Contributions to the Theory of the Anomalous Hall Effect in Ferro- and Antiferromagnetic Materials

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An interaction mechanism is proposed that can account for the anomalous Hall effect in different magnetic materials. In particular, the sign and the temperature dependence of the anomalous Hall resistivity are obtained for ferromagnetic metals. Moreover, a partial explanation is provided for the anomalies in the paramagnetic region of antiferromagnets. The difficulties of the present theory are discussed.

I. INTRODUCTION

THE present paper contributes to the theory of the Hall effect in magnetic materials. The Introduction briefly reviews the pertinent experimental evidence and the existing theories and presents an outline of the paper.

Anomalies of the Hall effect were observed long ago in ferromagnetic metals and more recently in antiferromagnetic metals and semiconductors. The behavior of the Hall resistivity as a function of temperature and type of conduction in representatives of each of these types of materials will be discussed. Iron and nickel are typical ferromagnetic metals. Jan,¹ among many other authors, reports that in these materials a strongly temperature-dependent effect is superimposed on the normal Hall effect. It is apparently possible² to subdivide the observed Hall resistivity into a normal and an anomalous contribution, by measurements of the Hall effect as a function of the external magnetic field at temperatures that are low with respect to the Curie point. Indications of the type of conduction can be derived then from the normal Hall effect: Iron shows p-type conduction, nickel *n*-type conduction. At the same time, the anomalous contribution shows the same sign as the normal contribution,³ i.e., the effect is larger both in Fe and Ni than one would expect if only the Lorentz force were effective. The anomalous contribution is phenomenologically written as the magnetization times a coefficient. This anomalous Hall resistivity has experimentally the following temperature dependence: It tends to zero as T tends to zero in perfect lattices, and it increases with temperature up to a maximum occurring just below the Curie temperature. This was observed in Ni by Jan.¹

Chromium is known to be an antiferromagnetic metal.⁴ The Hall constant as a function of temperature decreases rather abruptly at about the Néel temperature for increasing temperatures.⁵ The sign of the Hall constant is found to be positive.

broad-band semiconductor,6 whereas the other compound is likely to be a narrow-band semi-conductor.⁷ The type of conduction in these materials is determined by the valence of the impurities incorporated into the lattice and/or by deviations from stoichiometry. The sign of the Seebeck coefficient^{6,7} is positive, as expected.⁸ The Hall coefficient of MnTe⁶ and NiO⁹ in the antiferromagnetic phase has the same sign as the Seebeck coefficient. However, the Hall coefficient of MnTe single crystals drops to zero in the vicinity of the Néel point and changes sign if it is measured with the magnetic field parallel to the crystallographic c axis; if the measurement is performed with the magnetic field perpendicular to the c axis, the Hall constant of MnTe decreases sharply but remains positive.¹⁰ In NiO⁹ too a sign reversal of the Hall coefficient is found in the vicinity of the Néel temperature. Above this transition point the Hall and Seebeck coefficients have opposite signs. The law of the inverse proportionality of the Hall constant to the charge-carrier concentration has been verified⁹ in NiO in the paramagnetic region too. Disregarding the anomalous sign of the Hall coefficient, the proportionality constant for NiO is two orders of magnitude smaller than the normal value. Further interesting evidence of anomalies of the type mentioned can be found in measurements¹¹ on α -Fe₂O₃. α -Fe₂O₃ is weakly ferromagnetic in a temperature region lying between the so-called Morin temperature and the transition temperature to the paramagnetic region. Below the Morin temperature, α -Fe₂O₃ is antiferromagnetic. The sign of the observed Seebeck coefficient is negative, as expected, in all temperature regions.

Finally, MnTe and NiO are known to be antiferromagnetic semiconductors. MnTe appears to be a

¹ J. P. Jan, Helv. Phys. Acta 25, 677 (1952); J. P. Jan and H. M. Gijsman, Physica 18, 339 (1952). ² See, for example, M. Pugh, N. Rostoker, and A. Schindler, Phys. Rev. 80, 688 (1950). ³ This is not true in general for alloys. ⁴ See, for example, G. E. Bacon, Acta Cryst. 14, 823 (1961). ⁵ G. de Vries and G. W. Rathenau, J. Phys. Chem. Solids 2, 339 (1957). 339 (1957).

⁶ J. D. Wasscher, A. M. J. H. Seuter, and C. Haas, in Proceed-ings of the 7th International Conference on the Physics of Semicon-

ductors, Paris, 1964 (Academic Press Inc., New York, 1964). ⁷ A. J. Bosman and C. Crevecoeur, Phys. Rev. 144, 763 (1966). ⁸ The existence of magnon drag in MnTe (Ref. 6) does not prevent conclusions from being drawn regarding the sign of the

ordinary Seebeck coefficient. ⁹ A. J. Bosman, H. J. van Daal, and G. F. Knuvers, Phys. Letters 19, 372 (1965).

¹⁰ The remarkable behavior of the Hall effect in MnTe as a function of temperature and of the direction of the magnetic field was the first clear-cut indication of the presence of anomalies in the Hall effect of antiferromagnetic semiconductors

¹¹H. J. van Daal and A. J. Bosman, Phys. Rev. 158, 736 (1967).

Notwithstanding this, the sign of the Hall effect is positive in the paramagnetic region. α -Fe₂O₃ provides an example of a material with expected *n*-type conductivity that shows a positive Hall effect, while all semiconductors mentioned previously showed p-type conduction. The law of the inverse proportionality of the Hall effect to the carrier concentration is verified also in the paramagnetic region of α -Fe₂O₃. The proportionality constant is in this case a factor of 4 too small, and, of course, it has the unexpected sign.

The present state of the theory of the Hall effect in magnetic materials will now be reviewed by referring only to authors who have proposed new interaction mechanisms to which the anomalous Hall effect could be attributed. No mention is made of later refinements within these models concerning, for instance, detailed band structure, etc. All available calculations refer exclusively to the case of ferromagnetic metals.

Karplus and Luttinger¹² constructed the following model: A gas of charge carriers is free to move in the periodic potential of magnetically inert ions; the carriers with spin up are more numerous than the carriers with spin down. This temperature-dependent difference in the occupation of spin states is the cause of the spontaneous magnetization of the ferromagnet. In this model the very same itinerant particles are responsible for the electrical and magnetic properties of the solid. The carriers are subject to the interaction of their spin with their orbital angular momentum which produces, in the opinion of Karplus and Luttinger, a stationary current of the right order of magnitude with the symmetry of a Hall current. Smit¹³ criticized the theory of Karplus and Luttinger on the grounds that a periodic potential, such as the spin-orbit interaction, cannot cause scattering, nor consequently a current perpendicular to the external electric field. Only the presence of impurities disturbs the periodicity of the spin-orbit field. In the vicinity of the impurities a force acts on the charge carriers, and the charge carrier is scattered asymmetrically with respect to a plane defined by the carrier's incoming direction and the direction of its spin. This scattering process, skew scattering in Smit's terms, provides a mechanism by which a Hall current is produced of the right order of magnitude. Even though Luttinger, in a succeeding paper,¹⁴ would not accept many of Smit's objections, he also obtained a cancelling of the effect he had previously considered, at least in the effective-mass approximation. Smit's calculation itself is open to criticism: His equation for the anomalous Hall angle changes sign according to whether the perturbing potential of the impurity is attractive or repulsive. This prediction is disproved by Smit's experiments with different impurities in Ni: Whether the impurities had higher or lower atomic numbers than Ni (Al or Si on one side, Sn or W on the other), the anomalous Hall effect remained negative. It should also be observed that the role of impurities is fundamental in Smit's calculation, while Lavine's measurements¹⁵ on different Ni specimens indicate no essential change in the effect at temperatures near the transition point. Only a residual anomalous contribution to the Hall effect at low temperatures seems to be dependent upon the impurity concentration.

A different model has been considered by Kondo¹⁶: The charge carriers (which will also be called "s" electrons) are equally distributed between states of opposite spin. The ions then have a nonvanishing total spin, which accounts for the magnetic properties of the material. This is due to the spin of the *d* electrons, which are localized on the ions. The spins of the magnetic ions are disordered by temperature and the charge carriers are scattered by the nonperiodic potential which is thus generated and which acts on their spins. In this model periodicity is destroyed by the disorder of the ionic magnetic moments, rather than by the introduction of impurities. The mechanism described is the s-d spin-spin interaction (Ruderman and Kittel⁷) and Kasuya¹⁸) which accounts in principle for the resistivity of magnetic materials in terms of scattering of s electrons by d electrons. The s-d interaction provides no skew scattering by itself, even though Kondo shows that it is anisotropic, if the orbital ground state of the d electrons is degenerate. (Skew scattering is, in this model, a scattering which produces a wave function of the scattered charge carrier which is not invariant with respect to mirroring along a plane defined by the incoming direction of the s electron and the direction of the spin of the scattering ion.) This anisotropy of the s-d interaction disappears in fact if the ground state mentioned is nondegenerate. If, however, the spinorbit interaction of the d electrons within the magnetic ions (not the s charge carriers) is added, skew scattering takes place and a Hall current appears. It must be stressed at this point that in Kondo's opinion the skew scattering is caused by an anisotropy of the s-d interaction. The function of the spin-orbit interaction of the d electrons within the ions is to permit an odd power of the s-d interaction proper to a degenerate ground state to appear in the transition probabilities. Kondo's calculation provides the correct temperature dependence of the anomalous Hall effect in metals. The right order of magnitude and the sign of the effect is obtained by determining ad hoc the value of an available parameter. With reference to Kondo's calculation, it should be observed that the anisotropy of the s-d interaction and the spin-orbit interaction within an

 ¹² R. Karplus and J. M. Luttinger, Phys. Rev. 95, 1154 (1954).
 ¹³ J. Smit, Physica 21, 877 (1955) 24, 39 (1958); thesis, University of Leiden, 1956 (unpublished).
 ¹⁴ J. M. Luttinger, Phys. Rev. 112, 739 (1958).

J. M. Lavine, Phys. Rev. 123, 1273 (1961).
 J. Kondo, Progr. Theoret. Phys. (Kyoto) 27, 772 (1962).
 M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1955).
 T. Kasuya, Progr. Theoret. Phys. (Kyoto) 22, 227 (1959).

ion can exist only if the orbital angular momentum of the electrons within the ions is not quenched. This momentum appears to be quenched in the transition metals and in gadolinium, where the effect found experimentally is nonetheless particularly large. This remark is due to Kondo himself.

Summarizing, it can be concluded that the mechanism responsible for the anomalies of the Hall effect in magnetic materials is not completely understood. This applies in particular to antiferromagnetic solids for which no theory exists.

An interaction mechanism is proposed in the following as a possible cause of the anomalous Hall effect.¹⁹ The model adopted by Kondo is utilized here: The ions possess a nonvanishing magnetic moment due to localized d electrons, which accounts for the magnetic properties of the solid; the charge carriers (s electrons) are equally distributed between states with spin up and spin down, and they are scattered by the disorder induced by temperature in the system of magnetic ions. In addition to an isotropic s-d interaction, which is responsible for the resistivity of the material, an interaction is considered here which, in combination with the s-d interaction, gives rise to skew scattering. This interaction describes the force acting on the moving electrons as a consequence of the magnetic field produced by the presence of the magnetic moment of the ions. This interaction could be called a d-spins-orbit interaction. Such an interaction is of necessity present in all magnetic materials, and in the model of the localized moments it describes the same interaction between moving charges and magnetization that is written in terms of the spin-orbit interaction in the models proposed by Karplus and Luttinger and by Smit. It will be shown in the following that this interaction mechanism produces the following results:

(a) The temperature dependence of the anomalous Hall resistivity agrees with experiment in the case of ferromagnetic metals (iron and nickel); the anomalous Hall resistivity has a maximum below the Curie temperature and drops rapidly to very low values; the anomalous Hall coefficient does not.

(b) The difference in the sign of the anomalous Hall effect in Fe and Ni is attributed to the fact that Fe shows p-type conduction and Ni n-type conduction. In general, the anomalous Hall effect in ferromagnetic metals has the same sign as the normal Hall effect within the limitations of this theory.

(c) An abrupt decrease in the Hall coefficient is predicted in antiferromagnets near the Néel point, when the external field is parallel to the axis of easy magnetization (the complementary case, H normal to the axis of easy magnetization cannot be treated simply).

(d) In the paramagnetic region of antiferromagnets an extraordinary Hall effect is subtracted from the ordinary Hall effect. This applies to both orientations of the magnetic field mentioned in (c). For antiferromagnetic semiconductors this extraordinary effect is almost temperature-independent above the Néel temperature.

(e) The Hall coefficient remains inversely proportional to the carrier concentration in the paramagnetic region of antiferromagnetic semiconductors.

On the basis of these results it would appear that a unified explanation may be provided for the experimental observations on materials of varied magnetic and electrical properties. Some caution must be exercised, nevertheless, when judging the general applicability of the theory. It appears, first of all, from the measurements of Foner²⁰ on cobalt at room temperature that the anomalous and the normal Hall effect in this metal have opposite signs. These observations are at variance with the present theory, which is incapable of explaining them. More recent measurements²¹ of the Hall effect in Co show that the mentioned difference in signs is temperature-dependent. The explanation of the Hall effect in Co obviously requires further study. The sign of the effect in alloys, on the contrary, can be understood within the present theory.

There remains moreover a dubious point relating to the s-d interaction. The description of this interaction in terms of a spin-dependent potential [Eq. (6) of this paper, for instance] can be a questionable procedure. A rigorous treatment of the electron-electron Coulomb interaction should make use of electron eigenfunctions antisymmetrized with respect to all coordinates of the carrier electron and of the electrons residing on localized orbitals of the ion. In this way the Coulomb interaction between pairs of electrons would be explicitly taken into account. However, it seems probable that the standard procedure, followed also in this paper, is adequate.

Special attention had to be devoted to order-of-magnitude considerations: The present effect is approximately two orders of magnitude too small both for ferromagnets and antiferromagnets. The origin of this serious discrepancy is discussed in the third section of this paper.

The interaction to be considered in the following along with the s-d interaction will now be derived.²² Gaussian units are utilized throughout this paper. A magnetic moment M situated at the origin of coordinates generates a magnetic field whose vector potential

¹⁹ The same interaction mechanism has been considered independently by A. N. Voloshinskiy {Fiz. Metal. Metalloved. 18, 492 (1964) [English transl.: Phys. Metals Metallog. (USSR) 18, 13 (1964)]} for the case of ferromagnetic metals. See also the references included in the cited article.

 ²⁰ S. Foner and E. M. Pugh, Phys. Rev. 91, 20 (1953).
 ²¹ N. V. Volkenshtein and G. V. Fedorov, Zh. Eksperim, i Teor. Fiz. 38, 64 (1960) [English transl.: Soviet Phys.-JEPT 11, 48 (1960)]. ²² A. Messiah, *Mécanique Quantique* (Dunod Cie., Paris, 1964),

p. 809.

 \mathbf{A} is

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$$\mathbf{A} = \mathbf{M} \times \mathbf{r}/r^3 = \operatorname{curl}(\mathbf{M}/r). \tag{1}$$

This vector potential introduces a new term in the Hamiltonian describing the motion of a charge carrier (e, m, p; carrier's charge, mass, and momentum, respectively):

$$\mathfrak{H} = -\frac{e}{2mc} \left(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p} \right) = -\frac{e}{mc} \left(\mathbf{p} \cdot \mathbf{A} \right); \quad (\operatorname{div} \mathbf{A} = 0).$$
(2)

If the orbital angular momentum L of the charge carrier around the origin is introduced, this final result is obtained:

$$\mathfrak{H} = -(e/mc)\mathbf{M} \cdot \mathbf{L}/r^3 \tag{3}$$

In the case under consideration, \mathbf{M} is the magnetic moment proportional to the sum of the spins of the *d* electrons. \mathbf{M} equals $g\mu \mathbf{S}$, where \mathbf{S} is the total spin of the ion, *g* is the Landé factor, and μ is the Bohr magneton. As indicated previously, (3) is a *d* spin, "s" orbit interaction. It is apparent that (3) changes sign if the coordinate \mathbf{r} is changed into its specular image by mirroring along a plane containing \mathbf{M} and \mathbf{p} . This implies that the matrix elements of (3) between quasifree-electron states of wave vectors \mathbf{k} and \mathbf{k}' are antisymmetric under an exchange of \mathbf{k} and \mathbf{k}' . If an odd power of such a matrix element appears in a transition probability, skew scattering results.

In the following section a perturbation calculation of the skew scattering due to Hamiltonian (3) in combination with the *s-d* Hamiltonian and a transport calculation are carried out to obtain an expression for the anomalous Hall resistivity. The third section discusses the equations obtained with reference to experimental evidence. Finally, the fourth section emphasizes the limitations of the theory.

II. CALCULATION OF THE HALL RESISTIVITY

A. Transition Probabilities

The transition probabilities between quasi-freeelectron states will be obtained by the application of the methods of S-matrix theory.²³ The first-order S-matrix element will be considered to obtain an expression for the isotropic transition probability leading to resistivity, the second-order S-matrix element will be considered in combination with the first-order matrix element to obtain an expression for the transition probability leading to skew scattering and to a contribution to the Hall effect. Higher-order S-matrix elements will be disregarded. This is permissible only if the interaction energies under consideration, namely the energies related to the *s*-*d* Hamiltonian and Hamiltonian (3), are small with respect to the kinetic energy of the scattered charge carriers. The results of the calculation sketched will then be utilized to calculate the Hall resistivity for metals and semiconductors by introducing them into the transport equation. This calculation follows rather closely the method used by Kondo.¹⁶ The essential difference between the two calculations resides in the fact that the perturbation Hamiltonians are different in the two cases. Expressed in equation form, the following first- and second-order *S*-matrix elements shall be computed:

$$\langle \alpha' \mid S^{(1)} \mid \alpha \rangle = -2i\pi\delta(E_{\alpha'} - E_{\alpha}) \langle \alpha' \mid \mathfrak{F}_{1} + \mathfrak{F}_{2} \mid \alpha \rangle, \quad (4)$$

$$\langle \alpha' \mid S^{(2)} \mid \alpha \rangle = -2i\pi\delta(E_{\alpha'} - E_{\alpha})$$

$$\times \sum_{\alpha''} \langle \alpha \mid \mathfrak{F}_{1} + \mathfrak{F}_{2} \mid \alpha'' \rangle$$

$$\times \langle \alpha'' \mid \mathfrak{F}_{1} + \mathfrak{F}_{2} \mid \alpha' \rangle / (E_{\alpha} - E_{\alpha''} + i\eta), \quad (5)$$

where

$$\mathfrak{H}_1 = -\sum_{n=1}^N J(\mathbf{r} - \mathbf{R}_n) \, \boldsymbol{o} \cdot \mathbf{S}_n \tag{6}$$

and

$$\mathfrak{G}_{2} = \left(-eg\mu/mc\right) \sum_{n=1}^{N} \left(\mathbf{S}_{n} \cdot \mathbf{L}_{n}\right) / |\mathbf{r} - \mathbf{R}_{n}|^{3} \qquad (7)$$

represent the interaction terms. \mathfrak{H}_1 is a formal representation of the *s*-*d* interaction between the spin \mathfrak{d} of the carrier and the spins \mathbf{S}_n of the *N* magnetic ions present in the solid. $J(\mathbf{r}-\mathbf{R}_n)$, the exchange integral, is assumed to be isotropic.²⁴ In Eq. (7) \mathbf{L}_n is the angular momentum of the charge carrier with respect to the *n*th ion, *m* is the effective mass of the carrier, and \mathbf{R}_n is the position coordinate of the carrier. The interaction Hamiltonians (6) and (7) cause transitions between states that are the products of a quasi-free-electron eigenfunction $V^{-1/2} \exp(i\mathbf{k}\cdot\mathbf{r})$ (*V* is the volume of the specimen), of an eigenfunction

$$\begin{bmatrix} 0 \\ 1 \end{bmatrix} \text{ or } \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

of the z component of the spin \mathfrak{d} , and of eigenfunctions of the operators S_n^z relative to each ion. The spins of all ions have modulus equal to $[S(S+1)]^{1/2}$. These unperturbed states are labeled $|\alpha\rangle = |\mathbf{k}, \sigma, m_1, \cdots, m_N\rangle$, where m_n is the magnetic quantum number relative to the *n*th ion. The direction of quantization of angular momentum is chosen to coincide with the direction $\boldsymbol{\zeta}$ of the external magnetic field **H**. The spin σ can take

²³ See, for example, A. S. Davydov, *Quantum Mechanics* (Pergamon Press, Inc., New York, 1965), p. 330.

 $^{^{24}\,\}mathrm{The}$ difficulties relative to this exchange integral have been mentioned in the Introduction.

$$W_1(\mathbf{k}', \mathbf{k}) = (2\pi/\hbar) \,\delta(E_{\mathbf{k}} - E_{\mathbf{k}'}) \mid \langle \alpha' \mid \mathfrak{H}_1 + \mathfrak{H}_2 \mid \alpha \rangle \mid^2, \tag{8}$$

$$W_{2}(\mathbf{k}',\mathbf{k}) = (2\pi/\hbar) \,\delta(E_{\mathbf{k}} - E_{\mathbf{k}'}) \left\{ \langle \alpha' \mid \mathfrak{G}_{1} + \mathfrak{G}_{2} \mid \alpha \rangle \sum_{\alpha''} \left[\langle \alpha \mid \mathfrak{G}_{1} + \mathfrak{G}_{2} \mid \alpha'' \rangle \langle \alpha'' \mid \mathfrak{G}_{1} + \mathfrak{G}_{2} \mid \alpha' \rangle / (E_{\mathbf{k}} - E_{\mathbf{k}''} + i\eta) \right] + \text{c.c.} \right\}.$$
(9)

The matrix elements $\langle \alpha' | \mathfrak{G}_1 + \mathfrak{G}_2 | \alpha \rangle$ are easily calculated; it appears that the only nonvanishing ones are

 $\langle \mathbf{k}', \pm, m_1, \cdots, m_N \mid \mathfrak{H}_1 \mid \mathbf{k}, \pm, m_1, \cdots, m_N \rangle = \mp (J(\mathbf{k}, \mathbf{k}')/V) \sum_n \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_n] m_n,$ (10a)

$$\langle \mathbf{k}', \mp, m_1, \cdots, m_n \pm 1, \cdots, m_N \mid \mathfrak{H}_1 \mid \mathbf{k}, \pm, m_1, \cdots, m_n, \cdots, m_N \rangle$$

= $-(J(\mathbf{k}, \mathbf{k}')/2V) \exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n][S(S+1)-m_n(m_n\pm 1)]^{1/2}$ for every n , (10b)

$$\langle \mathbf{k}', \pm, m_1, \cdots, m_N \mid \mathfrak{F}_2 \mid \mathbf{k}, \pm, m_1, \cdots, m_N \rangle = -(4\pi i eg\mu\hbar/mcV)(\mathbf{k} \times \mathbf{k}')_{\mathfrak{f}} \mid \mathbf{k} - \mathbf{k}' \mid^{-2} \sum_n \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_n]m_n,$$

$$\langle \mathbf{k}^{1}, \pm, m_{1}, \cdots, m_{n} \pm 1, \cdots, m_{N} | \mathfrak{H}_{2} | \mathbf{k}, \pm, m_{1}, \cdots, m_{n}, \cdots, m_{N} \rangle$$

$$= -(2\pi i eg\mu\hbar/mcV) \exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{n}][S(S+1)-m_{n}(m_{n}\pm 1)]^{1/2} | \mathbf{k}-\mathbf{k}' |^{-2}(\mathbf{k}\times\mathbf{k}')\cdot[\xi\mp i\mathbf{n}] \quad \text{for every } n.$$
(10d)

Here $J(\mathbf{k}, \mathbf{k}') = \int \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] J(\mathbf{r}) d\mathbf{r}$. The expression $(\mathbf{k} \times \mathbf{k}')_{\zeta}$ indicates the component of $\mathbf{k} \times \mathbf{k}'$ in the direction ζ . ξ and \mathbf{n} are unit vectors normal to ζ .

In the following calculation only those matrix elements which induce no transitions in the system of magnetic ions [namely matrix elements (10a) and (10c)] shall be retained. This approximation was also adopted by Kondo. Furthermore, only \mathfrak{H}_1 shall be retained in Eq. (8) because it is argued that the square of the matrix element of \mathfrak{H}_2 is but a small correction to the square of the matrix element of \mathfrak{H}_1 . The cross products cancel in (8), as it is apparent from Eqs. (10a) and (10c).

The transition probability of Eq. (9) is the sum of eight terms containing different combinations of three matrix elements of either \mathfrak{H}_1 or \mathfrak{H}_2 . All the terms containing the square of the matrix element of \mathfrak{H}_2 are not relevant because they cannot cause skew scattering. Only three terms contain linearly the matrix element of \mathfrak{H}_2 : Two of them contain a matrix element of \mathfrak{H}_2 which must be summed over α'' ; one term contains $\langle \alpha' | \mathfrak{H}_2 | \alpha \rangle$. Only this last-mentioned term shall be retained in the calculation. The two other terms linear in the matrix element of \mathfrak{H}_2 are believed to be smaller than the one to be retained. The term containing the third power of the matrix element of \mathfrak{H}_2 is neglected because it is small with respect to terms containing linearly the matrix element of \mathfrak{H}_2 . The calculation of the transition probabilities can now proceed. Substitution of (10a) into (8) gives, if $J(\mathbf{k}, \mathbf{k}')$ is real,

$$W_{1}(\mathbf{k}', \mathbf{k}) = (2\pi/\hbar) \,\delta(E_{\mathbf{k}'} - E_{\mathbf{k}}) \, (J(\mathbf{k}, \mathbf{k}') \, J(\mathbf{k}', \mathbf{k})/V^{2})$$
$$\sum_{nn'} m_{n} m_{n'} \exp[i(\mathbf{k} - \mathbf{k}') \cdot (\mathbf{R}_{n} - \mathbf{R}_{n'})]. \quad (11)$$

If correlations among different magnetic momenta are disregarded, with the exception of the cumulative

influence on one momentum of all the others as described by a molecular field, then the sum in (11) can be computed; it equals

$$N\langle (m - \langle m \rangle)^{2} \rangle + N^{2} \langle m \rangle^{2} \delta^{2}(\mathbf{k} - \mathbf{k}') \quad \text{for a ferromagnet,}$$

$$(12a)$$

$$\frac{1}{2} N(\langle (m_{1} - \langle m_{1} \rangle)^{2} \rangle + \langle (m_{2} - \langle m_{2} \rangle)^{2} \rangle) + (\frac{1}{2} N)^{2} \delta^{2}(\mathbf{k} - \mathbf{k}') [\langle m_{1} \rangle^{2} + \langle m_{2} \rangle^{2} + \langle m_{1} \rangle \langle m_{2} \rangle]$$

In the case of a ferromagnet, $\langle m^n \rangle$ is defined as the average value of the *n*th power of the magnetic quantum number of an ion. This is calculated within the molecular-field approximation and it is the same for all the ions. $\langle (m - \langle m \rangle)^2 \rangle$ is defined in terms of $\langle m^n \rangle$ by the algebraic relation $\langle (m - \langle m \rangle)^2 \rangle = \langle m^2 \rangle - \langle m \rangle^2$. The antiferromagnet to be considered here is made up of two sublattices. All the ions belonging to the first sublattice have an average magnetic quantum number equal to $\langle m_1 \rangle$; all the ions belonging to the second sublattice have an average magnetic quantum number equal to $\langle m_2 \rangle$. Within each sublattice the same definitions given for ferromagnets apply.

The terms containing δ 's in Eqs. (12) do not describe a scattering process. They rather describe the modification of the carrier band as a consequence of the presence of the interaction terms (6) and (7). Such a modification is considered small and it is neglected. The transition probability $W_1(\mathbf{k}', \mathbf{k})$ then equals

$$W_{1}(\mathbf{k}', \mathbf{k}) = (2\pi/\hbar) \,\delta(E_{\mathbf{k}'} - E_{\mathbf{k}}) \\ \times (J(\mathbf{k}, \mathbf{k}') \,J(\mathbf{k}', \mathbf{k})/V^{2})\mathfrak{M}_{2}, \quad (13)$$

where $\mathfrak{M}_2 = N\langle (m - \langle m \rangle)^2 \rangle$ for a ferromagnet and $\mathfrak{M}_2 = \frac{1}{2}N(\langle (m_1 - \langle m_1 \rangle)^2 \rangle + \langle (m_2 - \langle m_2 \rangle)^2 \rangle)$ for an anti-ferromagnet.

(10c)

Substitution of (10c) and (10a) into (5) gives the second-order S-matrix element:

$$\langle \alpha' \mid S^{(2)} \mid \alpha \rangle = -(2\pi i/V) \,\delta(E_{\alpha'} - E_{\alpha}) \, \sum_{nn'} m_n m_{n'} I_{nn'}(\mathbf{k}, \mathbf{k}') \, \exp[i(\mathbf{k} \cdot \mathbf{R}_n - \mathbf{k}' \cdot \mathbf{R}_{n'})], \tag{14}$$

where

$$I_{nn'}(\mathbf{k}, \mathbf{k}') = (2\pi)^{-3} \int d\mathbf{k}'' \ J(\mathbf{k}, \mathbf{k}'') \ J(\mathbf{k}'', \mathbf{k}') \ \exp[i\mathbf{k}'' \cdot (\mathbf{R}_{n'} - \mathbf{R}_n)] / (E_{\mathbf{k}} - E_{\mathbf{k}''} + i\eta) = R_{nn'}(\mathbf{k}, \mathbf{k}') + i\Im_{nn'}(\mathbf{k}, \mathbf{k}').$$
(15)

Then the transition probability (9) equals

$$W_{2}(\mathbf{k}', \mathbf{k}) = (2\pi/\hbar) \,\delta(E_{\mathbf{k}'} - E_{\mathbf{k}}) \,i Q(\mathbf{k} \times \mathbf{k}')_{\zeta} \mid \mathbf{k} - \mathbf{k}' \mid^{-2} \sum_{nn'n''} m_{n} m_{n'} m_{n'} m_{n'} M_{nn'} M_{nn'} (\mathbf{k}, \mathbf{k}') [\exp(i\alpha) + \exp(-i\alpha)]/V + i \Im_{nn'}(\mathbf{k}, \mathbf{k}') [\exp(i\alpha) + \exp(-i\alpha)]/V \}, \quad (16)$$

where

$$O = 4\pi eg\mu\hbar/mcV, \alpha = (\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}_{n''} - \mathbf{k}' \cdot \mathbf{R}_{n'} + \mathbf{k} \cdot \mathbf{R}_{n}.$$

 $R_{nn'}(\mathbf{k}, \mathbf{k}')$ and $\mathfrak{F}_{nn'}(\mathbf{k}, \mathbf{k}')$ are now substituted by the values of $R(\mathbf{k}, \mathbf{k}')$ and $\mathfrak{F}(\mathbf{k}, \mathbf{k}')$ that they have when n and n' label ions that are nearest neighbors. This approximation eases the progress of calculation and it does not change the order of magnitude of the effect. This approximation is essential to let \mathfrak{M}_3 appear in the following equation. Then Eq. (16) reduces to

$$W_{2}(\mathbf{k}', \mathbf{k}) = (2\pi/\hbar) \,\delta(E_{\mathbf{k}'} - E_{\mathbf{k}})$$
$$\times (-Q) \,(\mathbf{k} \times \mathbf{k}')_{\varsigma} \mid \mathbf{k} - \mathbf{k}' \mid^{-2} \mathfrak{N}(\mathbf{k}, \mathbf{k}') \mathfrak{M}_{3}/V, \quad (17)$$

where $\mathfrak{M}_3 = N\langle (\mathbf{m} - \langle \mathbf{m} \rangle)^3 \rangle$ for ferromagnets, $\mathfrak{M}_3 = \frac{1}{2}N(\langle zm_1 - \langle m_1 \rangle z^3 \rangle + \langle zm_2 - \langle m_2 \rangle z^3 \rangle)$ for antiferromagnets. Also in the case of $W_2(\mathbf{k}', \mathbf{k})$ the molecular-field approximation has been adopted and the δ 's which should appear in \mathfrak{M}_3 have been neglected for the reasons given above Eq. (13).

The ratio $|W_2/W_1|$ is a measure of the Hall angle ϕ_H' caused by skew scattering. Estimates of the order of magnitude of the effect considered in this paper will be based on a comparison of this ratio with the ordinary Hall angle. The ratio $|W_2/W_1|$ is equal to

$$\phi_{H}' = | W_2/W_1 | = 2Q(k \times k')_{\mathfrak{f}} | \mathbf{k} - \mathbf{k}' |^{-2} \times V \Im(\mathbf{k}, \mathbf{k}') J^{-1}(\mathbf{k}, \mathbf{k}') J^{-1}(\mathbf{k}', \mathbf{k}) \mathfrak{M}_3/\mathfrak{M}_2.$$
(18)

An estimate of this ratio is possible if $J(\mathbf{k}, \mathbf{k}')$ is independent of \mathbf{k} and \mathbf{k}' and is equal to J. $[J(\mathbf{r})$ in Eq. (6) is a delta function times J.] Then $\mathfrak{F}_{nn'}(\mathbf{k}, \mathbf{k}')$ can be computed as

$$\mathfrak{F}_{nn'}(\mathbf{k}, \mathbf{k}') = -(J^2 m/2\pi^2 \hbar^2) \sin(k \mid \mathbf{R}_{n'} - \mathbf{R}_n \mid) / |\mathbf{R}_{n'} - \mathbf{R}_n|. \quad (19)$$

If $|\mathbf{R}_{n'}-\mathbf{R}_{n}|$ equals the nearest-neighbor distance a, then

$$\phi_{H}' = (4eg\mu/\pi c\hbar) (\sin ka/a) (\mathfrak{M}_{3}/\mathfrak{M}_{2}) \simeq 2 \times 10^{-5} \mathfrak{M}_{3}/\mathfrak{M}_{2}.$$
(20)

The Hall angle due to the external magnetic field is roughly $\phi \simeq \tan \phi = H\mu/c$, where μ indicates in this particular case the mobility of the carriers. ϕ is of the order of 10⁻⁵ for H=5 kOe, $\mu=1$ cm²/V sec as it is observed experimentally in the magnetic materials of interest. The following section contains an estimate of the ratio of the average values appearing in (20) and a study based on (20) of the relative magnitudes of the normal and anomalous Hall effects.

B. Transport Calculations

The transition probabilities obtained in the preceding subsection will now be introduced in the transport equation in order to obtain an expression for the Hall resistivity. From now on $J(\mathbf{k}, \mathbf{k}') = J$, independent of \mathbf{k} and \mathbf{k}' . The ordinary Hall effect will not be calculated in this subsection. The equations that will be obtained for the Hall resistivity will refer only to the skew-scattering contribution. The procedure used follows the article by Kondo.¹⁶ Attention will be devoted first of all to metals for which all integrations are performed on the Fermi surface. The carrier distribution among states of wave vector \mathbf{k}^{25} is approximated by

$$f_{\mathbf{k}} = f_{\mathbf{k}^{0}} - \mathcal{E}g_{\mathbf{k}}(\partial f_{\mathbf{k}^{0}}/\partial E_{\mathbf{k}}).$$
(21)

 ε u is the external electric field, and $g_k = g_k^{(1)} + g_k^{(2)}$, where $g_k^{(1)}$ and $g_k^{(2)}$ are the corrections relative to the transition probabilities (13) and (17), respectively. f_k^0 is the Fermi-Dirac distribution. Then the equation for $g_k^{(1)}$ is

$$\sum_{k'} W_1(\mathbf{k}', \mathbf{k}) \left(g_{\mathbf{k}^{(1)}} - g_{\mathbf{k}'}{}^{(1)} \right) + (\hbar e/m) \mathbf{u} \cdot \mathbf{k} = 0.$$
(22)

A solution is found for $g_{\mathbf{k}}^{(1)} = \phi(\mathbf{u} \cdot \mathbf{k})$, where

$$\phi = -\pi \hbar^4 e V / m^2 k J^2 N \mathfrak{M}_2. \tag{23}$$

The equation for $g_k^{(2)}$ is

$$\sum_{\mathbf{k}'} \left[W_1(\mathbf{k}', \mathbf{k}) \{ g_{\mathbf{k}^{(2)}} - g_{\mathbf{k}'^{(2)}} \} - W_2(\mathbf{k}', \mathbf{k}) \{ g_{\mathbf{k}^{(1)}} + g_{\mathbf{k}'^{(1)}} \} \right] = 0. \quad (24)$$

²⁵ Carriers with spin up and down are assumed to reside in the same spherical band, with equal effective mass *m*. This assumption, amounting to the neglect of energy corrections due to $\mathfrak{H}_1+\mathfrak{H}_2$, has already been used to neglect the δ 's in Eq. (12). It is argued in the usual way that the difference between the two bands is small enough to be disregarded in the case at hand. Moreover, the charge carriers are skew scattered in the same direction whether they have spin up or spin down. The contributions of the two bands then add up and the small difference between the two bands does not appear in the calculation in a relevant way.

A solution for $g_{\mathbf{k}^{(2)}}$ is found such that $g_{\mathbf{k}^{(2)}} = \psi(\zeta \times \mathbf{u}) \cdot \mathbf{k}$, where

$$\psi/\phi = -\pi^{-1}(\sin ka/a) \left(eg\mu/c\hbar \right) \mathfrak{M}_3/\mathfrak{M}_2.$$
(25)

Such results lead simply to the calculation of the current density:

$$\mathbf{j} = (e\hbar \mathcal{E}/mV) \sum_{\mathbf{k}} (\partial f_{\mathbf{k}}^{0}/\partial E_{\mathbf{k}}) (g_{\mathbf{k}}^{(1)} + g_{\mathbf{k}}^{(2)})$$
$$= -(ek_{F}^{3}/6\pi^{2}\hbar) \phi_{F} \mathcal{E} [\mathbf{u} + (\psi_{F}/\phi_{F}) (\boldsymbol{\zeta} \times \mathbf{u})]. \quad (26)$$

 $\hbar \mathbf{k}_F$ is the Fermi momentum; ψ_F and ϕ_F equal ψ and ϕ at the Fermi surface. The Hall resistivity is defined by

$$\rho_H = E_{\perp}/j_{\parallel \parallel} = (-3/ec) (N/V) \\ \times (\operatorname{sink}_F a/a E_F) (m/\hbar^2) J^2 g \mu \mathfrak{M}_3. \quad (27)$$

The Hall resistivity observed experimentally is of opposite sign, because it refers to the electric field that compensates the field perpendicular to \mathbf{u} that drives j. Then

$$\rho_H = (3/ec) \left(N/V \right) \left(\sin k_F a/a E_F \right) \left(m/\hbar^2 \right) J^2 g \mu \mathfrak{M}_3. \tag{28}$$

A discussion of this result will follow in the next section. A similar formula for semiconductors is now derived. If it is assumed that

$$f_{\rm k}^{0} = (16\mu/V) (\pi\hbar^2/2mk_BT)^{3/2} \exp(-E_{\rm k}/k_BT),$$

where n is the total number of carriers present in the solid and k_B is Boltzmann constant, then, by the same calculation performed for metals, the following Hall resistivity is obtained for semiconductors:

$$\rho_{H} = (45/16\pi) (nec)^{-1}N \exp(-ma^{2}k_{B}T/2\hbar^{2}) \\ \times (1 - ma^{2}k_{B}T/6\hbar^{2}) (m^{3}/\hbar^{6}) J^{2}g\mu\mathfrak{M}_{3}k_{B}T.$$
(29)

III. DISCUSSION OF THE RESULTS

It will now be shown that Eqs. (28) and (29) obtained for the anomalous Hall resistivities in metals and semiconductors have the features listed in the introduction.

A. Results (a) and (b)

From Eq. (28) it appears that for metals the temperature dependence of the anomalous contribution to the Hall resistivity is contained in \mathfrak{M}_3 . It will be shown that this quantity is positive at all temperatures for a ferromagnet in a molecular-field approximation. Then ρ_H anomalous has the sign of the charge carriers [μ being negative in Eq. (28)] if $\sin k_F a < 0$. A ferromagnetic crystal is considered consisting of one domain. Interactions among nearest neighbors are considered. The reduced magnetization σ (which is negative, ranging from zero to minus one) is given in a molecular-field approximation by $\sigma = B_S(y)$, where

$$y = [3S/(S+1)](T_c/T)\sigma + g\mu SH/k_BT.$$

 B_S is a Brillouin function. It is easy to see that $\mathfrak{M}_3 = S^3 B_S''(y)$. \mathfrak{M}_3 is easily expressed in terms of the



FIG. 1. The temperature dependence of \mathfrak{M}_3/S^3 .

spontaneous and induced magnetizations:

$$\mathfrak{M}_{3} = S^{3} [B_{S}''(y_{0}) + B_{S}'''(y_{0}) (y - y_{0})]$$

= $S^{3} [B_{S}''(y_{0}) + (B_{S}'''(y_{0}) / B_{S}'(y_{0})) \delta\sigma]$
= $S^{3} [(B_{S}''(y_{0}) / B_{S}(y_{0})) \sigma_{0} + (B_{S}'''(y_{0}) / B_{S}'(y_{0})) \delta\sigma]]$
 $\sigma = \sigma_{0} + \delta\sigma; \qquad y_{0} = [3S/(S+1)](Tc/T)\sigma_{0}.$ (30)

Of the two terms that are present in \mathfrak{M}_3 , the former is proportional to the spontaneous magnetization and the latter is proportional to the induced magnetization. The proportionality constants are not equal. The sign of the two contributions to \mathfrak{M}_3 mentioned is the same near T_c, but is opposite below $0.88T_c$, for $S=\frac{1}{2}$, because of the signs of $B_{s}^{\prime\prime}$ and $B_{s}^{\prime\prime\prime}$. The diagram of Fig. 1 displays the temperature dependence of \mathfrak{M}^3/S^3 for $S = \frac{1}{2}$ and H = 0; $B_{S''}(y)$ is positive for all negative y. The appearance of a maximum below T_c is due to the presence of two factors in \mathfrak{M}_3 : the spontaneous magnetization, which is zero at T_c , and the coefficient of σ_0 in (30), which is zero at T=0, and which takes care that, when the magnetic system is ordered, no scattering takes place. It must be remarked that the spontaneous Hall resistivity vanishes for $T = T_c$ because of σ_0 , while the spontaneous Hall coefficient, which was mentioned in the Introduction, remains finite. The temperature dependence of \mathfrak{M}_3 should be compared with the data of Ref. 1 for the anomalous Hall resistivity. The agreement is satisfactory. The same temperature dependence was obtained by Kondo¹⁶; moreover, this author compares his result with that of Karplus and Luttinger.¹²

B. Results (c), (d), and (e)

In the case of antiferromagnets the measured quantity R_H equals the normal Hall coefficient plus ρ_H of Eq. (29) divided by H, the magnitude of the external magnetic field:

$$R_H = (nec)^{-1}(1+\alpha),$$
 (31)

where

$$\alpha = (45/16\pi) N(m^3/\hbar^6) J^2 g \mu \mathfrak{M}_3 k_B T/H.$$
(32)

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Equation (31) is the transcription for antiferromagnetic semiconductors of the phenomenological formula mentioned in the Introduction for ferromagnets. It will be shown that α is independent of H. The expression $\exp(-mk_BTa^2/\hbar^2)(1-ma^2k_BT/6\hbar^2)$ has been dropped from (32) because it is practically one in the temperature regions of interest.

The fact that the anomalous contribution to the Hall effect in semiconductors is inversely proportional to the carrier concentration is apparent from Eq. (31). The temperature dependence of \mathfrak{M}_3 , which determines the temperature dependence of α , is now investigated for an antiferromagnet, for the case of H parallel to the axis of easy magnetization Δ .²⁶ The simplest antiferromagnet is considered, consisting of two sublattices such that all neighbors of an ion in one sublattice reside on the other sublattice. Nearest-neighbor interactions only are considered. The following equations apply to the two sublattices (the index + refers to the sublattice whose total magnetic moment is parallel to the external magnetic field; the index - refers to the sublattice whose total magnetic moment is antiparallel to the external magnetic field):

$$\sigma_{\pm} = B_S(y_{\pm}), \qquad (33)$$

$$y_{\pm} = [3S/(S+1)](T_N/T)\sigma_{\mp\pm}g\mu SH/k_BT,$$
 (34)

$$\mathfrak{M}_{3\pm} = S^{3} \{ [B_{S}^{\prime\prime}(y_{0})/B_{S}(y_{0})]\sigma_{0\pm} + [B_{S}^{\prime\prime\prime}(y_{0})/B_{S}^{\prime}(y_{0})]\delta\sigma_{\pm} \}.$$
(35)

The equations apply

$$\sigma_{0+} = -\sigma_{0-},$$

$$\delta\sigma_{+} = \delta\sigma_{-} = \delta\sigma. \tag{36}$$

Then

$$\mathfrak{M}_{3} = \mathfrak{M}_{3+} + \mathfrak{M}_{3-} = 2 S^{3} \delta \sigma B_{S}^{\prime \prime \prime}(y_{0}) / B_{S}^{\prime}(y_{0}). \quad (37)$$

 $\delta\sigma$ is expressed in terms of the susceptibility:

$$\delta \sigma = \chi_{||} H / N g \mu S$$

Then

$$\mathfrak{M}_{3} = \frac{(2S^{4}g\mu H/k_{B}T)B_{S}^{\prime\prime\prime}(y_{0})}{[1 + \{3S/(S+1)\}(T_{N}/T)B_{S}^{\prime}(y_{0})]}.$$
 (38)

It is clear that α is independent of H. The temperature dependence of

$$B_{S'''}(y_{0})/[1+\{3S/(S+1)\}(T_{N}/T)B_{S'}(y_{0})]$$

is given in Fig. 2. These results are now compared with the experimental evidence. It shall be observed first of all that the equations derived above apply in general only above the Néel temperature, where the spins of the sublattices are parallel to \mathbf{H} ; also, the molecular-field theory is certainly not appropriate much below the Néel temperature.

It is, however, possible to say that α is negative²⁷ in the paramagnetic region, after changing sign rather abruptly in the vicinity of the Néel temperature. This is in remarkable qualitative agreement with experiments in MnTe and NiO, provided α is very close to -1 in the paramagnetic region. It should be emphasized here that Fig. 2 shows the temperature dependence of a quantity proportional to α , and that the appearance of -1 in Fig. 2 does not mean that $\alpha = -1$. α is very insensitive to changes in temperature above the Néel temperature. This is also in striking agreement with experiment in the mentioned materials.

The anisotropy of the effect in MnTe cannot be explained because it is not possible to treat the case H perpendicular to Δ within the present theory. The presence of the maximum below the Néel temperature in Fig. 2 is not very disturbing: This means that the Hall effect in that temperature region contains an added term which is 30% of the effect that is subtracted in the paramagnetic region. If α equals -1 in the paramagnetic region, then the extra effect below the Néel temperature may be included in the measuring errors with some good will. Moreover, it may be argued that the maximum falls into a region in which the molecular-field theory cannot be applied. On the other hand, it should be mentioned that in the case of chromium [which is a metal; consequently Eq. (28) would apply if the model proposed here could be used for chromium] there are indications of the presence of a maximum.

Some attention should be paid to the order of magnitude of the effect just calculated. It has been ob-



²⁷ \mathfrak{M}_3 is positive, μ is negative in (32).

²⁶ T. Nagamiya, K. Yosida, and R. Kubo, Advan. Phys. 4, 1 (1955).

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served [following Eq. (20)] that the ratio of ordinary and anomalous Hall angles is of the order of $\mathfrak{M}_3/\mathfrak{M}_2$. This quantity is of order one in ferromagnets, and of order 10^{-2} in antiferromagnets. Experimentally, the anomalous Hall effect is about a hundred times larger than the normal effect¹³ in Ni in the vicinity of the Curie temperature. In antiferromagnets, normal and anomalous Hall effects should roughly be of the same order of magnitude at the Néel temperature. The computed effect is, in all cases, two orders of magnitude too small.²⁸ The following provides a possible explanation for the difficulty discussed.

Only interaction (7) is relevant in connection with the estimate of the order of magnitude; in fact Hamiltonian (6) cancels out in the expression for the anomalous Hall angle. Interaction (7) describes the effect of the magnetic field caused by the current of the s electrons on the total spin of the d electrons. With the assumption that the s electrons reside in states described by plane waves, this magnetic field is probably underestimated. Suppose in fact that the conduction electrons orbited somewhat around the ions, as described, for instance, by a tight-binding combination of proper atomic orbitals. It appears immediately that the presence of such circular currents around the ions would produce a much larger magnetic field on the ion sites than the field generated by a current described by a plane wave. A refinement of the model in the indicated direction seems promising. It is not unlikely that the difficulties in the order of magnitude are a consequence of the limitations of the model rather than an indication of the fact that the effect considered is much too small to be the cause of the anomalies of the Hall effect.

CONCLUSION

A number of objections are gathered in the following conclusion; these indicate the drastic limitations of the theory and permit a more objective evaluation of the remarkable qualitative agreement of the predictions made by the theory with experiment.

The treatment of a Hamiltonian as a perturbation is always open to question when the scattering due to this Hamiltonian limits the mean free path of the charge carriers to distances comparable with the interatomic distance; this is actually the case for all materials considered here, for temperatures close to the transition temperature. This fact follows immediately from the knowledge of the mobility in magnetic materials at the transition temperature.

Consequently, all results derived here suffer from the possible consequences of the unjustified adoption of a calculation technique which is in reality not applicable to the physical situation at hand.

The major objection now mentioned applies to all materials cited in the Introduction in the vicinity of the transition point. Moreover, in the case of the transition-metal oxides, the mobility is low at all temperatures, so that the consideration of Hamiltonian (6) as a perturbation is not allowed, in consideration of the fact that the energy related to Hamiltonian (6) exceeds the band width in such compounds. Even the formal expression of Hamiltonian (6) is questionable in such a physical situation: A different model should be considered, one in which the interaction between the spin of the carrier and the spin of the carrier is treated in its turn as a perturbation.

The conclusion is, of course, that the theory is by no means adequate to give a detailed explanation of the observed phenomena, especially in the case of transition-metal oxides.

A number of qualitative experimental features are nevertheless reproduced by the theory, as listed above. This fact is a clear indication that the mechanisms described by Hamiltonians (6) and (7) are probably responsible for the anomalous Hall effect. This is the only result the theory may claim at present. A different description of the mechanisms here described by Hamiltonians (6) and (7), and a different calculation procedure are to be adopted in general, and in particular for transition-metal oxides, to produce a more suitable theory. This approach appears nevertheless extremely difficult at present.

One more drawback of the theory should be mentioned in conclusion: It is experimentally established that α in Eq. (30) is very close to -1 for all the semiconducting compounds considered. In the theory, as it stands in this paper, this can only be coincidental, while there is evidence to indicate that, on the contrary, a more fundamental reason for this interesting behavior of α in different materials must exist.

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²⁸ In the opinion of the present author, the effect considered by Kondo (Ref. 16) is also two orders of magnitude too small. If the parameter appearing in Kondo's theory is estimated on the basis of the rough knowledge of the order of magnitude of the quantities appearing in it, the values obtained by Kondo by adjusting the parameter to fit experiment are a hundred times too large. Kondo's parameter is $\lambda F_2(F_0^2 - \frac{4}{3}F_0F_1)/(E_{F_2} - E_0)$. λ is the spin-orbit constant; this is approximately 600 cm⁻¹ for Ni and 400 cm⁻¹ for Fe. The difference $E_{F_2} - E_0$ is of the order of 10⁴ cm⁻¹. F_0 , F_1 , and F_2 are defined by Kondo as exchange integrals in which a Bessel function and the radial part of a localized wave function appear. It is difficult to estimate such integrals from the information available in the literature. One may attempt to establish an upper limit by considering the average 4s-3dexchange integral for F_0 . In this case F_0 is 0.16 eV. This agrees with the estimates of Goodings [J. Appl. Phys. **34**, 1370 (1963)] obtained from optical spectra. F_1 and F_2 should be smaller than F_0 . If one takes $F_0 = F_1 = F_2 = 0.2$ eV, and estimates Kondo's parameter, a result is obtained of the order $1.6 \times 10^{-4} \text{ eV}^3$, while the values cited by Kondo are 0.03 and 0.12 eV³ for Ni and Fe, respectively.