### Hall Effect in Ferromagnetics<sup>\*</sup>

ROBERT KARPLUS,<sup>†</sup> Department of Physics, University of California, Berkeley, California

AND

J. M. LUTTINGER, Department of Physics, University of Michigan, Ann Arbor, Michigan (Received May 21, 1954)

Both the unusually large magnitude and strong temperature dependence of the extraordinary Hall effect in ferromagnetic materials can be understood as effects of the spin-orbit interaction of polarized conduction electrons. It is shown that the interband matrix elements of the applied electric potential energy combine with the spin-orbit perturbation to give a current perpendicular to both the field and the magnetization. Since the net effect of the spin-orbit interaction is proportional to the extent to which the electron spins are aligned, this current is proportional to the magnetization. The magnitude of the Hall constant is equal to the square of the ordinary resistivity multiplied by functions that are not very sensitive to temperature and impurity content. The experimental results behave in such a way also.

### I. INTRODUCTION

**I**<sup>T</sup> is well known that the Hall effect in ferromagnetic and strongly paramagnetic substances shows some quite anomalous characteristics. In recent years Pugh and his collaborators<sup>1</sup> have done much to clarify the experimental situation. This may be summarized in the following way: if one uses instead of the external magnetic field  $H_0$  an "effective" field  $H_e$ , then the Hall effect in ferromagnetics behaves very much like the Hall effect in other metals as far as order of magnitude goes. The effective field is given by

# $H_e = H_0 + 4\pi M \alpha$ ,

where M is the macroscopic magnetization of the sample and  $\alpha$  is a parameter. The entire anomalous behavior is buried in  $\alpha$ . Wannier<sup>2</sup> has shown that one may expect an effective internal field due to the magnetization of  $2\pi(1+p)M$ , where p measures the relative probability of a conduction electron penetrating into the interior of a polarized electron. Thus  $p \gtrsim 1$  at most and one would expect a constant  $\alpha$  of the order of unity. Experimentally  $\alpha$  is extremely temperature dependent and can be considerably larger than unity. In very pure nickel, for example,  $\alpha$  varies from 1 at very low temperatures<sup>3</sup> to about 100 at the Curie temperature. It is this huge magnitude and strong temperature dependence which has remained a puzzle until now.

It is convenient to express the experimental results a little differently. From the foregoing, the Hall field  $e_H$ per unit current density is

$$e_H = R_0 H_e = R_0 (H_0 + 4\pi M\alpha), \qquad (1.1)$$

† On leave of absence from Harvard University, Cambridge, Massachusetts.

where  $R_0$  is the "ordinary" Hall coefficient. We may write this expression as

$$e_H = R_0 H_0 + R_1 M, \tag{1.2}$$

where  $R_1 = 4\pi \alpha R_0$  is called the "extraordinary" Hall constant. To separate the anomalous part we write Eq. (1.2),

$$e_{H} = R_{0} [H_{0} + 2\pi (1 + p)M] + R_{1}'M, \qquad (1.3)$$

 $R_1' = R_1 - R_0 2\pi (1 + p)$ .  $R_1'$  describes only the anomalous effects. We shall be concerned with the calculation of  $R_1'$ , which differs only insignificantly from  $R_1$  at all but the very lowest temperatures.

In this paper we shall show that it is possible to understand all the unusual properties of  $R_1'$  (or  $\alpha$ ) as a consequence of the spin-orbit interaction of the magnetic electrons. The principle of the method is very simple. As a result of the spin-orbit interaction the stationary states of the system acquire a left-right asymmetry. When an external electric field is applied there results a current perpendicular both to the field and to the mean direction of spin of the particles. This current will therefore be proportional to the magnetization and its coefficient will yield  $R_1'$  or  $\alpha$ . The result will depend in an intricate way on the Bloch functions of the electrons in a ferromagnetic. It is therefore only possible to make rough estimates of the final answer. Reasonable estimates, however, give results in excellent qualitative agreement with experiment.

### **II. METHOD OF CALCULATION**

We now must develop a formalism capable of dealing with the consequences of spin-orbit interaction. The Hamiltonian  $\mathcal{R}_T$  of an electron is a sum of three terms

$$\mathfrak{K}_T = \mathfrak{K}_0 + \mathfrak{K}' + \mathfrak{K}'';$$
 (2.1)

 $\mathcal{K}_0 = p^2/2m + V(\mathbf{r})$  is the Hamiltonian of an electron in the crystal potential energy  $V(\mathbf{r})$ ;  $\mathfrak{K}' = [\boldsymbol{\sigma} \times \boldsymbol{\nabla} V(\mathbf{r})] \cdot \mathbf{p}/\mathbf{r}$  $4m^2c^2$  is the spin-orbit interaction,<sup>4,5</sup>  $\sigma$  being the Pauli

<sup>\*</sup> This work was assisted in part by the U.S. Office of Naval Research and the U.S. Signal Corps.

<sup>&</sup>lt;sup>1</sup>An excellent recent summary on the ferromagnetics may be found in E. M. Pugh and N. Rostoker, Revs. Modern Phys. 25, 151 (1953). The strongly paramagnetic rare earths have been investigated by Kevane, Legvold, and Spedding, Phys. Rev. 91, 1372 (1953). <sup>2</sup> G. Wannier, Phys. Rev. 72, 304 (1947).

<sup>&</sup>lt;sup>8</sup> E. M. Pugh (private communication).

<sup>&</sup>lt;sup>4</sup> Units have been chosen such that  $\hbar = 1$ . <sup>5</sup> See for example D. Bohm, *Quantum Theory* (Prentice-Hall, Inc., New York, 1951), p. 405. Spin-orbit interaction has been

matrix vector. If the electrons are polarized (say by exchange forces) in the direction of the magnetization, the average value of  $\mathcal{H}'$  for a magnetic electron is

$$3C' = \frac{1}{4m^2c^2} \frac{(\mathbf{M} \times \boldsymbol{\nabla} V) \cdot \mathbf{p}}{M_s}, \qquad (2.2)$$

where  $M_s$  is the magnetization one would have if the magnetic electrons were lined up to their maximum extent. For other electrons  $\mathcal{K}'$  averages to zero.  $\mathcal{K}'' = -e\mathbf{E}\cdot\mathbf{r}$  is the Hamiltonian of the electrons in the external electric field E.

Since  $V(\mathbf{r})$  is periodic and p is translationally invariant,  $\mathfrak{K} \equiv \mathfrak{K}_0 + \mathfrak{K}'$  will have stationary solutions which are of the form of Bloch waves, and whose energy levels fall into bands. Let us label the states of  $\mathfrak{K}$  by an index l which tells the band (n) and the pseudomomentum  $(\mathbf{k})$ , i.e.,  $l \equiv (n, \mathbf{k})$ . Call these stationary states  $\phi_l$  and the corresponding energy  $\epsilon_l$ ;

$$\Im \mathcal{C} \phi_l = (\Im \mathcal{C}_0 + \Im \mathcal{C}') \phi_l = \epsilon_l \phi_l. \tag{2.3}$$

The  $\phi_l$  are chosen normalized over the entire crystal; that is,

$$(\phi_{l},\phi_{l'}) = \int_{\Omega} \phi_{l}^{*}(\mathbf{r})\phi_{l'}(\mathbf{r})d^{3}x = \delta_{ll'}, \qquad (2.4)$$

 $\Omega$  being the volume of the crystal.

It is now necessary to compute the effect of the spinorbit coupling on the transverse conductivity of the substance. The usual theory of conductivity based on the Boltzmann transport equation<sup>6</sup> proves to be insufficient for our purposes, yielding in fact a vanishing result (Appendix A). To see the necessary extension let us consider the interaction  $\mathcal{K}''$  with the electric field in detail. In the representation based on the wave functions  $\phi_i$ , the matrix elements of  $\mathcal{K}''$  may be written

$$(n\mathbf{k}|3\mathcal{C}''|n'\mathbf{k}') = -eE_{b}(n\mathbf{k}|x_{b}|n'\mathbf{k}')$$
$$= -eE_{b}\left\{i\delta_{nn'}\frac{\partial}{\partial k_{b}}\delta_{\mathbf{kk}'} + i\delta_{\mathbf{kk}'}J_{b}^{nn'}(\mathbf{k})\right\}, \quad (2.5)$$

where

$$J_{b^{nn'}}(\mathbf{k}) = \int_{\Omega} w_{nk}^{*}(\mathbf{r}) \frac{\partial}{\partial k_{b}} w_{n'k}(\mathbf{r}) d^{3}x,$$
  
$$J_{b^{nn}}(\mathbf{k}) = J_{b}(l) \neq 0,$$
 (2.6)

with  $\phi_l = e^{i\mathbf{k}\cdot\mathbf{r}}w_{n\mathbf{k}}(\mathbf{r})$  (see Appendix B). This second term in the expression for  $\mathcal{K}''$  is completely regular.

It is usually ignored because in the absence of spinorbit coupling the only effects of it are second order in the electric field  $E_b$  and thus of no interest for the conductivity problem. We shall show that actually it is entirely responsible for the anomalous Hall effect. Since it has nonvanishing matrix elements only if k = k', it represents a periodic potential. Let us write

$$\mathfrak{K}'' = \mathfrak{K}_1'' + \mathfrak{K}_i'', \qquad (2.7)$$

where  $\mathfrak{W}_{1}^{\prime\prime}$  is the regular periodic perturbation whose matrix elements are  $-ie\delta_{\mathbf{k}\mathbf{k}'}E_bJ_b{}^{nn'}(\mathbf{k})$  and  $\mathfrak{W}_{i}^{\prime\prime}$  is the singular operator responsible for the usual conductivity effects. It is easy to see by direct computation that in any representation with Bloch functions  $H_{i}^{\prime\prime}$ has the same form and  $H_{1}^{\prime\prime}$  transforms according to the usual transformation theory. Hence the decomposition is unique. We therefore introduce the periodic Hamiltonian,

$$\mathfrak{K}_p = \mathfrak{K} + \mathfrak{K}_1'', \qquad (2.8)$$

whose eigenfunctions comprise the stationary oneelectron states.  $H_i''$  causes transitions among these states and must be treated by time-dependent methods together with the effects of the lattice vibrations.

The electron distribution is described by the density matrix<sup>7</sup>  $\rho$  which consists of two parts,

$$\rho = \rho_0(\mathfrak{R}_p) + \rho_1, \qquad (2.9)$$

where  $\rho_0(\mathfrak{SC}_p)$  is the Fermi distribution at the lattice temperature T,

$$\rho_0(\mathcal{K}_p) = \{ \exp[(\mathcal{K}_p - E_F)/kT] + 1 \}^{-1}, \ \operatorname{Tr}\{\rho_0\} = 1, \ (2.10)$$

and  $\rho_1$  contains the deviation from thermal equilibrium caused by the combined effect of  $\mathcal{C}_i''$  and collisions with the lattice. It leads only to the ordinary conductivity formula discussed in Appendix A. The Hall effect must therefore be contained in the average velocity

$$\bar{v}_a = \operatorname{Tr}\{\rho_0 v_a\},\tag{2.11}$$

where  $v_a$  is the velocity operator,

$$v_a = i [\mathfrak{K}_T, x_a] = i [\mathfrak{K}, x_a] = i [\mathfrak{K}_p, x_a] - i [\mathfrak{K}_1'', x_a]. \quad (2.12)$$

The first term in  $v_a$  averages to zero because

$$\operatorname{Tr}\{\rho_0(\mathcal{K}_p)[\mathcal{K}_p, x_a]\} = \operatorname{Tr}\{[\rho_0(\mathcal{K}_p), \mathcal{K}_p]x_a\} \equiv 0. \quad (2.13)$$

In the calculation of the second term, which is already linear in the electric field, one may use the distribution function  $\rho_0(3\mathfrak{C})$  and the wave functions  $\phi_i$  in the absence of the field to calculate the average velocity,

$$\bar{v}_{a} = -i \operatorname{Tr}\{\rho_{0}(3\mathbb{C})[\mathbb{C}\mathbb{C}_{1}'', x_{a}]\} = -i \operatorname{Tr}\{[x_{a}, \rho_{0}(3\mathbb{C})]\mathbb{C}_{1}''\}$$

$$= -i \sum_{n\mathbf{k}} (n\mathbf{k} | [x_{a}, \rho_{0}(3\mathbb{C})] | n\mathbf{k}) (n\mathbf{k} | \mathbb{C}_{1}'' | n\mathbf{k})$$

$$-i \sum_{n\mathbf{k}} \sum_{n' \neq n} (n\mathbf{k} | [x_{a}, \rho_{0}(3\mathbb{C})] | n'\mathbf{k}) \times (n'\mathbf{k} | \mathbb{C}_{1}'' | n\mathbf{k}). \quad (2.14)$$

<sup>7</sup> See R. C. Tolman, *Principles of Statistical Mechanics* (Oxford University Press, New York, 1930), Chap. IX.

proposed previously for this problem by A. Samoilovich and U. Kon'Kov, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, 782 (1950). However, their treatment of the spin-orbit interaction which neglects the fact that it has the lattice periodicity is quite incorrect and consequently leads to a temperature-independent  $\alpha$ , in conflict with experiment.

conflict with experiment. <sup>6</sup> N. F. Mott and H. Jones, *Theory of the Properties of Metals* and Alloys (The Clarendon Press, Oxford, 1936), pp. 189 ff.

The sum over the diagonal matrix elements in Eq. (2.14) can be simplified with the help of the formula in Appendix C and the definition of  $\Im C_1''$  to yield  $(\rho' = \partial \rho / \partial \epsilon)$ 

$$-ieE_b\sum_l \rho_0'(\epsilon_l)v_a(l)J_b(l). \qquad (2.15)$$

The sum over the off-diagonal elements, on the other hand, does not involve any singular matrix elements at all. If the  $J^{nn'}(k)$  are used to express the matrix elements of  $x_a$  and  $\mathfrak{R}_1''$ , this sum becomes equal to

$$ieE_b \sum_{l} \rho_0(\epsilon_l) \sum_{n'} \{J_a^{nn'}(\mathbf{k})J_b^{n'n}(\mathbf{k}) -J_b^{nn'}(\mathbf{k})J_a^{n'n}(\mathbf{k})\}. \quad (2.16)$$

The sum has now been extended to include the term n'=n which vanishes because  $J^{nn}$  is finite. The completeness of the functions  $w_{nk}(\mathbf{r})$  implies that

$$\sum_{n'} J_{b}^{nn'}(\mathbf{k}) J_{a}^{n'n}(\mathbf{k})$$

$$= -\int_{\Omega} \frac{\partial w_{n\mathbf{k}}^{*}(\mathbf{r})}{\partial k_{b}} (\sum_{n'} w_{n'\mathbf{k}}(\mathbf{r}) w_{n'\mathbf{k}}^{*}(\mathbf{r}')) \frac{\partial w_{n\mathbf{k}}(\mathbf{r}')}{\partial k_{a}} d^{3}x d^{3}x'$$

$$= -\int_{\Omega} \frac{\partial w_{n\mathbf{k}}^{*}(\mathbf{r})}{\partial k_{b}} \frac{\partial w_{n\mathbf{k}}(\mathbf{r})}{\partial k_{a}} d^{3}x$$

$$= -\frac{\partial}{\partial k_{b}} J_{a}(l) + \int_{\Omega} w_{n\mathbf{k}}^{*}(\mathbf{r}) \frac{\partial^{2}}{\partial k_{a}\partial k_{b}} w_{n\mathbf{k}}(\mathbf{r}) d^{3}x. \quad (2.17)$$

Since only the antisymmetric part of the product enters in Eq. (2.16), the second term cancels and leaves us with

$$-ieE_b\sum_{l}\rho_0'(\epsilon_l)[v_b(l)J_a(l)-v_a(l)J_b(l)], \quad (2.18)$$

after an integration by parts with respect to k. If we add this result to Eq. (2.15), we obtain the average velocity

$$\bar{v}_a = -ieE_b \sum_l \rho_0'(\epsilon_l) v_b(l) J_a(l). \qquad (2.19)$$

Formally speaking, we may say that our effect arises from the consideration of the interband matrix elements of the electric interaction and of the velocity operator, whereas the usual theory only treats the intraband matrix elements.

In the next section we shall show that the transverse current contained in Eq. (2.19) is perpendicular to both the magnetization and the electric field and that it vanishes in the absence of the spin orbit coupling. We can therefore write

$$J_y = rM_z E_x, \qquad (2.20)$$

where r is obtained by carrying out the summation over matrix elements in Eq. (2.14). From its structure we can see that r depends on temperature only weakly through the distribution function  $\rho_0(\epsilon_l)$ . If we therefore express the Hall voltage which prevents a current from flowing in the y direction,

$$E_y = -\rho J_y (\rho = \text{resistivity}),$$
 (2.21)

as a voltage per unit current density,

$$e_H = E_y / J_x = -\rho r M_z E_x / J_x = -\rho^2 r M_z,$$
 (2.22)

we see that the Hall constant  $R_1' = -\rho^2 r$  should depend strongly on temperature like the square of the resistivity. Such a temperature dependence is actually the most striking feature of the experimentally determined Hall constants  $R_1$ . It follows in our theory from the approximate constancy of r. We now turn to an estimate of the magnitude of the extraordinary Hall effect.

# III. THE HALL EFFECT FORMULA

The first step is to express the  $J_a(l)$  in terms of the eigenfunctions  $\psi_l = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$  and eigenvalues  $\epsilon_l^0$  of the electrons unperturbed by spin-orbit coupling. The matrix element in this representation will be denoted by a subscript zero. First-order perturbation theory on the energy gives  $\epsilon_l = \epsilon_l^0$  (Appendix D), while the wave function is

$$w_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}) + \sum_{n' \neq n} u_{n'\mathbf{k}}(\mathbf{r}) (n'\mathbf{k} | \mathfrak{IC}' | n\mathbf{k})_0 / \epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}, \quad (3.1)$$

since the periodic character of 3C' gives matrix elements only between states with the wave vector **k**. From now on all equations will have a common index **k** which we shall suppress, writing Eq. (3.1), for example,

$$w_n = u_n + \sum_{n'} u_{n'} (n' | \mathcal{C}' |_n)_0 / \epsilon_n - \epsilon_{n'}. \qquad (3.2)$$

Substitution in the definition of  $J_a(l)$  gives

$$J_{a}(l) = 2 \sum_{n' \neq n} I_{a}^{nn'}(n' | \mathfrak{K}' | n)_{0} / \omega_{nn'}, \qquad (3.3)$$

where

$$I_{a^{nn}} = 0, \quad \omega_{nn'} = \epsilon_n - \epsilon_{n'},$$

$$I_{a^{nn'}} = \int_{\Omega} u_n^* \frac{\partial u_{n'}}{\partial k_a} d^3x$$

$$= -(n | p_a | n')_0 / m \omega_{nn'} (n \neq n'). \quad (3.4)$$

 $I_a^{nn'}$  is the same as  $J_a^{nn'}$  except that it is evaluated with the functions  $u_n$  in the absence of spin-orbit coupling. It is discussed in Appendix D.

These expressions used in Eq. (3.3) finally yield the formula,

$$\bar{v}_{a} = -2ieE_{b}\sum_{l}\rho_{0}{'}(\epsilon_{l})\sum_{n'\neq n}v_{a}(l)(n|p_{b}|n')_{0} \times (n'|\mathcal{SC}'|n)_{0}\omega_{nn'}^{-2}, \quad (3.5)$$

in which no approximations have been made other than the use of perturbation theory.

To proceed further with Eq. (3.5) one has to make additional and cruder approximations. The magnetic electrons belong to different "d bands" made up of the fivefold degenerate d state of the free atom. Let n be in one of these d bands. Then we would expect that those  $n' \ (\neq n)$  which are also in d bands contribute most to Eq. (3.5). If n' represents a higher band (say the "s band") where the electrons are almost free,  $(n'|p_b|n)_0$  is almost zero, since it is exactly zero for n'representing a band where the electrons are free. On the other hand for n' in a lower band the matrix elements are approximately just those for transitions of the isolated atoms, and therefore independent of k. For these though the sum over k vanishes, since  $\sum_l \rho_0'(l)v_a(l)=0$ . We shall then assume that the main contribution to the n' sum in Eq. (3.5) comes from transitions between the "d bands." Assuming this, we may replace  $\omega_{nn'}^2$  by  $\Delta^2$ , where  $\Delta^2$  is some mean square energy separation between different d bands for the same  $\mathbf{k}$  at the top of their Fermi surfaces. Thus Eq. (3.5) becomes

$$\bar{v}_{a} = -\frac{2ieE_{b}}{m\Delta^{2}} \sum_{l(d)} \rho_{0}'(l) \sum_{n' \neq n} v_{a}(l)(n \mid p_{b} \mid n')_{0} \times (n' \mid 3C' \mid n)_{0}, \quad (3.6)$$

where the sum over *l* only covers the polarized *d* bands. Using  $(u \mid t \mid u')_{0} = (u' \mid t \mid u)_{0}$ 

and

$$(n | p_a| n)_0 - (n' | p_a| n)_0$$
$$(n | 3C' | n')_0 = -(n' | 3C' | n)_0,$$

we can rewrite Eq. (3.6),

$$\bar{v}_{a} = -\frac{eE_{b}}{\Delta^{2}m} \sum_{l(d)} \rho_{0}{}'(l) (n | i [ \mathfrak{IC}', p_{a} ] | n)_{0} v_{b}(l). \quad (3.7)$$

Equation (3.7) may be put into a much more transparent form, since the quantity  $(n|i[\mathfrak{K}',p_a]|n)_0$  is just the expectation value of the force due to spin-orbit interaction on an electron in an unperturbed state *l*. To see this we write the *a* component of the force  $F_a$  as

$$F_a = i[3C, mv_a] = i[3C_0, mv_a] + i[3C', p_a],$$

to the first order in 3C'. Then

$$(n | F_a| n)_0 = (n | i [\mathfrak{M}_0, mv_a] | n_0 + (n | i [\mathfrak{M}', p_a] | n)_0 = (n | i [\mathfrak{M}', p_a] | n)_0 \equiv F_a(l), \quad (3.8)$$

since the diagonal matrix elements in the  $\mathfrak{K}_0$  representation of the commutator of  $\mathfrak{K}_0$  with a regular operator vanish. Therefore substitution of Eq. (3.8) into Eq. (3.7) gives

$$\bar{v}_{a}' = -\frac{eE_{b}}{\Delta^{2}m} \sum_{l(d)} \rho_{0}'(l) F_{a}(l) v_{b}(l), \qquad (3.9)$$

the entire result being expressed by averages within a band. Equation (3.9) may also be written as the vector equation,

$$\bar{\mathbf{v}} = -\frac{e}{m\Delta^2} \sum_{l(d)} \rho_0'(\epsilon_l) [\mathbf{E} \cdot \mathbf{v}(l)] \mathbf{F}(l), \qquad (3.10)$$

which shows that the additional current is in the direction of the spin-orbit force.

#### **IV. CONCLUSIONS**

For the final evaluation of the spin-orbit contribution to the Hall effect one must estimate Eq. (3.10). The chief difficulty is that the wave functions are so poorly known that it is impossible to find a really reliable estimate for F(l). A very rough estimate however can be obtained by setting

$$\mathbf{F}(l) = + (e/c) [\mathbf{v}(l) \times \mathbf{H}], \qquad (4.1)$$

where H is of the order of the mean value of the magnetic field giving rise to the spin-orbit interaction<sup>8</sup> times the ratio of the magnetization to saturation magnetization [see Eq. (2.2)],

$$\mathbf{H} = H_{s.o.} \mathbf{M} / M_s. \tag{4.2}$$

We obtain

$$\bar{\mathbf{v}} = -\frac{e^2}{\Delta^2 mc} H_{\text{s.o.}} \mathbf{E} \cdot \left[\sum_{l(d)} \mathbf{v}(l) \rho_0'(\epsilon_l) \mathbf{v}(l)\right] \times \mathbf{M}/M_s. \quad (4.3)$$

Comparison with Appendix A reveals that the sum in Eq. (4.3) is just the same one as that which occurs in the ordinary conductivity tensor. In a cubic crystal it is diagonal and

$$\bar{\mathbf{v}} = \frac{e^2}{\Delta^2 mc} H_{\text{s.o.}} \frac{\mathbf{M} \times \mathbf{E}}{M_s} \sum_{l(d)} \rho_0'(\epsilon_0) v_x^{\ 2}(l). \tag{4.4}$$

The velocity is perpendicular to both the electric and magnetic fields. It therefore represents a Hall effect. With the electric and magnetic fields in the x and z directions, respectively, the velocity has only a y component. Hence the resultant transverse current is

$$J_y = N_d e \bar{v}_y = r M_z E_x, \qquad (4.5)$$

where  $N_d$  is the total number of magnetic electrons contributing to the current; the constant of proportionality r defined in Eq. (2.20) is

$$r = -\frac{e^3}{mc\Delta^2} H_{\rm s.o.} \frac{N^d}{M_s} \sum_{l(d)} \rho_0'(\epsilon l) v_x^{\ 2}(l).$$
(4.6)

The sum can be simplified by the usual methods employed in discussions of the conductivity. It yields

$$-\sum_{l(d)} \rho_0'(l) v_x^2(l) = \delta \left\langle \frac{1}{m^*} \right\rangle_{d \text{ Av}}, \qquad (4.7)$$

where  $m^*$  is the effective mass and  $\delta$  is the number of incompletely filled d bands.<sup>9</sup> The maximum possible

<sup>&</sup>lt;sup>8</sup> This field can be estimated by the condition that it should produce the correct separation for the spin-orbit doublets. Since for Fe or Ni these separations are of the order of 500 cm<sup>-1</sup> or  $10^{-13}$  erg, we have  $H_{s.o.}\mu_B \sim 10^{-13}$ ,  $H_{s.o.} \sim 10^7$  gauss. <sup>9</sup> The effective mass has been discussed in connection with the

<sup>&</sup>lt;sup>9</sup> The effective mass has been discussed in connection with the large electronic heat capacity of transition metals [F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 153 ff.] In our notation, the effective mass  $m_t$  of the electrons near the top of the Fermi distribution can be written  $m_t = \delta \langle m^* \rangle_{dAv}$  or  $\langle 1/m^* \rangle_{dAv} \sim \delta / m_t$  if only a narrow band of levels is either occupied or unoccupied.



FIG. 1. Experimental results for iron. The equation of the straight line is  $R'=0.7\times 10^{-10} (\rho/\rho_0)^{1.94}$ , with  $\rho_0=10$  micro-ohm cm.

magnetization  $M_{*}$  is equal to

$$M_s = e N_d / 2mc \Omega. \tag{4.8}$$

As a result Eq. (4.6) yields the extraordinary Hall constant

$$R_1' = \frac{2e^2 H_{\text{s.o.}}}{m\Delta^2} \delta \left\langle \frac{m}{m^*} \right\rangle_{d\,kv} \rho^2. \tag{4.9}$$

If we know the ordinary Hall constant  $R_0$ , we may compute the field parameter  $\alpha(\alpha \gg 1)$  from

$$\alpha = \frac{R_1'}{4\pi R_0} = \delta \left\langle \frac{m}{m^*} \right\rangle_{d \text{ }_{N}} \frac{e^2 H_{\text{s.o.}}}{m \Delta^2 R_0} \rho^2$$
$$\cong 0.7 \times 10^{-7} \left\langle \frac{m}{m^*} \right\rangle_{d \text{ }_{N}} \frac{H_{\text{s.o.}}}{\Delta^2 R_0} \rho^2 \delta, \quad (4.10)$$

where  $H_{\text{s.o.}}$ ,  $\Delta$ ,  $R_0$ , and  $\rho$  are expressed in the usual units: gauss, electron volts, volt cm/amp gauss, and ohm cm, respectively. To get an idea of the magnitude of  $\alpha$ , we insert the measured values  $H_{\text{s.o.}} \sim 10^7$  gauss,<sup>8</sup>  $\Delta \sim 2 \text{ ev}$ ,<sup>10</sup>  $R_0 \sim \frac{1}{2} \times 10^{-12}$  volt cm/amp gauss,  $\rho(0^\circ) \sim 10^{-5}$ ohm cm= $\rho_0$ ,  $\delta \sim 3$  and  $\langle m/m^* \rangle_{d \, k'} \sim 1/10$ :

$$\alpha(0^{\circ}C) \sim 10,$$
 (4.11)

at room temperature, which agrees quite well with the observed values for Fe and Ni.

Actually from the entire calculation we see that the quantity  $4\pi M\alpha$  is not really an effective field at all, and the anomalous temperature dependence arises solely out of our desire to write the effect as we would an ordinary Hall effect. It is therefore more natural perhaps to compare  $R_1'$  with experiment, since that is

what one actually measures. Then Eq. (4.9) becomes

 $R_1' \approx 0.7 \times 10^{-10} (\rho/\rho_0)^2$  volt cm/amp gauss. (4.12) The most striking prediction of our theory is the fact that the extraordinary Hall coefficient should be proportional to the square of the resistivity. If one takes the measurements of Jan,<sup>11</sup> Jan and Gijsman,<sup>12</sup> and Butler and Pugh,<sup>13</sup> Figs. 1 and 2, one finds

and

$$R_1' = 1.3 \times 10^{-10} (\rho_T / \rho_0)^{1.42}$$
 for Ni

 $R_1' = 0.7 \times 10^{-10} (\rho_T / \rho_0)^{1.94}$  for Fe,

For iron especially the agreement is excellent, though for nickel it is only qualitatively right. The agreement is good enough however to convince us that we have found the proper mechanism of the extraordinary Hall effect. The deviations from straight lines to low Hall constant values have to do with the fact that  $R_1$  and  $R_1'$  differ significantly in this region.  $R_1'$ , of course, will be less than  $R_1$ , and may be no more than one-half as big.

We should like to thank C. Kittel, who called this problem to our attention, for many stimulating discussions. One of us (J. M. Luttinger) would also like to thank the staff of the Physics Department of the University of California for their hospitality during the summer of 1953, where this work was begun.

# APPENDIX A

The transport theory result<sup>6</sup> for the average velocity of an electron in a crystal subject to an electric field E is

$$\bar{v}_{a} = -eE_{b}\tau \sum_{l} \rho_{0}'(\epsilon_{l}) \frac{\partial \epsilon_{l}}{\partial k_{b}} v_{a}(l), \qquad (A.1)$$



FIG. 2. Experimental results for nickel. The equation of the straight line is  $R' = 1.3 \times 10^{-10} (\rho/\rho_0)^{1.42}$ , with  $\rho_0 = 10$  micro-ohm cm.

<sup>11</sup> J.-P. Jan, Helv. Phys. Acta. 25, 677 (1952).

<sup>12</sup> J.-P. Jan and J. M. Gijsman, Physica 18, 339 (1952).

<sup>13</sup> E. H. Butler and E. M. Pugh, Phys. Rev. 57, 916 (1940).

<sup>&</sup>lt;sup>10</sup> G. C. Fletcher, Proc. Phys. Soc. (London) A65, 192 (1952).

where v(l) and  $\epsilon_l$  are the diagonal elements of the velocity and Hamiltonian operators including spin-orbit coupling in the state l;  $\rho_0(\epsilon_l)$  is the Fermi distribution function at the lattice temperature. It is shown in Appendix C that

$$v_a(l) = \partial \epsilon_l / \partial k_a \tag{A.2}$$

in the general case of an electron subject to a periodic Hamiltonian. This applies in our case because the spinorbit interaction is periodic. Any spin-orbit effects on the current through the velocity in Eq. (A.1) therefore depend on the energy shifts caused by this perturbation. Since the first-order effect of the spin-orbit coupling on the energy vanishes (Appendix D), there is no linear dependence on the magnetization in Eq. (A.1), and this expression can never contain a Hall effect.

#### APPENDIX B. PROPERTIES OF THE VELOCITY AND COORDINATE MATRICES

The velocity operator is given by the rate of change of the corresponding coordinate

$$v_a = i [\mathfrak{H}, x_a]. \tag{B.1}$$

When 3C is given by Eq. (4), then

$$v_a = \frac{p_a}{m} + \frac{1}{4m^2c^2} \frac{(\mathbf{M} \times \boldsymbol{\nabla} V)_a}{M_s}.$$
 (B.2)

Since  $p_a$  and V both have the lattice periodicity,  $v_a$  will only connect states with the same k. Further, all the operators in Eq. (B.2) are regular in the sense that they have diagonal matrix elements for Bloch functions. If we express the velocity matrix in terms of the co-ordinate matrix, we get

$$(l | v_a | l') = i \omega_{ll'} (l | x_a | l'),$$
 (B.3)

from Eq. (B.1). This equation is not very convenient for the diagonal elements, since those of  $x_a$  do not exist, strictly speaking. However, for off-diagonal elements (that is, interband matrix elements) it is useful since in this case  $(l|x_a|l')$  may be expressed simply.

In general we may write:

$$(n\mathbf{k} | x_{a} | n'\mathbf{k}')$$

$$= \int_{\Omega} e^{-i\mathbf{k}\cdot\mathbf{r}} w_{n\mathbf{k}}^{*} x_{a} e^{i\mathbf{k}\cdot\mathbf{r}} w_{n'\mathbf{k}'} d^{3}x$$

$$= \int_{\Omega} e^{-i\mathbf{k}\cdot\mathbf{r}} w_{n\mathbf{k}}^{*} \frac{1}{i} \frac{\partial e^{i\mathbf{k}\cdot\mathbf{r}}}{\partial k_{a}'} w_{n'\mathbf{k}'} d^{3}x$$

$$= \int_{\Omega} e^{i\mathbf{k}\cdot\mathbf{r}} w_{n\mathbf{k}}^{*} \frac{1}{i} \left[ \frac{\partial}{\partial k_{a}'} (e^{i\mathbf{k}'\cdot\mathbf{r}} w_{n'\mathbf{k}'}) - e^{i\mathbf{k}'\cdot\mathbf{r}} \frac{\partial w_{n'\mathbf{k}'}}{\partial k_{a}'} \right] d^{3}x$$

$$=\frac{1}{i}\frac{\partial}{\partial k_{a}'}\int_{\Omega}\phi_{n\mathbf{k}}^{*}\phi_{n'\mathbf{k}'}d^{3}x$$

$$+i\int_{\Omega}e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}w_{n\mathbf{k}}^{*}\frac{\partial w_{n'\mathbf{k}'}}{\partial k_{a}'}d^{3}x$$

$$=-i\frac{\partial}{\partial k_{a}'}(\delta_{nn'}\delta_{\mathbf{k}\mathbf{k}'})$$

$$+i\int_{\Omega}e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}w_{n\mathbf{k}}^{*}\frac{\partial w_{n'\mathbf{k}'}}{\partial k_{a}'}d^{3}x, \quad (B.4)$$

since the  $w_{n\mathbf{k}}$  are orthonormal. However, the fact that the  $w_{n\mathbf{k}}(r)$  are periodic means that the exponential factor will cause the remaining integral to vanish unless  $\mathbf{k} = \mathbf{k}'$ . Thus

$$(n\mathbf{k} | x_a | n'\mathbf{k}') = i\delta_{nn'} \frac{\partial}{\partial k_a} \delta_{\mathbf{k}\mathbf{k}'} + iJ_a^{nn'}(\mathbf{k}), \quad (B.5)$$

where J is defined in Eq. (2.6).

imply that

## APPENDIX C

We shall prove that no matter what the nature of the interaction of the electrons and another system, so long as Bloch-like solutions,

$$\phi_{n\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}},\tag{C.1}$$

exist with energy  $\epsilon_n(\mathbf{k})$ , then the expectation value of the commutator of a function  $f(\mathcal{K})$  of the electronic Hamiltonian with the coordinate vector  $x_a$  is given by the derivative with respect to  $k_a$ ,

$$\partial f(\boldsymbol{\epsilon}_n(\mathbf{k}))/\partial k_a = +i\langle [f(\mathcal{GC}), x_a] \rangle_{n, \mathbf{k}}.$$
 (C.2)

To show this identity, we recognize that Eq. (C.1) and

$$\mathfrak{K}(\mathbf{p},\mathbf{r})\phi_{n\mathbf{k}} = \epsilon_n(\mathbf{k})\phi_{n\mathbf{k}} \qquad (C.3)$$

$$\mathfrak{K}(\mathbf{p}+\mathbf{k})u_{n\mathbf{k}} = \epsilon_n(\mathbf{k})u_{n\mathbf{k}}.$$
 (C.4)

Consequently the matrix element in Eq. (C.2) becomes

$$\begin{split} [f(\mathfrak{F}), x_{a}]\rangle_{nk} \\ &= \int d^{3}x u_{nk}^{*} e^{-i\mathbf{k}\cdot\mathbf{r}} [f(\mathfrak{F}(\mathbf{p}, \mathbf{r})) x_{a} \\ &- x_{a} f(\mathfrak{F}(\mathbf{p}, \mathbf{r}))] e^{i\mathbf{k}\cdot\mathbf{r}} u_{nk} \\ &= -i \int d^{3}x u_{nk}^{*} \frac{\partial}{\partial k_{a}} [e^{-i\mathbf{k}\cdot\mathbf{r}} f(\mathfrak{F}(\mathbf{p}, \mathbf{r})) e^{i\mathbf{k}\cdot\mathbf{r}}] u_{nk} \\ &= -i \int d^{3}x u_{nk}^{*} \frac{\partial}{\partial k_{a}} [f(\mathfrak{F}(\mathbf{p}, \mathbf{k}, \mathbf{r}))] u_{nk}. \end{split}$$
(C.5)

Because the normalization integral  $\int d^3x u_{nk}^* u_{nk} = 1$  is independent of  $k_a$ , and  $u_{nk}$  is an eigenfunction of the differentiated operator by Eq. (C.4), the derivative may be taken outside the integral. The matrix element then immediately yields Eq. (C.2). We obtain a well-known special case of the relationship if we choose

$$f(\mathfrak{FC}) = \mathfrak{FC}, \quad f(\boldsymbol{\epsilon}_n(\mathbf{k})) = \boldsymbol{\epsilon}_n(\mathbf{k}).$$
 (C.6)

Then Eq. (C.2) states

$$\langle +i[\Im c, x_a] \rangle_{n\mathbf{k}} = \langle \dot{x}_a \rangle_{n\mathbf{k}} = \langle v_a \rangle_{n\mathbf{k}} = \partial \epsilon_n(\mathbf{k}) / \partial k_a.$$
 (C.7)

In the general case we can then express the derivative in a simpler way,

$$\frac{\partial f(\boldsymbol{\epsilon}_{n}(\mathbf{k}))}{\partial k_{a}} = \frac{\partial f(\boldsymbol{\epsilon}_{n}(\mathbf{k}))}{\partial \boldsymbol{\epsilon}_{n}(\mathbf{k})} \langle \boldsymbol{v}_{a} \rangle_{n\mathbf{k}}.$$
(C.8)

#### APPENDIX D. SYMMETRY PROPERTIES

We consider here the symmetry properties of various matrix elements with respect to the eigenfunctions  $\psi_{nk}$  of 3C<sub>0</sub>. It follows at once from the reality of 3C<sub>0</sub> that one may always choose

$$\chi_{n,-k}^{*} = \chi_{n,k}, \qquad (D.1)$$

which is equivalent to time-reversal invariance. Further, if the crystal has a center of symmetry—which is true for all cases that we consider—then we also may choose

$$\chi_{n,-\mathbf{k}}(-\mathbf{r}) = \chi_{n,\mathbf{k}}(\mathbf{r}). \qquad (D.2)$$

Since H' (see Eq. (2.2)) is pure imaginary and reflection invariant, we have

$$\mathfrak{K}^{\prime *} = -\mathfrak{K}^{\prime}, \qquad (D.3)$$

$$\mathfrak{K}'(-\mathbf{r}) = \mathfrak{K}'(\mathbf{r}).$$
 (D.4)

From Eqs. (D.1) and (D.3) we obtain at once

$$(n'\mathbf{k} | \mathfrak{C}' | n\mathbf{k})_0 = \int \chi_{n'\mathbf{k}} \mathfrak{C}' \chi_{n\mathbf{k}} d^3x = \int (\mathfrak{C}' \chi_{n'\mathbf{k}})^* \chi_{n\mathbf{k}} d^3x$$
$$= \int (\mathfrak{C}'^* \chi_{n'\mathbf{k}}) \chi_{n\mathbf{k}} d^3x$$
$$= -\int (\mathfrak{C}' \chi_{n',-\mathbf{k}}) \chi_{n,-\mathbf{k}} d^3x$$
$$= -\int \chi_{n,-\mathbf{k}} \mathfrak{C}' \chi_{n',-\mathbf{k}} d^3x.$$
Thus

Thus

$$(n'\mathbf{k}|\mathcal{3C}'|n\mathbf{k})_{0} = -(n, -\mathbf{k}|\mathcal{3C}'|n', -\mathbf{k})_{0}$$
  
=  $(n', -\mathbf{k}|\mathcal{3C}'|n, -\mathbf{k})_{0}.$  (D.5)

We obtain a well-known special case of the relation- From Eqs. (D.2) and (D.4), on the other hand, we have

$$(n'\mathbf{k} | \mathbf{3C}' | n\mathbf{k})_{0} = \int \chi_{n'\mathbf{k}}^{*} \mathbf{3C}' \chi_{n'\mathbf{k}} d^{3}x$$
  
=  $\int \chi_{n',+\mathbf{k}}^{*} (-\mathbf{r}) \mathbf{3C}' (-\mathbf{r}) \chi_{n,+\mathbf{k}} (-\mathbf{r}) d^{3}x$   
=  $\int \chi_{n',-\mathbf{k}}^{*} (\mathbf{r}) \mathbf{3C}' (\mathbf{r}) \chi_{n,-\mathbf{k}} (\mathbf{r}) d^{3}x,$   
or,  
 $(n'\mathbf{k} | \mathbf{3C}' | n\mathbf{k})_{0} = (n',-\mathbf{k} | \mathbf{3C}' | n,-\mathbf{k})_{0}.$  (D.6)

Combining (D.5) with (D.6) we have

$$(n'\mathbf{k}| 3C'| n\mathbf{k})_0 = -(n\mathbf{k}| 3C'| n'\mathbf{k})_0.$$
 (D.7)

From this we see at once that the diagonal elements of 3C' vanish, and therefore there is no first-order correction to the energy due to the perturbation 3C'.

We may also use Eq. (D.1) and Eq. (D.2) to obtain some properties of the  $I_a^{nn'}(\mathbf{k})$ . By writing  $\psi_{n\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}$ , Eqs. (D.1) and (D.2) become

$$u_{n,-k}^{*} = u_{nk}, \qquad (D.8)$$

$$u_{n,-\mathbf{k}}(-\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r}). \tag{D.9}$$

From Eq. (D.8) we have

$$I_{a^{nn'}}(\mathbf{k}) = \int u_{n\mathbf{k}}^{*} \frac{\partial u_{n'\mathbf{k}}}{\partial k_{a}} d^{3}x = \int u_{n,-\mathbf{k}} \frac{\partial u_{n',-\mathbf{k}}}{\partial k_{a}} d^{3}x$$
$$= -\int u_{n,-\mathbf{k}} \frac{\partial u_{n',-\mathbf{k}}}{\partial (-k_{a})} d^{3}x = -(I_{a^{nn'}}(-\mathbf{k}))^{*},$$
$$I_{a^{nn'}}(\mathbf{k}) = I_{a^{n'n}}(-\mathbf{k}).$$
(D.10)

Similarly from Eq. (D.9),

$$I_{a}^{nn'}(\mathbf{k}) = \int u_{n\mathbf{k}}^{*}(\mathbf{r}) \frac{\partial u_{n'\mathbf{k}}(\mathbf{r})}{\partial k_{a}} d^{3}x$$

$$= \int u_{n\mathbf{k}}^{*}(-\mathbf{r}) \frac{\partial u_{n'\mathbf{k}}(-\mathbf{r})}{\partial k_{a}} d^{3}x$$

$$= \int u_{n,-\mathbf{k}}^{*}(\mathbf{r}) \frac{\partial u_{n',-\mathbf{k}}(\mathbf{r})}{\partial k_{a}} d^{3}x$$

$$= -\int u_{n,-\mathbf{k}}^{*} \frac{\partial u_{n',-\mathbf{k}}}{(-k_{a})} d^{3}x,$$

$$I_{a}^{nn'}(\mathbf{k}) = -I_{a}^{n'n}(\mathbf{k}).$$
(D.11)

Thus the diagonal elements  $I_a^{nn}(\mathbf{k})$  vanish identically.

1160