NOVEMBER 15, 1940 PHYSICAL REVIEW VOLUME 58

Ferromagnetic Anisotropy and the Itinerant Electron Model

HARVEY BROOKS
Harvard University, Cambridge, Massachusetts

(Received October 3, 1940)

The purpose of the present investigation is to explore the possibilities of the "itinerant" or "collective" electron picture in the theory of metals to explain the quenching of orbital angular momentum in solids and, through the introduction of l,s coupling, the phenomenon of ferromagnetic anisotropy in cubic crystals. The approach used is that of the Bloch "approximation of tight binding" in the theory of metals, the exchange energy being treated as a Weiss internal field as in the work of Stoner and Slater, and the spin-orbit coupling being introduced as a perturbation. The anisotropy is shown to appear in the fourth approximation, and to have the correct order of magnitude for iron and nickel. The model also predicts the correct sign of K_1 in nickel and iron, but this prediction is not entirely satisfactory because computational difficulties prevent the inclusion of all the d-wave functions in the calculation. A qualitative discussion of the behavior of iron-nickel alloys is given. The chief weakness of the model is its failure to take account adequately of Russell-Saunders coupling within the atom, and the dependence of many of its predictions on details of the model which are not very well established.

INTRODUCTION

A CONSIDERABLE amount of experimental data has accumulated in recent years on the magnetic anisotropy of ferromagnetic cubic crystals.[1] Most of the observed effects can be interpreted on the assumption that the crystal is composed of a number of magnetized domains,[2] whose energy depends upon the orientation of the magnetic intensity in the domain relative to the crystalline axes. Thus the energy of a domain takes the form

$$E=E_0+f(\alpha_1, \alpha_2, \alpha_3), \tag{1}$$

where $\alpha_1, \alpha_2, \alpha_3$ are the direction cosines of the magnetization. Fortunately the form of the function $f(\alpha_1, \alpha_2, \alpha_3)$ may be deduced from the symmetry class[3] of the crystal without any assumptions as to the mechanism responsible for the anisotropy. In a cubic crystal, for example, it may be shown that the energy must take the form

$$E=E_0+K_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_1^2\alpha_3^2)+K_2(\alpha_1^2\alpha_2^2\alpha_3^2) \tag{2}$$

plus higher degree terms which have never been found necessary in practice. The magnitude and general properties of the coefficients K_1 and K_2 are not, of course, determined by the symmetry, but may be deduced from experiment.[1] The elucidation of the magnitude, sign, and temperature and alloy composition dependence of K_1 and K_2 is a task for the electron theory of metals. The Heisenberg exchange coupling, which accounts so nicely for the existence and general properties of the ferromagnetic state,[4] is of no use in explaining the anisotropy since it depends only on the relative orientations of neighboring spins and not on their absolute orientation with respect to the crystal. The earliest such mechanism proposed was the magnetic dipole interaction between spins. This interaction contains a term depending on the orientation of the spins with respect to the line joining them, and such terms are naturally structure dependent since they depend on the actual positions of the spins in the lattice. In cubic crystals, however, the magnetic interaction vanishes in first approximation because of the symmetrical arrangement of nearest neighbors, and the second approximation of perturbation theory gives much too small a magnitude for the anisotropy constants.[5] Bloch and Gentile[5] suggested instead that the spin-orbit coupling, acting in conjunction with the electrostatic coupling of the orbit to the crystal, would provide an anisotropy of the proper magnitude, and at present this is the generally accepted view. The two models are not dissimilar from the mathematical viewpoint, since, as Van Vleck[6] has

---

[1] R. M. Bozorth, J. App. Phys. **8**, 575 (1937); E. C. Stoner, *Magnetism and Matter* (Methuen, 1933).

[2] Cf., for example, W. Heisenberg, Zeits. f. Physik **69**, 287 (1931); R. M. Bozorth and E. C. Stoner, reference 1.

[3] F. Bitter, *Introduction to Ferromagnetism* (McGraw-Hill, 1938).

[4] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928).

[5] R. Becker, Zeits. f. Physik **62**, 253 (1930); F. Bloch and G. Gentile, Zeits. f. Physik **70**, 395 (1931).

[6] J. H. Van Vleck, Phys. Rev. **52**, 1178 (1937).

indicated, the mechanism of Bloch and Gentile gives rise to an apparent dipole-dipole as well as quadrupole-quadrupole coupling which is of much greater magnitude than the purely magnetic interaction. Calculations using this somewhat phenomenological substitute for the true mechanism were undertaken from different viewpoints by Van Vleck and van Peype, a pupil of Kramers.[7]

In spite of their success these methods are not entirely satisfactory because of their semiphenomenological approach, and it therefore seems worth while to attempt a calculation with a more explicit model, which gives a more detailed insight into the origin of the coupling terms. Van Vleck's theory is based on the many-electron (Heisenberg) model, which is too complicated for rigorous solution. At Professor Van Vleck's suggestion, accordingly, we have treated ferromagnetic anisotropy from the standpoint of the "itinerant" or "collective" electron model of Bloch, Stoner, and Slater,[8] in which each electron is treated as belonging to the metal as a whole and as moving independently of the other electrons in a self-consistent field determined by the potential of the ions and the "time exposure" field of the other electrons. Although this model is a far poorer approximation for the tightly bound d electrons involved in ferromagnetism than the Heisenberg model, it leads to a secular equation which is reasonably manageable, and which, with the introduction of spin-orbit interaction, gives rise to ferromagnetic anisotropy in a straightforward manner.

Quenching of Orbital Momentum

The whole mechanism of ferromagnetic anisotropy bears an intimate relation to the quenching of the orbital angular momentum in solids. Determinations of the gyromagnetic ratio for the ferromagnetic metals and alloys give a g factor only slightly less than 2, showing that even though the electrons involved in the magnetic properties are d electrons, their orbital angular momentum is not free to orient and precess in an external field. This means that there is a powerful force within the crystal tending to orient the charge cloud around each atom in a definite manner with respect to the crystal axes. The weak magnetic coupling of the spin to the orbit insures that this force will be "felt" slightly by the spin, whose energy is therefore not entirely independent of orientation. The most obvious orienting or "quenching" mechanism would be the crystalline Stark effect,[9] lifting as it does the degeneracy between the various magnetic substates of a given total angular momentum, but unfortunately this is not an adequate mechanism for cubic crystals, where the asymmetry of the electrostatic field is not sufficient completely to destroy the degeneracy with respect to the magnetic quantum number. In a cubic field, as shown by Bethe,[9] an atomic d level subdivides into two levels, forming the representations Γ_3 and Γ_5 of the cubic group. The Γ_3 level is doubly degenerate but magnetically inactive, but the Γ_5 level is triply degenerate and possesses matrix elements of the magnetic moment between its substates. If the level is not completely filled in the solid state, therefore, we should expect contributions to the magnetic moment from the orbit as well as the spin, and a g factor considerably less than 2. In order to remove this discrepancy Sommerfeld and Bethe[10] suggested an additional quenching arising from an antiferromagnetic coupling between orbital angular momenta on different atoms, and this is the sort of quenching postulated by Van Vleck and van Peype. In the itinerant electron picture the quenching arises naturally from the hopping of electrons between adjacent atoms. Even in the tightly bound d band the hopping takes place with sufficient frequency to destroy any orientation in an external magnetic field. In more quantum-mechanical language, the situation may be described as follows. In the Heisenberg model each electron is confined to its own atom, and its energy levels are determined by a field having the symmetry of the point group about a fixed atom. In this field the representations and energy levels are degenerate as described above. In the

---

[7] W. van Peype, Physica **5**, 465 (1938).

[8] F. Bloch, Zeits. f. Physik **57**, 545 (1929); J. C. Slater, Phys. Rev. **49**, 537 (1936); E. C. Stoner, Proc. Roy. Soc. **A165**, 372 (1938).

[9] H. Bethe, Ann. d. Physik **3**, 137 (1929); Zeits. f. Physik **60**, 218 (1930); H. Kramers, Proc. Amst. Acad. **32**, 1176 (1929); **33**, 959 (1930); W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932); **42**, 166 (1932); J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford, 1932), Section 73.

[10] A. Sommerfeld and H. Bethe, *Handbuch der Physik* (second edition, Berlin, 1933), Vol. 24/2, p. 613.

itinerant model, on the other hand, each electron moves in a field whose symmetry is determined by the space group of the whole crystal, including translations as well as rotations. For the majority of wave vectors **k** the representations are nondegenerate, the space-group insuring the removal of the degeneracy which may exist under the point group alone. The reality of the resultant nondegenerate wave functions then precludes the existence of diagonal matrix elements of the magnetic moment, and such nondiagonal elements as there may be join states whose energy differences are large compared to the magnetic perturbation.

Approximate Structure of *D* Bands

In order to put these ideas on a quantitative basis it is necessary to say something about the form of the *d* bands in cubic crystals. This is a case where the Bloch "approximation of tight binding"[11] is reasonably reliable, since the overlapping of the *d* shells is small. The energy levels are just those of the single atom subject to the crystalline Stark effect, except that each level is broadened out into a band, arising from the possibility of leakage of electrons between atoms. When the original atomic levels are degenerate, however, the substates give rise to a number of overlapping bands, and considerable care is necessary in choosing the correct linear combinations of wave functions which diagonalize the perturbing energy.

In setting up the secular equation we confine ourselves to the Γ_5 level, although this is a poor assumption, in that there are matrix elements of the magnetic moment between the Γ_3 and Γ_5 levels as well as between the substates of Γ_5. For the purposes of this paper we shall assume that the separation between Γ_3 and Γ_5 is large compared to the broadening of the individual levels. The atomic wave functions of the Γ_5 level are:

$$\phi_1=yzf(r),\quad \phi_2=zxf(r),\quad \phi_3=xyf(r). \tag{3}$$

In the approximation of tight binding we start with the linear combinations:[11]

$$\psi_n(\mathbf{k})=N^{-\frac{1}{2}}\sum_{\mathbf{l}}\exp(ia\mathbf{l}\cdot\mathbf{k})\phi_n(\mathbf{r}-a\mathbf{l}), \tag{4}$$

where a is the lattice constant, N the total number of atoms in a domain, **l** a vector representing the lattice points. With these wave functions and a perturbing potential equal to the difference between the crystalline self-consistent field and the potential due to the free ion, the secular equation factors according to **k**, but for each value of **k** there are in general matrix elements of the "hopping" energy (perturbing potential) between states of different n. Thus for each value of **k**, the wave vector, the energy is obtained as a root of a third-degree secular equation:

$$\begin{vmatrix} H_1-E & H_{12} & H_{13} \\ H_{12} & H_2-E & H_{23} \\ H_{13} & H_{23} & H_3-E \end{vmatrix}=0,\qquad \begin{aligned} H_1&=\int\psi_1^*(\mathbf{k})H\psi_1(\mathbf{k})d\tau, \\ H_{12}&=\int\psi_1^*(\mathbf{k})H\psi_2(\mathbf{k})d\tau. \end{aligned} \tag{5}$$

This equation was first obtained by Jones and Mott[12] for the body-centered cubic lattice. In this case the matrix elements are:

$$\begin{aligned} &H_1=H_2=H_3=-8A\cos\xi\cos\eta\cos\zeta, && H_{12}=8B\sin\xi\sin\eta\cos\zeta, \\ &H_{23}=8B\cos\xi\sin\eta\sin\zeta, && H_{13}=8B\sin\xi\cos\eta\sin\zeta \end{aligned} \tag{6}$$

---

[11] F. Bloch, Zeits. f. Physik **52**, 55 (1928); N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford, 1936), Chapter II.

[12] H. Jones and N. F. Mott, Proc. Roy. Soc. **A162**, 49 (1937).

where ξ, η, ζ are defined by $\xi=\frac{1}{2}k_xa$, $\eta=\frac{1}{2}k_ya$, $\zeta=\frac{1}{2}k_za$ and where

$$\begin{aligned} A&=-\int\phi_1(xyz)H'\phi_1(x+\tfrac{1}{2}a,\, y+\tfrac{1}{2}a,\, z+\tfrac{1}{2}a)dV,\\ B&=-\int\phi_1(xyz)H'\phi_2(x+\tfrac{1}{2}a,\, y+\tfrac{1}{2}a,\, z+\tfrac{1}{2}a)dV. \end{aligned}\tag{7}$$

Since the perturbing potential is negative, A and B are positive.[13]

For the face-centered cubic the matrix elements are readily obtained. The diagonal elements are:

$$\begin{aligned} H_1&=4A_1(\cos\xi\cos\eta+\cos\xi\cos\zeta)-4A_2\cos\eta\cos\zeta,\\ H_2&=4A_1(\cos\xi\cos\eta+\cos\eta\cos\zeta)-4A_2\cos\xi\cos\zeta,\\ H_3&=4A_1(\cos\xi\cos\zeta+\cos\eta\cos\zeta)-4A_2\cos\xi\cos\eta,\\ A_1&=\int xyf(r)H'(x+\tfrac{1}{2}a)yf(|(x+\tfrac{1}{2}a)^2+y^2+(z+\tfrac{1}{2}a)^2|^{\frac{1}{2}})dV,\\ A_2&=-\int xyf(r)H'(x+\tfrac{1}{2}a)(y+\tfrac{1}{2}a)f(|(x+\tfrac{1}{2}a)^2+(y+\tfrac{1}{2}a)^2+z^2|^{\frac{1}{2}})dV. \end{aligned}\tag{8}$$

A simple argument shows that A_1 and A_2 are positive as defined and that $A_2>A_1$.[14]

The off-diagonal elements are

$$H_{12}=-4B\sin\xi\sin\eta,\quad H_{23}=-4B\sin\eta\sin\zeta,\quad H_{13}=-4B\sin\xi\sin\zeta\tag{9}$$

and B as defined is positive.

Solutions of Secular Equation

1. Body-centered cubic

The solution has been obtained in approximate form by Jones and Mott.[12] The result is expressed in terms of a variable $x=(E/8B)+(A/B)\cos\xi\cos\eta\cos\zeta$. For most values of the wave vector the approximate solutions are:

$$x=0,\quad x=\pm\epsilon=\pm(a^2+b^2+c^2)^{\frac{1}{2}},\tag{10}$$

where

$$a=\sin\xi\sin\eta\cos\zeta,\quad b=\sin\xi\cos\eta\sin\zeta,\quad c=\cos\xi\sin\eta\sin\zeta.$$

With these energies the approximate form of the diagonalizing transformation is:

$$\begin{array}{c|ccc} & \phi_1 & \phi_2 & \phi_3\\ \hline 0 & -c\epsilon^{-1} & b\epsilon^{-1} & a\epsilon^{-1}\\ + & \frac{1}{2}\sqrt{2}\tau\epsilon^{-1} & \frac{1}{2}\sqrt{2}\tau^{-1}(a+bc\epsilon^{-1}) & \frac{1}{2}\sqrt{2}\tau^{-1}(b+ac\epsilon^{-1})\\ - & -\frac{1}{2}\sqrt{2}\tau\epsilon^{-1} & \frac{1}{2}\sqrt{2}\tau^{-1}(a-bc\epsilon^{-1}) & \frac{1}{2}\sqrt{2}\tau^{-1}(b-ac\epsilon^{-1}) \end{array}\tag{11}$$

where

$$\tau=(a^2+b^2)^{\frac{1}{2}},\quad \epsilon=(a^2+b^2+c^2)^{\frac{1}{2}}.$$

This gives the energy correctly except for terms of order abc/ϵ^2, which happens to be small for most values of the wave vector **k**. Thus the continuum generated by the three Γ_5 functions really consists of three overlapping bands. Each band is referred to an atomic function which is a linear combination of the functions (3), and which is different for each choice of propagation vector.

2. Face-centered cubic

We divide the secular equation through by $4B$ and define

$$x=(E/4B)-(A_1/B)(\cos\xi\cos\eta+\cos\xi\cos\zeta+\cos\eta\cos\zeta),\quad Q=(A_1+A_2)/B.\tag{12}$$

Here it must be remembered that $B<(A_1+A_2)$, and that therefore Q is large compared to unity. This being the case, the secular equation is largely dominated by its diagonal elements, except for the special values of **k** for which they become nearly equal. This means that in the face-centered cubic the original ϕ_1, ϕ_2, ϕ_3 are nearly the true atomic wave functions for the three bands of the Γ_5 level.

Similar results apply in the simple cubic lattice, but here it may be shown that the off-diagonal matrix elements vanish altogether so that the functions (3) are just correct.

---

[13] This follows from the fact that $xyf(r)$, $yzf(r)$, and $zxf(r)$ are even with respect to reflections along the body diagonal.

[14] A_1 is positive since the perturbing potential is negative while x and $x+\frac{1}{2}a$ have opposite signs on nearest neighbors. A_2 is positive because the integrand is positive in the region between nearest neighbors. $A_2>A_1$ because $y\sim 0$, i.e., the wave function has a node in the region of maximum perturbing potential.

SPIN-ORBIT INTERACTION

In order to carry on the discussion it is necessary to obtain the matrix elements of the spin-orbit interaction in the system of representation in which the band or "hopping" energy is diagonal. This interaction may be expressed in the form

$$O'=\sum_{\mathbf{l}} \zeta(|\mathbf{r}-a\mathbf{l}|)\mathbf{S}\cdot\mathbf{L}(\mathbf{r}-a\mathbf{l}), \tag{13}$$

where $\mathbf{L}(\mathbf{r}-a\mathbf{l})$ is the angular momentum operator about the atom at lattice position $\mathbf{l}$, and $\zeta(|\mathbf{r}-a\mathbf{l}|)$ is a function falling off as $1/r^3$ at large distances and depending only on the absolute magnitude of the radius vector.[15] O' is an operator which is periodic in the fundamental lattice translations, and hence is rigorously diagonal in $\mathbf{k}$.[16] Its matrix elements between Bloch functions of the same $\mathbf{k}$ and different n are furthermore independent of $\mathbf{k}$ to a first approximation. It is easily shown that

$$(n\mathbf{k}|\zeta(|\mathbf{r}-a\mathbf{l}|)\mathbf{S}\cdot\mathbf{L}(\mathbf{r}-a\mathbf{l})|n'\mathbf{k})=\sum_{\mathbf{l}} \exp(-ia\mathbf{l}\cdot\mathbf{k})\int\phi_{n'}(\mathbf{r}-a\mathbf{l})\zeta(r)\mathbf{S}\cdot\mathbf{L}\phi_n(\mathbf{r})dV. \tag{14}$$

If $\zeta(r)$ falls off sufficiently rapidly the integral in (14) will be inappreciable unless $\mathbf{l}=0$.[17] Thus we see that the matrix elements of the spin-orbit interaction with respect to Bloch functions are practically the same as between the corresponding atomic functions, that is

$$\int\psi_{n'}(\mathbf{k})O'\psi_n(\mathbf{k})dV=A(n'm_s'|\mathbf{S}\cdot\mathbf{L}|nm_s). \tag{15}$$

In this equation A is the ordinary spin-orbit interaction parameter for free atoms. It is the interaction for an individual electron, corresponding to the small a_i in Goudsmit's[18] notation, and must not be confused with the spin-orbit interaction parameter for the atom as a whole. The point is that we are here assuming the "hopping" energy sufficient completely to destroy the Russell-Saunders coupling within the atom, so that there is no question of the individual electronic angular momenta combining to form a resultant $\mathbf{L}$ and $\mathbf{S}$. This is a poor approximation since, owing to the tight binding of the d shell, there must be a rather high degree of internal coupling, but so far no way has been developed of taking it into account in the itinerant electron model, where the electrons are treated as essentially independent. We assume that the secular equation for the Γ_5 bands is diagonalized by a set of real transformation coefficients $a(\tau, n)$. In terms of this diagonal representation (labeled by the index τ), we find for the matrix elements of the spin-orbit interaction

$$\begin{aligned}(\tau m_s|\mathbf{S}\cdot\mathbf{L}|\tau' m_s')&=\sum a(\tau, n)(nm_s|\mathbf{S}\cdot\mathbf{L}|n'm_s')a(\tau', n')\\&=\sum_{n<n'}\{a(\tau, n)a(\tau', n')-a(\tau', n)a(\tau, n')\}(nm_s|\mathbf{S}\cdot\mathbf{L}|n'm_s'),\end{aligned} \tag{16}$$

where the index n refers to the original set of atomic wave functions [Eq. (3)]. In this representation the spin is quantized along the z axis. In practice, however, the spin must be quantized parallel to the external field. In this new system of representation the matrix elements are as follows:

$$\begin{aligned}&(\tau_1, \tfrac{1}{2}|\mathbf{S}\cdot\mathbf{L}|\tau_2, \tfrac{1}{2})=-i\cos\theta', \qquad (\tau_1, \tfrac{1}{2}|\mathbf{S}\cdot\mathbf{L}|\tau_3, \tfrac{1}{2})=i\sin\theta'\sin\phi',\\&(\tau_2, \tfrac{1}{2}|\mathbf{S}\cdot\mathbf{L}|\tau_3, \tfrac{1}{2})=-i\sin\theta'\cos\phi', \quad (\tau_1, \tfrac{1}{2}|\mathbf{S}\cdot\mathbf{L}|\tau_2, -\tfrac{1}{2})=\exp(-i\phi')[-i\sin\theta'],\\&(\tau_1, \tfrac{1}{2}|\mathbf{S}\cdot\mathbf{L}|\tau_3, -\tfrac{1}{2})=\exp(-i\phi')[-\cos\phi'-i\cos\theta'\sin\phi'],\\&(\tau_2, \tfrac{1}{2}|\mathbf{S}\cdot\mathbf{L}|\tau_3, -\tfrac{1}{2})=\exp(-i\phi')[-\sin\phi'+i\cos\theta'\cos\phi'].\end{aligned} \tag{17}$$

The angles θ', ϕ' are measured not with respect to the x, y, z axes but with respect to a new set of axes determined by the unit vectors $\mathbf{i}'$, $\mathbf{j}'$, $\mathbf{k}'$, which are defined in terms of the transformation coefficients as follows:

$$\mathbf{i}'=[a(\tau_1, 1), a(\tau_1, 2), a(\tau_1, 3)], \quad \mathbf{j}'=[a(\tau_2, 1), a(\tau_2, 2), a(\tau_2, 3)], \quad \mathbf{k}'=[a(\tau_3, 1), a(\tau_3, 2), a(\tau_3, 3)]. \tag{18}$$

---

[15] E. U. Condon and G. Shortley, *Theory of Atomic Spectra* (Cambridge, 1936), p. 120.

[16] N. F. Mott and H. Jones, reference 11, p. 59.

[17] A more detailed analysis of the spin-orbit effects would necessitate inclusion of the spin-other-orbit interaction. For atoms distant from the one in question this would tend to cancel out almost exactly the $1/r^3$ term arising from the ions, and so in effect $\zeta(r)$ would probably fall off exponentially rather than as $1/r^3$.

[18] S. Goudsmit, Phys. Rev. **31**, 946 (1928).

TABLE I. *Secular equation for ferromagnetic anisotropy, including spin-orbit interaction. Angles measured with respect to special skew axes determined by transformation coefficients, as shown in Eq. (18).*

	$\tau 1, \frac{1}{2}$	$\tau 2, \frac{1}{2}$	$\tau 3, \frac{1}{2}$	$\tau 1, -\frac{1}{2}$	$\tau 2, -\frac{1}{2}$	$\tau 3, -\frac{1}{2}$
$\tau 1, \frac{1}{2}$	$E_1+\delta-E$	$-iA\cos\theta'$	$iA\sin\theta'\sin\phi'$	0	$-iA\sin\theta'$	$-A\cos\phi'-iA\cos\theta'\sin\phi'$
$\tau 2, \frac{1}{2}$	$iA\cos\theta'$	$E_2+\delta-E$	$-iA\sin\theta'\cos\phi'$	$iA\sin\theta'$	0	$-A\sin\phi'+iA\cos\theta'\cos\phi'$
$\tau 3, \frac{1}{2}$	$-iA\sin\theta'\sin\phi'$	$iA\sin\theta'\cos\phi'$	$E_3+\delta-E$	$A\cos\phi'+iA\cos\theta'\sin\phi'$	$A\sin\phi'-iA\cos\theta'\cos\phi'$	0
$\tau 1, -\frac{1}{2}$	0	$-iA\sin\theta'$	$A\cos\phi'-iA\cos\theta'\sin\phi'$	$E_1-\delta-E$	$iA\cos\theta'$	$-iA\sin\theta'\sin\phi'$
$\tau 2, -\frac{1}{2}$	$iA\sin\theta'$	0	$A\sin\phi'+iA\cos\theta'\cos\phi'$	$-iA\cos\theta'$	$E_2-\delta-E$	$iA\sin\theta'\cos\phi'$
$\tau 3, -\frac{1}{2}$	$-A\cos\phi'+iA\cos\theta'\sin\phi'$	$-A\sin\phi'-iA\cos\theta'\cos\phi'$	0	$+iA\sin\theta'\sin\phi'$	$-iA\sin\theta'\cos\phi'$	$E_3-\delta-E$

Because of the unitary property of the transformation matrix the vectors $\mathbf{i}'$, $\mathbf{j}'$, $\mathbf{k}'$ form an orthogonal unit set, and θ', ϕ' are the polar angles of the magnetic field vector measured with respect to this set.

The complete secular problem, including the spin-orbit interaction, is of the sixth order, corresponding to the three overlapping bands of the Γ_5 level, and the two possible orientations of the spin. The secular determinant is shown in Table I. E_1, E_2, and E_3 are the energies of the three bands, and are, of course, functions of the wave vector $\mathbf{k}$. In this problem we have made the usual approximation of replacing the exchange energy by an internal "molecular" field $\delta=k\tau'\lambda$. Here λ is the fractional magnetization I/I_0, where I_0 is the saturation intensity, and $k\tau'$ is n_BJ, where n_B is the number of free spins per atom (electrons or holes) corresponding to the saturation magnetization; also J is the atomic exchange integral,[19] that is, the exchange integral between electronic wave functions normalized per unit cell rather than for the whole crystal. In the system of representation we have chosen, the energy matrix is diagonal in everything except the spin-orbit interaction, which may be considered as small compared to the difference between diagonal elements in Table I. Thus the solutions of the secular problem may readily be expanded in powers of the spin-orbit parameter A, the successive powers being obtained in the successive orders of perturbation theory.

DETAILED DERIVATION OF G FACTOR

We have already seen that the removal of the degeneracy of the cubic levels under the space group accounts for the almost complete quenching of the orbital angular momentum. There is, however, a secondary effect which allows the g factor to differ slightly from 2. Owing to the spin-orbit interaction there is in effect a small internal field tending to orient the orbital angular momentum, in addition to the large field acting on the spins and arising from exchange. The result of this field is always to make the g factor slightly less than 2. From the secular equation we obtain the first-order correction to the wavefunctions by the usual perturbation method:

$$\psi=\phi_3{}^+-\frac{iA\sin\theta'\sin\phi'}{\epsilon_1}\phi_1{}^+ +\frac{iA\sin\theta'\cos\phi'}{\epsilon_2}\phi_2{}^+ +\frac{A\cos\phi'+iA\cos\theta'\sin\phi'}{\epsilon_1+2\delta}\phi_1{}^- +\frac{A\sin\phi'-iA\cos\theta'\cos\phi'}{\epsilon_2+2\delta}\phi_2{}^-, \qquad (19)$$

$$\epsilon_1=E_3-E_1,\quad \epsilon_2=E_3-E_2,$$

where ϕ_1, ϕ_2, ϕ_3 are the wave functions for the three bands and the indices $+$, $-$ stand for the spin directions. We must find the mean of the magnetic energy with respect to these wave functions. Unfortunately, since it is linear in the coordinates, the vector potential cannot be treated as a small perturbation throughout the crystal. This difficulty may be obviated by a method of gauge transformations due to Peierls and F. London,[20] in such a way that the magnetic energy for Bloch functions is the same as for the corresponding atomic functions.[21] The correction to the energy arising in this way is

$$\Delta E=-2\mu HA(\alpha_2'^2\epsilon_1^{-1}+\alpha_1'^2\epsilon_2^{-1})+O(A^2). \qquad (20)$$

Here α_1', α_2' are direction cosines with respect to the skew axes defined by (18). Equation (20) gives the energy correction for one electron. To obtain the magnetic energy for the crystal as a whole we must sum over the occupied electronic states of the Fermi distribution, taking proper account of the symmetry properties of the energy

---

[19] J. C. Slater, E. C. Stoner, reference 8.

[20] R. Peierls, Zeits. f. Physik **80**, 763 (1933); F. London, J. de phys. et rad. **8**, 397 (1937).

[21] One naturally neglects diamagnetic effects arising from the migration of electrons among many atoms.

surfaces.[22] Finally dividing by the total angular momentum leads to a g factor

$$g=2+\tfrac{2}{3}A\langle\epsilon_1^{-1}+\epsilon_2^{-1}\rangle_{\text{Av}}. \tag{21}$$

The average is taken over all the occupied states for both directions of spin. Since the second term of (21) averages to zero when all the d levels are fully occupied, we may replace the average over the occupied states by the negative of the average over unoccupied states or "holes" of the distribution. In nickel and iron the band is nearly full, and most of the holes are in the highest of the three energy bands so that the energy differences $\epsilon_1(=E_3-E_1)$ and $\epsilon_2(=E_3-E_2)$ are positive for the overwhelming majority of the states involved in the averaging processes. Thus the second term of (21) is always negative, and the g factor is slightly less than 2, since A is positive for single electrons. This is in agreement with observation, and means simply that there is a slight tendency for the orbit to aline itself parallel to the orienting fields (external and internal). Assuming a spin-orbit parameter of about 500 cm^{-1}, and a mean band width of about 20,000 cm^{-1}, we obtain a g factor in the neighborhood of 1.97. Experimentally the departures from 2 range between 0.1 given by Barnett[23] to 0.004 obtained by Sucksmith and Bates for Ni.[24] Our calculated departure of 0.03 is thus of the correct order of magnitude.

CALCULATION OF ANISOTROPY CONSTANT

The calculation of the anisotropy constant K_1 is made by applying fourth-order perturbation theory to the secular equation shown in Table I. The energy corrections arising from lower orders of perturbation theory are easily shown to possess no angular dependence when the summation is carried out over all the occupied states. This result follows from the symmetry properties of the energy surfaces and is analogous to the argument usually employed to fix the form of the angular dependence in cubic crystals.[25] In carrying out the fourth-order calculation, we need include only terms whose angular dependence is of the form $\alpha_i'^2\alpha_j'^2$.[26] In this way we obtain for the fourth-order energy an expression

$$A_{12}\alpha_1'^2\alpha_2'^2+A_{23}\alpha_2'^2\alpha_3'^2+A_{13}\alpha_1'^2\alpha_3'^2 \tag{22}$$

in which α_1', α_2', α_3' are the direction cosines of the magnetic field with respect to the skew axes defined by (18), and A_{12}, A_{13}, A_{23} are given by the following expressions:

$$\begin{aligned}
A_{12}&=\frac{A^4}{2\delta}\left\{\frac{1}{\epsilon_1}-\frac{1}{\epsilon_2}-\frac{1}{\epsilon_1+2\delta}+\frac{1}{\epsilon_2+2\delta}\right\}^2+A^4\left\{\frac{1}{\epsilon_1}-\frac{1}{\epsilon_2}-\frac{1}{\epsilon_1+2\delta}+\frac{1}{\epsilon_2+2\delta}\right\}\left\{\frac{1}{\epsilon_1^2}-\frac{1}{\epsilon_2^2}-\frac{1}{(\epsilon_1+2\delta)^2}+\frac{1}{(\epsilon_2+2\delta)^2}\right\},\\
A_{23}&=A^4\left\{\frac{1}{\epsilon_2}-\frac{1}{\epsilon_2+2\delta}+\frac{1}{2\delta}+\frac{1}{\epsilon_1}+\frac{1}{\epsilon_1+2\delta}\right\}\left\{\frac{1}{\epsilon_1}-\frac{1}{\epsilon_1+2\delta}\right\}^2,\\
A_{13}&=A^4\left\{\frac{1}{\epsilon_1}-\frac{1}{\epsilon_1+2\delta}+\frac{1}{2\delta}+\frac{1}{\epsilon_2}+\frac{1}{\epsilon_2+2\delta}\right\}\left\{\frac{1}{\epsilon_2}-\frac{1}{\epsilon_2+2\delta}\right\}^2,
\end{aligned} \tag{23}$$

where now $\epsilon_1=E_3-E_1$, $\epsilon_2=E_3-E_2$, $\delta=n_BJI/I_0$.

In Eq. (22) we must expand the primed direction cosines in terms of the unprimed ones, using the definition of the primed axes: $\alpha_\tau'=\sum_n a(\tau,n)\alpha_n$, where the α_n are defined so that $\alpha_1=\alpha_x$, $\alpha_2=\alpha_y$, $\alpha_3=\alpha_z$. Substituting into Eq. (22), and using the symmetry argument once again, as well as the unitary property of the transformation coefficients, we obtain a relatively simple formula for the anisotropy constant K_1, namely

$$K_1=\tfrac{1}{3}\sum_{\mu<\nu}A_{\mu\nu}[1-5J_{\mu\nu}]\times\{\alpha_x^2\alpha_y^2+\alpha_x^2\alpha_z^2+\alpha_y^2\alpha_z^2\}, \tag{24}$$

---

[22] Brouckaert, Wigner and Smoluchowski, Phys. Rev. **50**, 58 (1936); Conyers Herring, Phys. Rev. **52**, 365 (1937). Cf. particularly Manning and Chodorow, Phys. Rev. **56**, 787 (1939), discussion in fine print at end of paper.

[23] S. J. Barnett, Rev. Mod. Phys. **7**, 129 (1935).

[24] W. Sucksmith and L. F. Bates, Proc. Roy. Soc. **A104**, 499 (1923); L. F. Bates, *Modern Magnetism* (Cambridge, 1939).

[25] Details of this argument, which is really quite obvious physically, are included in the author's thesis, Harvard (1940).

[26] It is to be understood, however, that all terms in the fourth power of the direction cosines such as $\alpha_1'^4$ are to be expressed as: $\alpha_1'^2(1-\alpha_2'^2-\alpha_3'^2)$.

where the $J_{\mu\nu}$ are defined by a biquadratic expression in the transformation coefficients:

$$J_{\mu\nu}=\sum_{j}[a(\mu,j)]^2[a(\nu,j)]^2. \quad (25)$$

On account of the terms in $J_{\mu\nu}$ the anisotropy bears a very close relation to the structure of the energy bands. If the original wave functions $xyf(r)$, $yzf(r)$, $zxf(r)$ are a good set of atomic functions for setting up the Bloch waves which diagonalize the band energy, then the $J_{\mu\nu}$ will be small and the anisotropy, as will be shown, is negative. But if the bands are not well described by the functions $xyf(r)$, etc., but rather by linear combinations such as $\psi_\tau=\sum_n a(\tau,n)\phi_n$, then the $J_{\mu\nu}$ may become important, and the anisotropy may even change sign and become positive as we shall show to be the case for iron. This effect has no counterpart in the theories of Van Vleck and van Peype, but seems to be characteristic of the particular model we have adopted.

NICKEL

The above discussion is well illustrated by the two common ferromagnetics nickel and iron. As can be seen by reference to the section on the structure of the d bands, nickel is a good example of the case where the functions $xyf(r)$, etc., are a good approximation and the $J_{\mu\nu}$ are small. To simplify the discussion we shall consider only the case of magnetic saturation, i.e., very low temperatures. The expressions for the $A_{\mu\nu}$ in Eq. (23) must be summed over all the occupied states in the three bands. The summation is carried out most readily by expressing each of the $A_{\mu\nu}$ as a sum $f_1(\delta)+f_2(\delta)$ of an even function of δ plus an odd function of δ, respectively ($f_1(\delta)=f_1(-\delta)$, $f_2(\delta)=-f_2(-\delta)$). Here δ, it must be remembered, is a quantity proportional to the exchange energy, whose sign is negative for spins parallel to the external field and positive for spins antiparallel to this field. The terms in the summation of the odd function cancel out in pairs for all states which are occupied by both directions of spin, so that we are left with a summation over only those states which contribute directly to the magnetic moment, whose spins are parallel to the external field. On the other hand, the summation for the even function must be carried out over all occupied states since the function has the same sign for both spin directions. However, $\sum f_1(\delta)$ vanishes when taken over all states, unoccupied and occupied alike, as follows by application of the diagonal sum rule to the matrix of Table I. Thus the sum over occupied states may be replaced by the negative of the sum over unoccupied states, and since the sign of δ is immaterial for the function $f_1(\delta)$, the summation may be carried out over exactly the same states as f_2, namely, those contributing directly to the magnetic moment. Thus we have the result: K_1 = sum over all occupied states of $(A_{12}+A_{23}+A_{13})$ = sum over states of unpaired spin of $-f_1(\delta)+f_2(-\delta)=-[f_1(\delta)+f_2(\delta)]$. The last is just the negative of Eqs. (23) summed over all the magnetic states, but with δ treated as a positive quantity. Since we are dealing with a band which is well over half full, most of the unpaired spins lie in the uppermost of the three Γ_5 bands, so that both the quantities ϵ_1 and ϵ_2 are positive. With these facts it is readily shown that $A_{\mu\nu}$ in Eq. (23) are all positive, irrespective of the numerical magnitudes of ϵ_1, ϵ_2, and δ. Thus the sign of K_1 in nickel is proved to be negative under quite general conditions.

The most recent results on the anisotropy of iron and nickel are due, for nickel, to Bozorth and Williams[27] who find $K_1=8\times10^5$ ergs/cc by extrapolation to absolute zero; for iron to L. P. Tarasov[28] who gives $K_1=5.3\times10^5$ ergs/cc at room temperature. The latter value would probably not be increased by a factor of more than 2 on extrapolation to absolute zero. It is of course impossible to reproduce these values to within better than a factor of 10 by means of the theory, but with this accuracy the theory predicts the correct order of magnitude. In his paper on ferromagnetism Slater[29] has given curves showing the distribution of states in the d band for copper, which he assumes to be similar to that of nickel. The six highest energy electrons, which presumably correspond to those occupying the states of the Γ_5 level in our model, occupy an energy range of about 50,000 cm^{-1}. Thus we

---

[27] H. J. Williams and R. M. Bozorth, Phys. Rev. **56**, 837 (1939).

[28] L. P. Tarasov, Phys. Rev. **56**, 1231 (1939).

[29] J. C. Slater, Phys. Rev. **49**, 537 (1936).

should not be far off in taking as a mean value for the separation of levels of the same **k**, (i.e., the quantities ϵ_1 and ϵ_2 in Eq. (23)), a value of 10,000 cm^{-1}. Slater has also estimated the value of the exchange integral δ, assuming that it arises from intra-atomic exchange. On the face of it, this seems highly unlikely, but the work of Stoner,[30] on the other hand, certainly indicates that the exchange energy cannot be much less than the band spread if ferromagnetism is to occur at all. We should probably not be far off in taking 2δ equal to 8000 cm^{-1} for nickel. Estimates of the spin-orbit parameter A have been made for the transition elements by Goudsmit.[18] Again these estimates cannot be taken too seriously in the solid state, not only because of the uncertainty arising from the incomplete destruction of Russell-Saunders coupling, but also because of the entirely altered screening effect of the conduction electrons in the solid phase.[31] With Goudsmit's estimate of $A=630$ cm^{-1} for nickel, we obtain a value of K_1 between 10^5 and 10^6 ergs/cc, which is the correct order of magnitude. The screening effect of the conduction electrons would tend to reduce the estimate of the spin-orbit parameter somewhat, and provide worse agreement with experiment. For iron Goudsmit estimates $A=390$ cm^{-1}, which would give an anisotropy for iron less than $\frac{1}{5}$ that of nickel, other factors being equal. However, the order of magnitude is still correct, and most of the discrepancy can be accounted for by the greater exchange energy in iron, and the greater number of spins per cc.

SIGN OF K_1—IRON

Iron is a good example of the case where the $J_{\mu\nu}$ of Eqs. (24) and (25) are not negligible. This arises from the fact in the body-centered cubic the diagonal elements of the secular equation for the "hopping" energy are all the same. For the highest of the three Γ_5 bands, namely the band corresponding to $x=+\epsilon$ in Eq. (10), the $J_{\mu\nu}$ may be obtained from the transformation matrix (11) by means of (25), and are as follows:

$$J_{12}=R, \quad J_{23}=R, \quad J_{13}=\tfrac{1}{2}(1-R),$$
$$R=(a^2b^2+a^2c^2+b^2c^2)/\epsilon^4, \tag{26}$$
$$\epsilon=(a^2+b^2+c^2)^{\frac{1}{2}}.$$

a, b, c are defined in terms of the components of the wave vector, as shown in Eq. (10). The maximum value of R is $\frac{1}{3}$.

With these values of $J_{\mu\nu}$, the anisotropy constant follows from Eq. (24). The exact expression is very complicated, but it may be very closely approximated by the formula:

$$K_1=\frac{4\delta^2}{\epsilon^2(\epsilon+2\delta)^2}\left[\frac{1}{6\delta}+\frac{2}{3\epsilon}\right]. \tag{27}$$

This expression applies only to the uppermost of the three bands, in which most of the electrons will lie in practice. The expression is easily seen to be positive for all positive values of ϵ and δ, in agreement with the observed positive sign of K_1 in iron.

The theory is very attractive in that it makes a satisfactory unambiguous prediction of the correct sign of K_1 in nickel and iron. When we come to examine the data on alloys, however, some difficulties begin to appear. The theory suggests, for example, that the sign of the anisotropy is to be correlated with the crystal structure, the difference between iron and nickel arising from the difference in the form of the energy bands between the face-centered and the body-centered lattices. Yet the observations on the Fe-Ni alloy system[32] show no marked discontinuity in the anisotropy as we pass from the face-centered to the body-centered phase. In fact the change in sign of K_1 takes place well within the γ-phase (face-centered) at a composition corresponding to one free spin per atom. All the alloy data suggest a much closer correlation of the anisotropy with the number of free spins per atom than with the crystal structure. In spite of this it is possible to devise a crude qualitative explanation of the alloy data, based on the itinerant electron model, somewhat as follows. In our discussion of the band structure of nickel we assumed that the off-diagonal matrix elements of

---

[30] E. C. Stoner, Proc. Roy. Soc. **A165**, 372 (1938).

[31] This effect is discussed in detail by M. F. Manning and M. I. Chodorov, Phys. Rev. **56**, 787 (1939).

[32] R. M. Bozorth, reference 1.

the "hopping" energy could be neglected. This is true in the approximation of very tight binding, but at the lattice spacing which actually obtains in nickel it is probably a very poor assumption except in portions of the Brillouin Zone in which sin ξ, sin η, and sin ζ are very small, where, as a consequence, the off-diagonal matrix elements are negligible. The electrons or holes in the highest energy states occupy just such a portion of **k**-space. Now, nickel has only 0.6 free spin per atom, and most of these lie in states very near the maximum. We should therefore expect the anisotropy of nickel to be negative, since small off-diagonal elements of the "hopping" energy imply small $J_{\mu\nu}$ in Eq. (24) and hence negative K_1. As iron is added the number of free spins per atom increases rapidly. The additional holes are forced into parts of **k**-space where the off-diagonal "hopping" integrals are large, and these holes will therefore tend to have positive K_1, opposing the effect of holes higher in the band, until finally the interior holes predominate and cause the K_1 for the whole crystal to change sign. For the body-centered phase a somewhat similar explanation applies in reverse. Here the experiments indicate a gradual falling off of K_1 with increasing percentage of nickel. In our model of the body-centered structure we have neglected the effect of next nearest neighbors. This effect will indeed be small except when the off-diagonal elements of the hopping energy are small, namely, near the top of the band. In this case the secular equation for the hopping energy takes a form similar to that for the simple cubic, since the next nearest neighbors lie in the same relative positions as the nearest neighbors in the simple cubic. Thus holes very near the top of the band in iron may be expected to make a negative contribution to K_1, since K_1 for a simple cubic may easily be shown to be negative in our model. Now the addition of nickel to iron decreases the number of free holes, and so increases the relative number of states of negative anisotropy, as these lie closest to the top of the band and so tend to hang on to the bitter end, as it were. There will thus be a gradual decrease of the positive anisotropy of iron with increasing percentage of nickel, in agreement with experiment.

This explanation of the alloy data is very rough, and an attempt at quantitative verification of it with the present model did not prove successful. Nevertheless, the effects calculated were in the right direction, if not of sufficient magnitude to substantiate the qualitative discussion. This is hardly surprising in view of the very approximate nature of our treatment of the band structure.

It would be desirable to obtain some idea of the temperature variation of K_1. Unfortunately, this would involve integration over the distribution with a Fermi distribution function, a task in which the labor involved is hardly commensurate with the results obtainable from so crude a picture of the band structure. It was at first believed that the temperature variation could be represented by a formula such as (27), the anisotropy being expressed as a function of magnetization as in Van Vleck's theory. The variation obtained from this formula, however, is much too slow, being of the order of the square of the magnetization instead of the tenth power as observed experimentally for iron.[33] The agreement with experiment in this respect is considerably worse than in Van Vleck's theory. Probably most of the discrepancy can be taken care of under the assumption of variations of the $J_{\mu\nu}$ in Eq. (24) arising from thermal excitation of the band electrons.

In conclusion I should like to express my thanks to Professor Van Vleck for suggesting the problem and for many helpful discussions and suggestions during the course of the work.

---

[33] N. Akulov, Zeits. f. Physik **100**, 197 (1936).