q , this is given as

$$W_q^{(1)} = W_q - (\partial W_q^0 / \partial k_y) X_{qq}. \quad (b)$$

Now combining the terms $[-|X_{qq}|^2 (\partial W_q^0 / \partial k_y)^2 + 2X_{qq} W_q \partial W_q^0 / \partial k_y]$ from χ_2 and the term $(W_q)^2$ from χ_4 of HS, we obtain the term representing crystalline paramagnetism in our expression (16). Next we consider the terms involving off-diagonal matrix elements in χ_3 of HS,

$$-\frac{e^2}{2\pi^3 m c^2} \int \sum_{q \neq s} \frac{X_{sq}}{W_s^0 - W_q^0} \left[\frac{m}{\hbar^2} \frac{\partial W_q^0}{\partial k_x} Y_{qs} + \langle q | Y p_x - X p_y | s \rangle \right] \frac{\partial W_q^0}{\partial k_y} f(W_q^0 - \eta) d\mathbf{k}. \quad (c)$$

To proceed further, we need a second-order sum rule which is obtained with the help of the Hermitian adjoint of Eq. (31a) of Ref. 10 by taking matrix elements with respect to b_s^0 , where $s \neq q$, thus obtaining

$$(W_s^0 - W_q^0) \langle q | \xi^- \eta^- | s \rangle = i \langle q | Y \left(p_x - \frac{\partial W_q^0}{\partial k_x} \right) + X \left(p_y - \frac{\partial W_q^0}{\partial k_y} \right) | s \rangle. \quad (d)$$

Here ξ^\pm, η^\pm are the operators $x \pm i(\partial/\partial k_x)$, $y \pm i(\partial/\partial k_y)$, with the sign according to the direction of operation.¹⁰ Utilizing Eq. (d), expression (c) can be written as

$$-\frac{e^2}{2\pi^3 m c^2} \int \sum_{q \neq s} \frac{X_{sq}}{W_s^0 - W_q^0} \left[2 \langle q | Y p_x | s \rangle + \frac{m}{\hbar^2} \frac{\partial W_q^0}{\partial k_y} X_{qs} + i \langle q | \xi^- \eta^- | s \rangle (W_s^0 - W_q^0) \right] \frac{\partial W_q^0}{\partial k_y} f(W_q^0 - \eta) d\mathbf{k}. \quad (e)$$

The summation over s can be easily carried out for the third term in the above expression by adding and subtracting the term with $s=q$ and utilizing the fact that the b_q 's form a complete set. Thus, we obtain

$$-\frac{e^2}{2\pi^3 m c^2} \int \left[\sum_{q \neq s} \frac{X_{sq}}{W_s^0 - W_q^0} \left\{ 2 \langle q | Y p_x | s \rangle + \frac{m}{\hbar^2} \frac{\partial W_q^0}{\partial k_y} X_{qs} \right\} + i \langle q | \xi^- \eta^- \xi^+ | q \rangle - \frac{1}{2} i X_{qq} \left(\frac{\partial Y_{qq}}{\partial k_x} + \frac{\partial X_{qq}}{\partial k_y} \right) \right] \frac{\partial W_q^0}{\partial k_y} f(W_q^0 - \eta) d\mathbf{k}. \quad (f)$$

Combining the terms in the curly bracket in the above expression with the terms involving off diagonal matrix elements in χ_4 of HS yields

$$\frac{e^2}{2\pi^3 m^2 c^2} d\mathbf{k} f(W_q^0 - \eta) \sum_{s \neq q} \frac{1}{W_s^0 - W_q^0} \left| \langle s | p_x Y - \frac{m}{\hbar} \frac{\partial W_q^0}{\partial k_y} X | q \rangle \right|^2. \quad (g)$$

This term is readily seen to be present in our expression for χ as the contribution involving off-diagonal terms from $W_q^{(2)}$.

Finally, all the remaining terms of HS can be written as

$$\begin{aligned} & \frac{e^2}{4\pi^3 m c^2} \int d\mathbf{k} \left[\left\{ \frac{m}{\hbar^2} \frac{\partial W_q^0}{\partial k_y} \langle q | x^2 | q \rangle - \langle q | X p_x Y + Y p_x X | q \rangle \right\} \frac{\partial W_q^0}{\partial k_y} \frac{\partial f(W_q^0 - \eta)}{\partial W_q^0} \right. \\ & + \left\{ \frac{m}{\hbar^2} X_{qq} \left(\frac{\partial Y_{qq}}{\partial k_x} - \frac{\partial X_{qq}}{\partial k_y} \right) + X_{qq} \left(\frac{\partial Y_{qq}}{\partial k_x} + \frac{\partial X_{qq}}{\partial k_y} \right) \frac{m}{\hbar^2} - 2i \langle q | \xi^- \eta^- \xi^+ | q \rangle \right\} \frac{\partial W_q^0}{\partial k_y} f(W_q^0 - \eta) \\ & \left. - \left\{ \langle q | Y^2 | q \rangle + 2W_q \frac{\partial X_{qq}}{\partial k_y} \right\} f(W_q^0 - \eta) \right]. \quad (h) \end{aligned}$$

Here W_q occurs as defined by HS. The terms in the first curly bracket in the above expression can be combined with the other terms by integrating by parts with respect to k_y . Thus (h) reduces to the following form:

$$\frac{1}{2\pi^3} \int d\mathbf{k} f(W_q^0 - \eta) \frac{e^2}{2m\hbar c^2} \frac{\partial}{\partial k_y} \langle q | X p_x Y + Y p_x X | q \rangle - \frac{e^2}{\hbar^2 c^2} \frac{\partial W_q^0}{\partial k_y} \frac{\partial}{\partial k_y} \langle q | X^2 | q \rangle - \frac{e^2}{2mc^2} \langle q | Y^2 | q \rangle - \frac{e^2}{2\hbar^2 c^2} \frac{\partial^2 W_q^0}{\partial k_y^2} \langle q | X^2 | q \rangle - \frac{e}{\hbar c} W_q^{(1)} \frac{\partial X_q}{\partial k_y}. \quad (i)$$

This is exactly the same expression as the contributions to χ from the remaining terms in (31), thus proving the equivalence of our result to that of HS.

Nuclear Magnetic Resonance Studies of the Metallic Transition in Doped Silicon*

R. K. SUNDFORS† AND D. F. HOLCOMB

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

(Received 12 June 1964)

The Si:P and Si:B systems have been studied using the methods of pulse and cw nuclear magnetic resonance. The purpose of this study is to investigate the transition of an impurity system in a solid from an array of isolated paramagnetic atoms or clusters of atoms to a superlattice of impurity atoms having strong wave-function overlap and metallic character. Knight shifts, line shapes, and nuclear spin relaxation times were measured for Si²⁹ and B¹¹ in *p*-type silicon and Si²⁹ and P³¹ in *n*-type silicon. Phosphorus concentrations vary from 10¹⁷ to 10²⁰ impurities/cm³ and the temperature range investigated extends from 1.4 to 300°K. Onset of metallic behavior in *n*-type silicon at 4×10¹⁸ phosphorus impurities/cm³ is indicated by the Si²⁹ T_1 becoming proportional to T^{-1} between 1.4 and 4.2°K and by the existence of a Knight shift for Si²⁹. Above a phosphorus concentration of approximately 3×10¹⁹ cm⁻³, Si²⁹ T_1 's and Knight shifts obey the Korringa relation. Broadening of the Si²⁹ resonance line by 5 times the dipolar width and of the P³¹ resonance line by 100 times the dipolar width at concentrations of 1.4×10²⁰ cm⁻³ is shown to be caused by fluctuations of the local Knight shift about the average Knight shift value. Such fluctuations are explained by a model of a Poisson distribution for the local P³¹ impurity density with a threshold local density of 3×10¹⁹ cm⁻³ for transition to metallic properties. This model agrees with the observed P³¹ resonance line shape and explains the transition to metallic behavior in *n*-type silicon. In *p*-type silicon, B¹¹ and Si²⁹ Knight shifts are measured for boron concentrations greater than 1×10¹⁹ cm⁻³. The B¹¹ T_1 's and Knight shifts agree with the Korringa relation within a 15% experimental error. However, both the B¹¹ T_1 and Knight shift are independent of concentration for boron concentrations between 2×10¹⁹ cm⁻³ and 8.5×10¹⁹ cm⁻³. Such concentration independence may be explained by postulating a clustering of boron atoms at an average local density in a cluster greater than 8.5×10¹⁹ cm⁻³. Wave function probability densities are calculated from Knight shifts with a free carrier density of states assumed valid. To facilitate comparison, wave-function densities are normalized per unit volume of the crystal and are 2600 cm⁻³ at P³¹ and 100 cm⁻³ at Si²⁹ in *n*-type silicon and 80 cm⁻³ at Si²⁹ in *p*-type silicon.

INTRODUCTION

THIS paper reports the experimental nuclear magnetic resonance (NMR) behavior of Si²⁹, P³¹, and B¹¹ nuclei in the silicon crystal lattice with increasing donor- or acceptor-impurity concentration. We are interested in those concentrations of impurities in which low-temperature electric resistivity and Hall-coefficient measurements indicate a transition from a nonmetal to a metal.¹ Graphs of the electrical resistivity as a function

of temperature in *n*- and *p*-type silicon²⁻⁶ and germanium^{7,8} show three qualitatively different classes of behavior as the impurity concentration is varied. In *n*-type silicon at donor-impurity concentrations less than about 4×10¹⁸ cm⁻³, the resistivity measurements^{2,5} indicate that most of the electrons are bound to the impurity system at temperatures less than 20°K. We shall call this concentration range the *semiconducting*

² G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).

³ F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).

⁴ R. O. Carlson, Phys. Rev. **100**, 1075 (1955).

⁵ R. K. Ray and H. Y. Fan, Phys. Rev. **121**, 768 (1961).

⁶ G. A. Swartz, Phys. Chem. Solids **12**, 245 (1960).

⁷ H. Fritzsche, Phys. Rev. **99**, 406 (1955).

⁸ H. Fritzsche, Phys. Chem. Solids **6**, 69 (1958).

* Work supported by the U. S. Office of Naval Research and the Advanced Research Projects Agency. The latter part of the work was also supported by the National Science Foundation.

† Present address: Washington University, St. Louis, Missouri.

¹ N. F. Mott and W. D. Twose, Advan. Phys. **10**, 107 (1961).