APPENDIX II

The scattering corrections to the various points of the spectrum measured in this experiment were calculated with a modification of the method used by Germain.[2] Table IV summarizes the results of these calculations. In this table the fraction of mesons lost by scattering is expressed in percent. Because the corrections are so small, they have not been applied to the results in Table III. The author is indebted to Dr. S. Fernbach for an enlightening discussion of these calculations.

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Energy of a Bloch Wall on the Band Picture. I. Spiral Approach

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It is shown that the band or itinerant electron model of a solid is capable of accounting for the "exchange stiffness" which determines the properties of the transition region, known as the Bloch wall, which separates adjacent ferromagnetic domains with different directions of magnetization. In this treatment the constant spin function usually assigned to each running electron wave is replaced by a variable spin function. At each point of space the spin of a moving electron is inclined at a small velocity-dependent angle to the mean spin direction of the other electrons, and this gives rise to an exchange torque which makes the spin direction of the given electron precess as it moves through the transition region, the precession rate being just sufficient to keep it in approximate alignment with the macroscopic magnetization. Physical insight into the mechanisms involved is provided by a rigorous solution of the wall problem for a ferromagnetic free electron gas in the Slater-Fock approximation, although it is known that the free electron gas is not likely to be ferromagnetic in higher approximations. Rough upper limits to the exchange stiffness constants for actual ferromagnetic metals can be calculated without using any empirical constants other than the saturation moment and the lattice constant. The results are only a few times larger than the observed values.

I. INTRODUCTION

IT has been shown by Bloch[1] and others that the change in the direction of magnetization of adjacent ferromagnetic domains takes place gradually, over a distance of the order of 10^{-5} cm; the transition layer is commonly known as the Bloch wall. The surface energy of this transition layer is a quantity of fundamental importance to the theory of ferromagnetic domains.[2] The occurrence of the transition layer represents a compromise between two tendencies, the tendency of the exchange effect to make the magnetization vector $\mathbf{M}$ vary as gradually as possible with position, and the tendency of anisotropy forces to force $\mathbf{M}$ into directions of easy magnetization. The former tendency can be described quantitatively by saying that when the spatial variation of the orientation of $\mathbf{M}$ is sufficiently gradual, it entails an increase ΔW in the energy per unit volume, given by

$$\Delta W = A|\nabla \mathbf{M}|^2/M^2, \tag{1}$$

where A is a numerical coefficient characteristic of the material. This coefficient A, which we shall refer to as the "Bloch wall coefficient," is also important in the theory of the temperature variation of the saturation magnetization at low temperatures (theory of spin waves),[3] and in the theory of the influence of skin effect on microwave resonance phenomena in ferromagnetics.[4]

In the papers cited under reference 1 the value of A is calculated on the Heitler-London or atomic model, according to which the electrons responsible for ferromagnetism are treated as localized on individual atoms of the crystal lattice. The calculation has not been carried out previously on the band or collective electron ferromagnetism model,[5] such as is employed in the work of Stoner and Slater, where the electrons are not localized, but are pictured as running waves moving through the lattice. In view of the well-known inadequacies of either model by itself it is rather unsatisfactory that the Bloch wall has not been treated on the running wave model, and it is with this gap that the present paper and a following one[6] are concerned. Specifically, we shall undertake to calculate A in the Slater-Fock approximation, i.e., assuming that the wave function of a crystal in which the spin direction varies slowly with position can be represented as a determinant of one-electron wave functions. Spin-orbit and other purely magnetic interactions will be neglected.

Two approaches to the problem of calculating A for

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[1] F. Bloch, Z. Physik **74**, 295 (1932); L. Landau and E. Lifshitz, Physik Z. Sowjetunion **8**, 153 (1935); E. Lifshitz, J. Phys. U.S.S.R. **8**, 337 (1944); L. Néel, Cahiers phys. **25**, 1 (1944). For a summary of wall theory and other aspects of domain theory, see C. Kittel, Revs. Modern Phys. **21**, 541 (1949).

[2] C. Kittel, Phys. Rev. **70**, 965 (1946); Williams, Bozorth, and Shockley, Phys. Rev. **75**, 155 (1949).

[3] C. Herring and C. Kittel, Phys. Rev. **81**, 869 (1951).

[4] C. Kittel and C. Herring, Phys. Rev. **77**, 725 (1950).

[5] For a discussion of the various models used in ferromagnetism the following review articles are suggested: J. H. Van Vleck, Revs. Modern Phys. **17**, 27 (1945); W. Shockley, Bell System Tech. J. **18**, 645 (1939); E. C. Stoner, Rep. Prog. Phys. **11**, 43 (1946–47).

[6] C. Herring (to be published).

the running-wave model will be employed, and shown to give equivalent results, at least for one case which can be calculated rigorously by both methods. The first and more obvious approach is to calculate the energy of a block of crystal on which periodic boundary conditions are imposed, with the macroscopic **M** lying always in the x-y plane and having an orientation φ proportional to z, with a factor sufficient to make φ increase by a multiple of 2π in the fundamental period. This, which may be called the "spiral approach," is the one used in the present paper. The second approach, to be used in the forthcoming paper,[6] is to calculate the response of a crystal to an externally imposed force which exerts a small torque $\mathbf{M}\times\mathbf{R}\sin\kappa x$ per unit volume tending to create a sinusoidal variation of the orientation of **M** with a wavelength $2\pi/\kappa$ large compared with atomic dimensions. This "perturbation approach" has already been discussed in application to the more general problem of relating A to the energies of spin waves.[3] The spiral approach, though less powerful, is better adapted to giving an understanding of the problem in elementary physical terms, and it is for this reason that discussion of the more complicated perturbation approach is deferred to a separate paper.

II. REMARKS ON FOCK'S EQUATIONS FOR A MAGNETIC CRYSTAL

In the Slater-Fock-Dirac approximation[7] one seeks the set of one-electron wave functions ψ_i which will make the energy of the determinant $|\psi_i(r_j, s_j)|$ a minimum. The functions of this set can be chosen in such a way as to satisfy the one-electron wave equations

$$(-\nabla^2+K+V-\mathcal{A})\psi_i=\lambda_i\psi_i, \tag{2}$$

where the λ_i are constants, $-\nabla^2$ is the kinetic energy operator T in atomic units, K is the potential field caused by all external sources (nuclei of atoms, etc.), V is the Coulomb potential of the electrons themselves, and $\mathcal{A}$ is their exchange operator. The energy in atomic units (rydbergs) is given by

$$\begin{aligned} E&=\sum_i(T_{ii}+K_{ii}+\tfrac{1}{2}V_{ii}-\tfrac{1}{2}\mathcal{A}_{ii})\\ &=\sum_i(i|-\nabla^2+K|i)+\tfrac{1}{2}\sum_{i,j}\left(ij\left|\frac{2}{|r-r'|}\right|ij\right)\\ &\qquad-\tfrac{1}{2}\sum_{i,j}\left(ij\left|\frac{2}{|r-r'|}\right|ji\right). \end{aligned} \tag{3}$$

It can be shown that, if the external potential K is invariant under a group G of symmetry transformations, there will always exist solutions of the self-consistent field Eqs. (2) for which V and $\mathcal{A}$ are also invariant under G, so that the ψ_i can be chosen to reduce G. For these solutions the determinant $|\psi_i(r_j, s_j)|$ is taken into a multiple of itself by all transformations of the group. In the band theory of nonferromagnetic metals one usually assumes that the solution which reduces the space group and the group of spin rotations has in fact the lowest energy of all solutions of the self-consistent field equations. For a ferromagnetic metal this is obviously not true, since the total wave function is not taken into itself by all operations of the spin rotation group, but belongs instead to a representation of very high multiplicity; it is also obvious that the exchange operator $\mathcal{A}$ will in this case not be invariant under spin rotations. It is reasonable to assume, however, that for a normal ferromagnetic crystal the lowest energy solutions include one which reduces the space group and the group of rotations of the spins about the z axis. Analogously, it will be equally reasonable to assume that if we wish to consider a ferromagnetic crystal with periodic boundary conditions and with **M** in the x-y plane with a constant $d\varphi/dz$, then the lowest energy solution of the self-consistent field equations will be one which reduces a group which is derived from the space group of the crystal by replacing each translation operation T by an operation TD_T where D_T is a spin rotation about the z axis through an angle $t_z d\varphi/dz$, where t_z is the z component of the vector describing the translation T. This is because the total wave function for this case is obviously invariant under this group. This fact will form the basis for the calculations of the present paper.

III. CORRELATION ENERGY

Since the calculations of the present paper are to be made using the Slater-Fock approximation, a few words on the limitations of this approximation are in place. In the Slater-Fock approximation the positions of the various electrons are statistically uncorrelated except for the correlations necessitated by the exclusion principle. In the ground state of a ferromagnetic crystal the ferromagnetic electrons will avoid each other fairly well, since the parallelism of their spins makes the probability of finding two of these electrons a distance r apart go to zero as $r\rightarrow 0$. In a state with varying spin direction, however, there will exist a nonzero probability density for finding two electrons of opposite spin at the same place. This probability of finding electrons of opposite spin close together will be greater for a determinantal wave function, where electrons of opposite spins are uncorrelated, than for the correct wave function, in which even electrons of opposite spins will avoid each other more than is possible in a determinantal wave function, and thereby lower their interaction energy. The difference between the energy of the true wave function and that of the determinantal solution of Fock's equations is called the "correlation energy"; from what has just been said it is clear that the correlation lowering will be greater for the state

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[7] J. C. Slater, Phys. Rev. **35**, 210 (1930); V. Fock, Z. Physik **61**, 126 (1930); P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930). An excellent summary is given by L. Brillouin, *Actualités Scientifiques et Industrielles* (Hermann et Cie., Paris, 1933–34), Nos. 71, 159, and 160.

with varying spin direction than for the state with constant spin direction. Therefore the methods of this paper and of reference 6 will lead to a value for the coefficient A in (1) which will be too large, at least if the calculations are carried out without the introduction of any empirical values for exchange integrals, etc.

It might therefore be supposed that almost any calculation made with wave functions of more general form than Slater determinants would give results superior to those obtainable by the Slater-Fock method. For example, Slater[8] has shown how the energy E_κ of a spin wave of wave vector $\boldsymbol{\kappa}$ can be calculated by solving a secular equation involving many determinantal wave functions, corresponding to the many possible states with a single reversed spin; since the Bloch wall coefficient A can be evaluated from a knowledge of E_κ, one might suppose that these calculations would provide a superior method of estimating A. However, this is not the case; as will be shown in the following paper, Slater's wave functions for the spin-wave state, though not of determinantal form, are related in a rather simple way to the determinantal wave functions used here, and the A values obtained by the two methods are the same.

IV. FORM OF THE WAVE FUNCTIONS

From what was said at the end of Sec. II it follows that the one-electron wave functions for the problem we wish to consider may be written in the form

$$\psi_k = \exp(i\mathbf{k}\cdot\mathbf{r})u_k(\mathbf{r})g_k(\mathbf{r}, s_z), \tag{4}$$

where u_k is a function with the periodicity of the lattice and where, for each point $\mathbf{r}$, g_k is a normalized spin function which is unchanged by all operators TD_T, i.e.,

$$\sum_{s_z=\pm\frac{1}{2}} |g_k(\mathbf{r}, s_z)|^2 = 1 \tag{5}$$

$$g_k(\mathbf{r}) = \exp[it_z(d\varphi/dz)(\sigma_z/2)]g_k(\mathbf{r}-\mathbf{t}), \tag{6}$$

where in the last line g_k is to be visualized as a two-row matrix and where σ_z is the Pauli spin matrix, the exponential being merely the operator D_T rotating the spin through the angle $t_z d\varphi/dz$.

Several qualitative properties of the wave function (4) are worth noting here.

(1) Whatever the form of g_k, there will exist at each point $\mathbf{r}$ some direction along which the component of spin has the eigenvalue $+\frac{1}{2}$; g_k may therefore be described by the polar angles $\theta_k(\mathbf{r})$, $\varphi_k(\mathbf{r})$ of this direction, and by a phase factor which, though the same for both values of the argument s_z, may depend in any way on $\mathbf{r}$. Different choices of this phase factor merely imply use of different functions u_k.

(2) For singly-occupied levels[9] $\mathbf{k}$, the deviations of θ_k, φ_k from the macroscopic spin direction $\theta=\pi/2$, $\varphi=\bar{\varphi}$, must be $O(d\bar{\varphi}/dz)$ as $d\bar{\varphi}/dz\rightarrow 0$. One consequence of this is that at a given point of space the angle between the directions θ_k, φ_k, and $\theta_{k'}$, $\varphi_{k'}$ is $O(d\bar{\varphi}/dz)$ whenever $\mathbf{k}$ and $\mathbf{k}'$ correspond to two different singly-occupied levels.

(3) The functions u_k can be taken to be of the form $u_k^{(0)}+O(d\bar{\varphi}/dz)$, where $u_k^{(0)}$ are the solutions of the self-consistent field problem for constant spin direction. This specifies the phases of the g_k to within terms of order $d\bar{\varphi}/dz$.

In the sections immediately following, we shall assume the spin function g_k going with any particular direction θ_k, φ_k (direction of quantization of the spin) to be defined by

$$g_k = \begin{pmatrix} \exp(-i\varphi_k/2)\cos\frac{1}{2}\theta_k \\ \exp(i\varphi_k/2)\sin\frac{1}{2}\theta_k \end{pmatrix}. \tag{7}$$

It will be verified below that the choice of the phase factor in (7) causes the u_k to coincide with the $u_k^{(0)}$ to within terms of order $(d\bar{\varphi}/dz)^2$. Using (7), the spin distribution is completely described by the set of functions $\theta_k(\mathbf{r})$, $\varphi_k(\mathbf{r})$, or equivalently by

$$\xi_k(\mathbf{r}) = \theta_k(\mathbf{r}) - \pi/2 \tag{8}$$

and

$$\eta_k(\mathbf{r}) = \varphi(\mathbf{r}) - \bar{\varphi}(\mathbf{r}), \tag{9}$$

where $\bar{\varphi}$ is a linear function of position defined so that $d\bar{\varphi}/dz=$ the macroscopic $d\varphi/dz$ and so that the average of η_k over a unit cell, weighted with the charge density $|u_k|^2$, vanishes when summed over all occupied states. The quantities ξ_k, η_k thus measure the deviation, in distance on the unit sphere, of the local spin direction from the mean direction $(\pi/2, \bar{\varphi})$. These quantities must obviously be periodic with the periodicity of the lattice; this follows mathematically from (6).

V. TERMS IN THE ENERGY

Let the function ψ_k given by (4) be written as

$$\psi_k = \chi_k(\mathbf{r})g_k(\mathbf{r}, s_z), \tag{10}$$

where now g_k is given by (7). The mean kinetic energy of ψ_k is, in atomic units,

$$\begin{aligned} T_{kk} &= \sum_{s_z}\int |\nabla\chi_k|^2 d\tau \\ &= \int [|\nabla\chi_k|^2 + 2\,\mathrm{Re}\chi_k^*\nabla\chi_k(\nabla g_k, g_k) \\ &\qquad + |\chi_k|^2(\nabla g_k, \nabla g_k)]d\tau, \end{aligned} \tag{11}$$

where the expressions in parentheses are spin scalar products at a given position $\mathbf{r}$. A straightforward

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[8] J. C. Slater, Phys. Rev. 52, 198 (1937).

[9] Strictly speaking it is not possible to separate the one-electron states of a ferromagnetic crystal into singly- and doubly-occupied levels, because the electrons of the two spins move in different exchange fields, and this makes the orbital parts of their wave functions slightly different. However, the distinction is obviously only of significance in calculations much more refined than those considered here.

calculation based on (7) and using (8) gives, to the second order in $d\bar{\varphi}/dz$ (i.e., to the second order in ξ_k and η_k),

$$(\nabla g_k, g_k) = -(i/2)\xi_k \nabla \varphi_k \qquad (12)$$

$$(\nabla g_k, \nabla g_k) = \tfrac{1}{4}[\,|\nabla \xi_k|^2 + |\nabla \varphi_k|^2]. \qquad (13)$$

Insertion of these into (11) gives T_{kk} in terms of χ_k, ξ_k, and φ_k or η_k.

Since the charge density for the state ψ_k is simply $|\chi_k|^2$ and is independent of ξ_k and φ_k, the Coulomb energy in the presence of a spin gradient will depend on the χ_k in the same way as for the case of constant spin direction. The exchange energy, however, will be different, unless ξ_k and φ_k happen to be independent of **k**. For the **kk′** contribution to the exchange energy is the self-energy of the distribution

$$\chi_{k'}^* \chi_k (g_{k'}, g_k), \qquad (14)$$

and we have from (7), to the second order in $d\bar{\varphi}/dz$,

$$(g_{k'}, g_k) = 1 - (i/4)(\eta_{k'} - \eta_k)(\xi_{k'} + \xi_k) - \tfrac{1}{8}(\eta_{k'} - \eta_k)^2 - \tfrac{1}{8}(\xi_{k'} - \xi_k)^2. \qquad (15)$$

The total exchange energy of the ferromagnetic electrons, which we shall not attempt to write down explicitly, is obtained by substituting (15) into (14), evaluating the self-energy, and summing over **k** and **k′**. Electronic states having the minority spin direction could be taken into account if necessary, by assigning to them spin functions of the form (7) but with (θ, φ) close to $(\frac{1}{2}\pi, \bar{\varphi}+\pi)$ instead of to $(\frac{1}{2}\pi, \bar{\varphi})$; spin scalar products of states with nearly opposite spins would then have to be evaluated, as well as those of the type (15).

The total energy is made up of kinetic, potential, Coulomb, and exchange contributions, and it is now clear that each of these contributions either is exactly the same function of the χ_k as when the spin direction is constant, or else equals this function plus something that is second order in the ξ's and η's, i.e., second order in the macroscopic $d\bar{\varphi}/dz$. Thus, as far as terms of the second order in $d\bar{\varphi}/dz$ are concerned, any change in χ_k would increase the energy, and so in the problem of minimizing the total energy by proper choice of the χ_k, ξ_k, and η_k we can assume the χ_k to be of the same form as when the spin direction is constant, and vary only the ξ_k and η_k. However, even the variational problem involved in finding the ξ_k and η_k which minimize the energy is quite a formidable once in the general case, and we shall here apply the approach just described to only two simplified cases:

(1) The free electron case. The simplification here arises, as will be shown below, from the fact that each ξ_k and η_k is independent of position, and from the related fact that cross terms between the ξ's and η's disappear from the exchange energy.

(2) The case where ξ_k and η_k are arbitrarily constrained to be independent of **k**. Though this assumption does not give as low an energy as when the ξ's and η's are unrestricted, it probably gives the right order of magnitude for the Bloch wall coefficient, and it is particularly simple because the exchange energy reduces to the same value as for constant spin direction, so that only the kinetic energy term need be considered. This case will be discussed in Secs. VIII and IX below. In the forthcoming paper[6] it will be shown that other, less drastic, simplifying assumptions can be used to make the problem tractable when the perturbation approach is used. However, I have not discovered any way of carrying through corresponding simplifications using the spiral approach.

VI. THE PROBLEM OF THE FREE ELECTRON GAS

Bloch[10] has shown that an assembly of free electrons moving in a volume pervaded by a uniform density of positive charge will be ferromagnetic, in the approximation of determinantal wave functions, if its density is sufficiently low. This case provides a convenient illustration of the physical principles involved in the Bloch wall problem, and, since the solution for this case can be obtained without any approximations beyond those involved in the use of determinantal wave functions, it offers an opportunity to assess the accuracy of various methods of calculation which involve additional simplifications. The utility of the free electron example is somewhat marred by the fact that the correlation energy for free electrons, which Wigner[11] has calculated, is so large that it will probably prevent a free electron gas of any density from being ferromagnetic.[12] Nevertheless, it is interesting to compare the results of different methods of estimating the Bloch wall coefficient for free electrons, starting from the (false) assumption that the ground state is a determinant of plane waves with parallel spins.

One such method is that based on the atomic approximation[13] as used in Heisenberg's theory of ferromagnetism, Bloch's theory of spin waves,[14] and previous theories of the Bloch wall.[1] The determinant of plane waves which approximates the ferromagnetic state for the free electron gas can be approximated by a determinant of "atomic" functions defined by Wannier's transformation[15]

$$w(\mathbf{r} - \mathbf{R}_n) = \textstyle\sum_k [\exp(-i\mathbf{k}\cdot\mathbf{R}_n)/N^{\frac{1}{2}}][\exp(i\mathbf{k}\cdot\mathbf{r})/\Omega^{\frac{1}{2}}], \qquad (16)$$

where Ω is the fundamental volume associated with the periodic boundary conditions and N is the number of electrons, and where the points $\mathbf{R}_n$ may refer to any arbitrary lattice of points in space. The quantity in brackets is a unitary matrix on the indices **k** and n if $\mathbf{k}/2\pi$ is allowed to run over a unit cell (Brillouin zone) in the lattice reciprocal to that of the $\mathbf{R}_n$. Since suitable

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[10] F. Bloch, Z. Physik **57**, 545 (1929).

[11] E. Wigner, Phys. Rev. **46**, 1002 (1934).

[12] E. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

[13] See, for example, the review by J. H. Van Vleck, Revs. Modern Phys. **17**, 27 (1945).

[14] F. Bloch, Z. Physik **61**, 206 (1931).

[15] G. H. Wannier, Phys. Rev. **52**, 191 (1937).

choice of this lattice will make the Brillouin zone nearly spherical, it is reasonable to try to estimate the value of the Bloch wall coefficient either by assuming the occupied $\mathbf{k}$ values to fill a Brillouin zone, or by assuming them to fill a sphere and ignoring the correction due to the fact that the w's defined by (16) will in the latter case not be exactly orthonormal. In this approximation the procedure used in previous theories of the Bloch wall corresponds to assuming the state with varying spin direction to consist of a determinant of w's, each with a spin function g_n which corresponds to eigenvalue $+\frac{1}{2}$ for the component of spin along a direction in the x-y plane and making an angle $\varphi_n = Z_n d\varphi/dz$ with the x axis, where Z_n is the z component of $\mathbf{R}_n$. Evaluating the contributions to the energy in (3), we see that the kinetic, potential, and Coulomb terms are the same as in the ground state, while the exchange term is numerically smaller. A rough estimation of this change in the exchange energy, given in Appendix I, indicates that the Bloch wall coefficient computed in this way has a value

$$A = \beta / r_e^2 \tag{17}$$

rydbergs per Bohr unit, where r_e is the radius in Bohr units of the sphere whose volume equals the volume per electron, and where β is a constant which is certainly greater than 0.026, perhaps by as much as a factor of two or so. A more accurate estimate of β could be made, but would hardly be worth while, since we shall see presently that the atomic approximation is a very poor one.

VII. APPLICATION OF THE SPIRAL APPROACH TO THE FREE ELECTRON GAS

We now return to the approach of Sec. V. For a free electron gas we may choose any vectors we please for the fundamental translations of the "crystal lattice"; the requirement that the ξ_k and η_k defined by (8) and (9) be periodic therefore implies that they must be independent of position. Therefore, the $(g_{k'}, g_k)$ in (14) is a constant, and the $\mathbf{k}\mathbf{k}'$ contribution to the exchange energy is just $|(g_{k'}, g_k)|^2$ times the corresponding contribution for the case of constant spin direction. Thus using (15) and ignoring terms of higher order than the second in the ξ's and η's,

exchange contribution to energy (3)

$$= -\frac{1}{\Omega}\sum_{k,k'}\frac{4\pi}{|\mathbf{k}-\mathbf{k}'|^2}\left[1-\frac{(\eta_{k'}-\eta_k)^2}{4}-\frac{(\xi_{k'}-\xi_k)^2}{4}\right], \tag{18}$$

where Ω is the fundamental volume associated with the periodic boundary conditions. From (11), (12), and (13) we have

$$\text{kinetic energy} = \sum_k[k^2 + (d\bar{\varphi}/dz)k_z\xi_k + (d\bar{\varphi}/dz)^2]. \tag{19}$$

The constants ξ_k, η_k must be chosen to minimize the sum of (18) and (19).

It is obvious from inspection that the proper choice of η_k is a value independent of $\mathbf{k}$, and since the mean of all the η_k must vanish, as specified under Eq. (9), we must take $\eta_k = 0$. The Euler equation for the ξ_k reduces to

$$\frac{d\bar{\varphi}}{dz}k_z + \frac{1}{\Omega}\sum_{k'}\frac{4\pi}{|\mathbf{k}-\mathbf{k}'|^2}(\xi_k - \xi_{k'}) = 0 \tag{20}$$

with the auxiliary condition that $\sum_k \xi_k = 0$. Since the possible values of $\mathbf{k}'$ are almost continuously distributed over the occupied sphere in $\mathbf{k}$-space, this is really an integral equation of the Fredholm type. It may be placed in a form convenient for computation by making the substitutions

$$\mathbf{y} = \mathbf{k}/k_{\max}, \quad \sum_k \to (3N/4\pi)\int_{S_1} d\mathbf{y},$$

where N is the total number of electrons in the fundamental volume Ω, supposed all to have the same spin when $d\varphi/dz = 0$, and where the region S_1 of integration is the unit sphere. The result is

$$\int_{S_1}\frac{[\xi(\mathbf{y}) - \xi(\mathbf{y}')]}{|\mathbf{y}-\mathbf{y}'|^2}d\mathbf{y}' = -2\pi^2\frac{d\bar{\varphi}}{dz}y_z, \tag{21}$$

where, it must be remembered, $d\bar{\varphi}/dz$ is to be evaluated in atomic units.

The integral Eq. (21) and its solution have a simple physical interpretation. Suppose that an electron moving with a given z component of velocity has a spin direction which at each point of space differs from the mean spin direction of the electrons to which it is coupled by the exchange effect. Then these other electrons will exert a torque on the spin of the given electron, in such direction as to tend to bring its spin into coincidence with theirs. Since the spin behaves gyroscopically, this torque will cause it to precess on the surface of the unit sphere in a direction at right angles to the line joining it to the mean spin direction of its fellows. An observer traveling with the moving electron would observe a constant magnitude for the discrepancy between his spin and that of the neighborhood, and would observe his own spin to precess in a very flat cone on the unit sphere, with a velocity proportional to $d\bar{\varphi}/dz$ times his z component of velocity. This is essentially the right of (21); the left of (21) corresponds to the suitably weighted average of the torques exerted by the various other electrons on the given one, each term in the average being proportional to the difference in the spin orientation of the two electrons concerned and to the strength of the exchange coupling between them. The equation thus expresses the proportionality of precessional velocity to torque. We shall see in the forthcoming paper[6] that the same integral equation results when the free electron problem is attacked by the perturbation method.

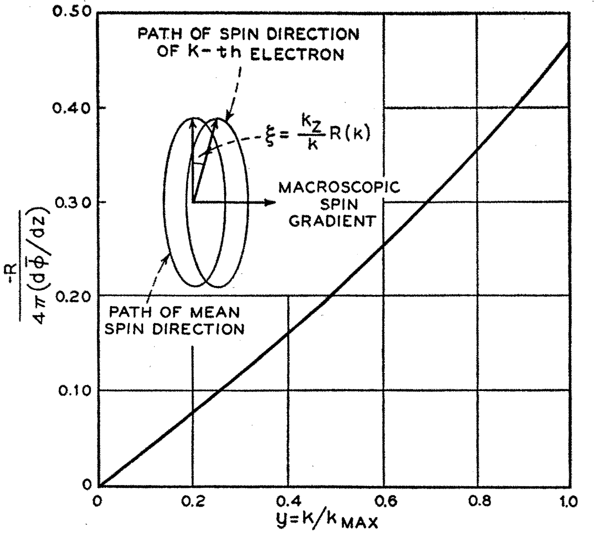

FIG. 1. Deviation of spin orientation from the mean orientation for free electrons, plotted as a function of wave number for electrons moving in the direction of the macroscopic gradient of spin direction.

The solution of (21) which has mean value zero is obviously of the form

$$\xi(y) = (y_z/y)R(y), \qquad (22)$$

since the spherical symmetry of the kernel causes each term in an expansion of ξ in spherical harmonics to be transformed into a term with the same angular dependence. A variational calculation, described in Appendix II, gives for R the approximate form shown in Fig. 1, *viz.*, the polynomial

$$R(y) = \gamma[-(243/610)y - (9/122)y^3], \qquad (23)$$

where

$$\gamma = 4\pi d\bar{\varphi}/dz. \qquad (24)$$

The increase in total energy, as compared with the state with all spins parallel, is the sum of (18) and (19) with the first term of each omitted. It thus consists of a term in $(d\bar{\varphi}/dz)^2$, one linear in ξ and $d\bar{\varphi}/dz$, and one quadratic in ξ; if the scale of ξ is so chosen as to minimize the sum of these three terms, this sum can be replaced by the term in $d\bar{\varphi}/dz$ plus half the term linear in ξ. Thus the energy increase is

$$E - E_0 = \tfrac{1}{2}(d\bar{\varphi}/dz)\textstyle\sum_k k_z\xi_k + (N/4)(d\bar{\varphi}/dz)^2. \qquad (25)$$

Combining (22), (23), and (25) gives

$$\begin{aligned} E - E_0 &= (N/4)(d\bar{\varphi}/dz)^2(1 - 0.72169\pi k_{\max}) \\ &= (N/4)(d\bar{\varphi}/dz)^2(1 - 5.4851/r_e), \end{aligned} \qquad (26)$$

which by (1) and with $4\pi r_e^3/3 = \Omega/N$ gives for the Bloch wall coefficient

$$\begin{aligned} A &= (E - E_0)/\Omega(d\bar{\varphi}/dz)^2 \\ &= (3/16\pi r_e^3)(1 - 5.4851/r_e). \end{aligned} \qquad (27)$$

The values (26) and (27), being obtained from a rigorous solution of the self-consistent field equations, may be expected to be lower than the energy or A value obtained by any other method based on determinantal wave functions. This is exemplified by the comparison of (27) with the value (17) obtained from the atomic approach, as illustrated in Fig. 2. It is clear that in spite of the uncertainty in the value of β in (17) the present value (27) is much the smaller. The simplification to be discussed in the next section, that of assuming all the spin functions the same, corresponds to replacing the last factor in (27) by unity; the resulting value of A is shown as the middle curve in Fig. 2.

According to (27), ferromagnetism should cease when the electron density exceeds the value for which $r_e = 5.4851$ Bohr units, even when only wave functions of determinantal form are considered. Bloch,[10] considering only determinants of plane waves each with constant spin direction, found that ferromagnetism should cease when r_e becomes less than $(2\pi/5)(9\pi/4)^{\frac{1}{3}} \times (2^{\frac{1}{3}}+1) = 5.4531$. Thus (27) gives a slightly more stringent criterion for ferromagnetism than Bloch's. (Improvement of the approximate solution (23) would merely increase the critical r_e, and probably only by a very small amount.) It is surprising that the critical r_e given by (27) comes so close to Bloch's value, since the former is the condition for stability with respect to a very gradual alteration of direction of magnetization with position, spin parallelism being preserved locally, while the latter is the condition for stability with respect to reversal of half the spins at every point of space. On Bloch's model the state with all spins parallel is stable with respect to removing a single electron at the top of the Fermi distribution and inserting it in the

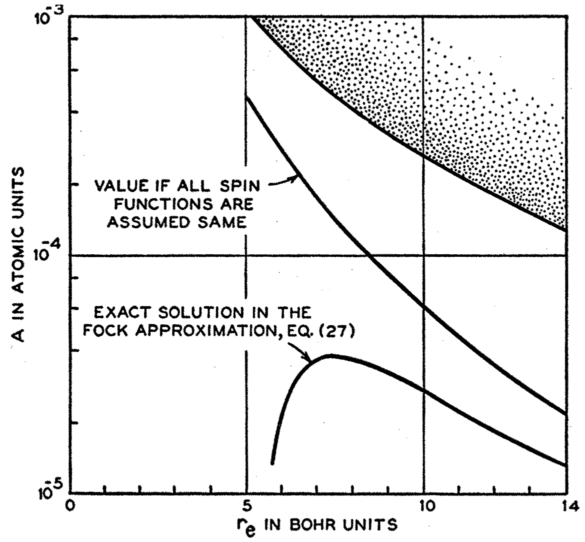

FIG. 2. Values of the Bloch wall coefficient A for a free electron gas, as computed by various methods of approximation. Bottom curve: best possible approximation using determinantal wave functions, as given by Eq. (27). Middle curve: approximation assuming all electrons to have the same spin function, given by replacing parentheses by unity in (27). Top curve: lower limit to value calculable from the atomic model, as given by Eq. (17).

state $k=0$ with reversed spin, whenever

$$r_e > 2^{-\frac{2}{3}}\pi(9\pi/4)^{\frac{1}{3}} = 3.8002.$$

VIII. APPROXIMATION OF ASSUMING ALL SPIN FUNCTIONS THE SAME

Although Fig. 2 shows that the correct value of A may be considerably less than that computed on the assumption that all electrons have the same spatially varying spin function, it does show that for free electrons the latter value is at least of the same order of magnitude as the best value that can be computed from determinantal wave functions, except near the critical density where ferromagnetism disappears. Moreover, the error is of course always in the direction of making the computed A too large. It therefore seems worth while to expend a little effort toward computing A for narrow bands of itinerant electrons, using this assumption that at each point of space all the ferromagnetic electrons $\mathbf{k}$ have the same spin orientation, i.e., the same $\theta_k(\mathbf{r})$, $\varphi_k(\mathbf{r})$, or the same $\eta_k(\mathbf{r})$, $\xi_k(\mathbf{r})$, in the notation of Sec. IV. With this assumption the exchange energy as well as the Coulomb energy is the same in the presence of a gradient of spin direction as when the spin direction is constant; this can be seen from the fact that the exchange charge density (14) reduces to $\chi_{k'}{}^*\chi_k$ if the ξ's and η's are the same for all $\mathbf{k}$.

Thus only the kinetic energy (11) needs to be considered; using (12) and (13) we have for the energy increase over the state with uniform spin direction

$$E-E_0 = -\int \xi\nabla\varphi\cdot\textstyle\sum_k \mathrm{Re}[i\chi_k{}^*\nabla\chi_k]d\tau$$

$$+\frac{1}{4}\int[|\nabla\xi|^2+|\nabla\varphi|^2]\textstyle\sum_k|\chi_k|^2 d\tau. \quad (28)$$

Here the summations extend over the singly filled orbitals: we shall suppose in the present section that the remaining electrons are paired off with two electrons of opposite spin to each orbital, and shall assume the latter levels to be unperturbed by the fact that the direction of magnetization is spatially varying. Now since we are neglecting spin-orbit interaction, the wave equation for each χ_k contains only real operators, and there will therefore be another orbital, with wave vector $-\mathbf{k}$, which is a multiple of $\chi_k{}^*$ and which has the same energy parameter λ_k in the one-electron wave equation (2). Thus for each $\mathbf{k}$

$$\chi_k{}^*\nabla\chi_k + \chi_{-k}{}^*\nabla\chi_{-k} = \nabla|\chi_k|^2$$

and is real; grouping the terms of the first integral of (28) in pairs in this way, the whole integral can be seen to vanish. We are left merely with the problem of choosing $\xi(\mathbf{r})$ and $\varphi(\mathbf{r})$ so as to minimize the second integral of (28) subject to the condition that the space average of $d\varphi/dz$ be fixed; obviously ξ must be chosen zero, while the variational equation for φ gives

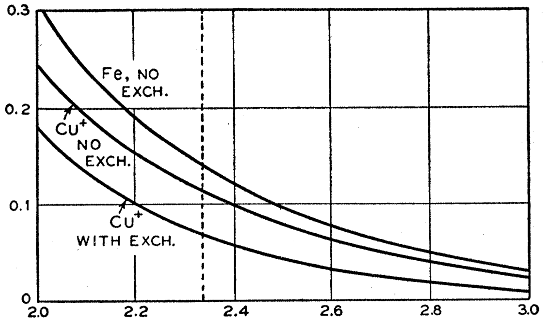

FIG. 3. Charge distributions for the $3d$ electrons of free atoms of Fe and Cu^+. The ordinate is the product of the $3d$ charge density ρ by the atomic volume Ω_0 of iron. The top curve is taken from the calculations of Manning and Goldberg (see reference 18) for Fe, made without exchange. The middle curve is taken from the calculations of Hartree (see reference 19) for Cu^+, without exchange, and the bottom curve from those of Hartree and Hartree for Cu^+, with exchange. The vertical dotted line is at the half-distance between nearest neighbors for Fe, which is also the same as that for Ni.

$$\nabla\cdot\rho\nabla\varphi = 0, \quad (29)$$

where $\rho=\sum|\chi_k|^2$ is the charge density of the ferromagnetic electrons in atomic units.

Although our primary concern in this paper is with the itinerant electron model, it is worth noting that the approximation of the present section, as represented by Eqs. (28) and (29), can be applied equally well to the atomic model. One has merely to assign to each atomic orbital a spatially varying spin function which is the same function of position for all atoms, instead of using spatially constant spin functions which are different for neighboring atoms, as is done in the conventional treatment, and as Fig. 2 shows, this may give a considerably lower energy. The results of this and the following section are in fact independent of whether an itinerant or an atomic model is used.

Equation (29) is the same as that for the electrostatic potential in a medium of variable dielectric constant ρ, when the mean field $\bar{\mathcal{E}}$ is $-d\bar{\varphi}/dz$. The problem of determining the Bloch wall coefficient A in the present approximation is therefore identical with that of determining the gross dielectric constant $\bar{\kappa}$ of an inhomogeneous medium, and it is in fact easy to show that

$$A = \bar{\kappa}/4 \text{ rydbergs per Bohr unit.} \quad (30)$$

While the exact calculation of $\bar{\kappa}$ from any given periodic density function $\rho(r)$ is difficult,[16] it is obvious that $\bar{\kappa}$ satisfies the inequalities[17]

$$\rho_{\min} < \bar{\kappa} < \bar{\rho}, \quad (31)$$

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[16] The problem of estimating gross dielectric constants, permeabilities, etc., for inhomogeneous media has received considerable attention in the literature. A comprehensive review has been given by K. Lichtenecker, Physik. Z. 27, 115 (1926).

[17] Note that the upper limit to A given by (30) and (31) is identical with that given in Eq. (44) of reference 3.

where $\rho_{\min}$ is the minimum value of the electron density ρ over a unit cell, and $\bar{\rho}$ is the mean electron density. More elaborate inequalities satisfied by $\bar{\kappa}$ can of course be derived. Of more interest to us, however, is the general picture of the variation of φ with position. If, as is doubtless the case, the charge density of the ferromagnetic electrons is much smaller in between the atoms than in the region well within an atomic cell, φ will be nearly constant over most of each atomic cell and will vary rapidly with position near the half-way point between nearest neighbor atoms. In fact, the closer the charge density hugs the atoms, the more nearly correct it is, in the approximation of this section, to picture each atomic cell as having its own constant spin orientation, different from that of its neighbors. We shall show in the next section how this fact makes possible a simple quantitative estimate of $\bar{\kappa}$, and hence of A.

IX. ESTIMATES FOR ACTUAL METALS, ASSUMING ALL SPIN FUNCTIONS THE SAME

To carry out the rough estimation of the Bloch wall coefficient outlined in the preceding section one must first make a reasonable guess at the charge density $\rho(r)$ of the ferromagnetic electrons. Figure 3 shows the d shell charge density calculated for the free iron atom by Manning and Goldberg[18] by the Hartree method. To illustrate the order of magnitude of the correction which might be introduced if exchange were included, charge densities calculated for Cu^+ by Hartree and Hartree[19] both with and without exchange are also shown.

Although the charge distributions in atom and metal certainly differ and although the decrease of d electron charge density at large distances from the nucleus is not overwhelmingly rapid, it will suffice for the present crude estimate to use an expression for the gross dielectric constant $\bar{\kappa}$ which can be derived by assuming that near the midpoint between two nearest neighbor atoms

$$\rho \propto \exp(-\lambda r_1)+\exp(-\lambda r_2),$$

where r_1 and r_2 are the distances from the two nuclei and λ is a very large constant. A little calculation based on this assumption gives

$$\bar{\kappa} \approx (3/2)^{\frac{1}{2}}\rho_0$$

for the body-centered cubic lattice, and twice this for the face-centered lattice, where ρ_0 is the charge density of ferromagnetic electrons at the midpoint between nearest neighbors. Substitution of this into (30) with a ρ_0 estimated by combining Fig. 3 with the known number of ferromagnetic electrons per atom gives values of A for Fe and Ni which are three or four times larger than the observed values of 2×10^{-6} ergs/cm for Fe,[20, 21] and 8×10^{-7} ergs/cm for Ni.[20]

When it is remembered that the calculations of the present section overestimate A, both by using the assumption that all spin functions are the same, and by neglecting correlation, this agreement to within a factor of 3 or 4 is about all that can be expected. Crude though it is, the agreement is gratifying in that no empirical magnetic constants except the saturation magnetization have been used in the present calculation. The ratio of A to the saturation moment has been estimated from h, m, e, and the lattice constant of iron, by use of a very simple physical model. However, the limitations of the model used in this section are severe; for example, it would be very risky to try to predict relative values of A for different metals from their respective values of ρ_0, since the correction factor corresponding to the expression in parentheses in the free electron Eq. (27) may vary considerably from one metal to another. The forthcoming paper[6] will present an alternative approach which throws some light on how this correction factor can be calculated.

I am very much indebted to Dr. C. Kittel for bringing this problem to my attention and for many helpful discussions in the course of the work, and to Dr. G. H. Wannier for suggestions on the calculations of Appendix II.

APPENDIX I. VALUE OF *A* FOR FREE ELECTRONS ON THE ATOMIC MODEL

We assume the wave function to be a determinant of functions of the form (16), each multiplied by a spin function g_n of the form (7) with $\theta_n=\pi/2$, $\varphi_n=Z_n d\varphi/dz$, where Z_n is the z component of the coordinate vector $\mathbf{R}_n$ of the nth lattice site. Using the subscript 0 for the state where all spins are parallel the contribution of the m, n pairs of w's to the exchange energy is

$$\left(mn\left|\frac{2}{|\mathbf{r}-\mathbf{r}'|}\right|nm\right)=\left(mn\left|\frac{2}{|\mathbf{r}-\mathbf{r}'|}\right|nm\right)_0 |(g_m, g_n)|^2$$

$$|(g_m, g_n)|^2=\cos^2\tfrac{1}{2}(\varphi_m-\varphi_n)\sim 1-\tfrac{1}{4}(Z_m-Z_n)^2(d\varphi/dz)^2.$$

Taking the origin of coordinates at one of the lattice sites we have for an assembly of N electrons, to order $(d\varphi/dz)^2$,

$$E-E_0=\frac{N}{8}\sum_n\left(0n\left|\frac{2}{|\mathbf{r}-\mathbf{r}'|}\right|n0\right)_0 Z_n^2\left(\frac{d\varphi}{dz}\right)^2. \quad (\mathrm{I}.1)$$

The exchange integrals $(0n|(2/|\mathbf{r}-\mathbf{r}'|)|n0)_0$ are messy to evaluate; however, they undoubtedly decrease with increasing $|\mathbf{R}_n|$, and their sum (including the term

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[18] M. F. Manning and L. Goldberg, Phys. Rev. **53**, 662 (1938).

[19] D. R. Hartree, Proc. Roy. Soc. (London) **A141**, 282 (1937); D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A157**, 490 (1936).

[20] M. Fallot, Ann. phys. **6**, 305 (1936); see also C. Kittel, Revs. Modern Phys. **21**, 541 (1949).

[21] Williams, Bozorth, and Shockley, Phys. Rev. **75**, 155 (1949).

$n=0$) satisfies

$$\sum_n \left(0n\left|\frac{2}{|\mathbf{r}-\mathbf{r}'|}\right|n0\right)_0=\frac{1}{N}\sum_{kk'}\left(\mathbf{kk}'\left|\frac{2}{|\mathbf{r}-\mathbf{r}'|}\right|\mathbf{k}'\mathbf{k}\right)_0 \quad \text{(I.2)}$$

$$=2.31/r_e \text{ rydbergs,}$$

where r_e is the radius in Bohr units of the sphere whose volume equals the volume per electron.[22]

It can be verified that the term $n=0$ contributes only a little over half of this sum. For by (16)

$$\left(00\left|\frac{2}{|\mathbf{r}-\mathbf{r}'|}\right|00\right)$$

$$=\text{self energy of } (\Omega N)^{-1}\sum_{kk'}\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}]$$

$$=(8\pi/\Omega N)\sum_{kk'}G(|\mathbf{k}-\mathbf{k}'|)/|\mathbf{k}-\mathbf{k}'|^2,$$

where $NG(|k-k'|)$ is the number of pairs of occupied states $\mathbf{k}, \mathbf{k}'$ which have a given value of $(\mathbf{k}-\mathbf{k}')$. A simple geometrical calculation gives

$$G(k)=1-(3k/4k_{\max})+(k^3/16k_{\max}{}^3).$$

When this is inserted into the preceding equation the double integrations can all be carried out analytically, and give the result

$$\left(00\left|\frac{2}{|\mathbf{r}-\mathbf{r}'|}\right|00\right)=66k_{\max}/35\pi=1.45/r_e. \quad \text{(I.3)}$$

Since all the terms in (I.1) are positive, we underestimate $(E-E_0)$ if we assume that the entire difference between (I.2) and (I.3) is due to those terms in whose $\mathbf{R}_n$ are nearest neighbors to the origin site. Therefore

$$A=\frac{E-E_0}{\Omega(d\bar{\varphi}/dz)^2}\geq\frac{N\bar{Z}_n{}^2}{8\Omega}\left(\frac{0.86}{r_e}\right), \quad \text{(I.4)}$$

where $\bar{Z}_n{}^2$ is the mean square distance of nearest neighbors in the z direction. For body-centered and face-centered cubic lattices the right of (I.4) has the values $0.026/r_e{}^2$ and $0.028/r_e{}^2$, respectively.

APPENDIX II. SOLUTION OF THE INTEGRAL EQUATION (21)

Equation (21) was derived by minimizing an expression equivalent to

$$\int_{S_1}\int_{S_1}\frac{(\xi-\xi')^2}{|\mathbf{y}-\mathbf{y}'|^2}d\mathbf{y}d\mathbf{y}'+8\pi^2\frac{d\bar{\varphi}}{dz}\int_{S_1}\xi\cdot\mathbf{y}d\mathbf{y}, \quad \text{(II.1)}$$

the ξ of (21) being merely the z component of the ξ of (II.1). Equation (22) becomes $\xi=R(y)\mathbf{y}/y$. The first integral in (II.1), which we may call I, is equal to twice the corresponding integral taken over the region of $\mathbf{yy}'$ space where $y\leq y'$. Throughout this region we may expand $1/|\mathbf{y}-\mathbf{y}'|$ as a series in Legendre functions of the cosine of the angle θ between $\mathbf{y}$ and $\mathbf{y}'$. Squaring this series and inserting it in I, only terms in $P_n{}^2$ and $P_nP_{n\pm1}$ will give a nonvanishing result after integration on θ. The result is

$$I=32\pi^2\sum_{n=0}^{\infty}\left[\frac{2}{(2n-1)(2n+3)}\int_0^1 R^2y^3dy\right.$$
$$-\frac{1}{(4n^2-1)}\int_0^1 R^2y^{2n+2}dy-\frac{2(2n+2)}{(2n+1)(2n+3)}$$
$$\left.\times\int_0^1\int_0^{y'}RR'(y^{2n+3}/y'^{2n+1})dydy'\right]. \quad \text{(II.2)}$$

Inserting a trial function of the form $R=ay+by^3$ into (II.1) and (II.2) there results a quadratic expression in a and b, with coefficients which are infinite series of terms containing products of factors of the type $(2n+s)$ in the denominator. These series can be summed by decomposing the general term into partial fractions. The choice of a and b which minimizes the quadratic resulting from (II.1) is $a=-243\gamma/610$, $b=-9\gamma/122$, where γ is given by (24). Since, as Fig. 1 shows, the cubic term in R is rather small compared to the linear one, and since an independent calculation using a linear trial function $R=a'y$ gives almost the same value for (II.1) as when the cubic term is included, it is likely that this approximate solution is quite close to the true one. The evaluation of I assuming $R=a'y$, or $\xi=a'y$, is very easy, of course, since the integrand becomes unity and $I=(4\pi/3)^2$.

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[22] See, for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), No. 75.