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Theory of Ferromagnetic Anisotropy

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By means of a virial theorem and perturbation theory, the anisotropy energy of a ferromagnetic crystal is expressed in terms of the Coulomb energy alone. This latter energy is approximated by a multipole expansion and the anisotropy constants are given in terms of electric multipole moments and crystalline-potential constants. The multipole moments, which arise from the orbital angular momentum induced by spin-orbit coupling, have been estimated from the known values of angular momentum. The method avoids explicitly carrying out high-order perturbations, and furnishes a physical interpretation of the anisotropy mechanism without the use of phenomenological couplings. In most cases, the principal mechanism leading to anisotropy is found to be different from those considered by Van Vleck.

THE free energy of a spherically shaped ferromagnetic crystal may be described by

$$F=F_0+K_1(\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2)+K_2\alpha_1^2\alpha_2^2\alpha_3^2+\cdots \quad (1)$$

for a cubic lattice and

$$F=F_0+K_1(1-\alpha_3^2)+K_2(1-\alpha_3^2)^2+\cdots \quad (2)$$

for the hexagonal case. The constants K_1 and K_2 are the first and second anisotropy constants; α_1, α_2, and α_3 are the direction cosines of the saturation magnetization with respect to the crystal axes. For the hexagonal lattice, α_3 is the cosine with respect to the c axis.

For most materials, in which the anisotropy has been measured, K_2 is smaller than K_1, and the above series converge rapidly.

The theoretical problem of describing anisotropy may be broken into two parts: (a) the problem of the intrinsic anisotropy at the absolute zero of temperature and (b) the temperature dependence, which, at least in part, is an effect that does not involve a change in the intrinsic values of K.[1] In the present calculation, only the first problem, (a), is considered.

It generally is agreed that the principal source of ferromagnetic anisotropy in most materials, particularly metals, comes from the electronic spin-orbit coupling, a suggestion which seems first to have been advanced by Powell,[2] and later in a more concrete form by Bloch and Gentile.[3] The inadequacy of exchange coupling and purely magnetic interactions is discussed by Van Vleck.[4]

Two noteworthy schemes have been used in attempting to calculate the effect of spin-orbit interaction in a ferromagnetic solid; one by Van Vleck[4,5] using an atomic approach, the other by Brooks[6] using an energy-band approximation.

The method of Van Vleck leads to a simple physical explanation of the cause of anisotropy, but has the weakness of being, to a large extent, phenomenological. Brooks' calculation avoids the latter objection but has the disadvantage of a straightforward perturbation approach, in that high orders[7] of perturbation are required, which tend to conceal the physical aspects of the problem. It also is evident that high-order perturbations can be carried out only on rather simple models. The recent calculation by Fletcher,[8] using an improved energy-band model, gives a result for nickel two orders of magnitude too large.

In the following calculation, some of the complications of perturbation theory are bypassed by the use of perturbation theory in conjunction with a virial theorem to express the result in terms of the Coulomb energy of the crystal. No explicit consideration of spin-orbit coupling is made. A multipole expansion has been used to calculate the Coulomb energy, and the principal approximations involved are those of estimating the crystalline potential and the effect of magnetization on the charge density about a lattice point. A rough approximation of the latter may be obtained from the known gyromagnetic ratio.

One of the principal mechanisms for anisotropy is found to be different from those considered by Van Vleck, and arises from the interaction between the orbital moment about a lattice site and the crystalline potential of the lattice.

FORMULATION OF THE PROBLEM

The Hamiltonian to be considered is

$$H=T+V+U, \quad (3)$$

where T, V, and U are, respectively, the kinetic energy, Coulomb energy, and spin-orbit interaction operators for all the electrons and nuclei of the solid. It was shown in a previous paper[9] that for each bound eigenstate of H a "virial" relationship exists among the mean values

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[1] C. Zener, Phys. Rev. **96**, 1335 (1954).

[2] F. C. Powell, Proc. Roy. Soc. (London) **A130**, 167 (1930).

[3] F. Bloch and G. Gentile, Z. Physik **70**, 395 (1931).

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

[5] Also W. F. Van Peype, Physica **5**, 465 (1938).

[6] H. Brooks, Phys. Rev. **58**, 909 (1940).

[7] For the correct Hamiltonian, fourth-order and sixth-order perturbation theory is necessary to obtain the K_1 and K_2 of cubic materials.

[8] G. C. Fletcher, Proc. Phys. Soc. (London) **A67**, 505 (1954).

[9] W. J. Carr, Jr., Phys. Rev. **106**, 414 (1957).

of these three quantities, given by

$$2\bar{T}+\bar{V}+3\bar{U}=0. \tag{4}$$

Equations (4) and (3) immediately allow the kinetic energy to be eliminated from the energy, E, leaving

$$E=(\bar{V}-\bar{U})/2. \tag{5}$$

Further, it can be shown[9] that if U is treated as a perturbation, leading to the energy

$$E=\sum_0^\infty E_n, \tag{6}$$

E_0 being the unperturbed energy and E_n the nth-order perturbation correction due to U, then

$$\bar{U}=\sum_0^\infty nE_n. \tag{7}$$

Thus, with (5), (6), and (7)

$$\sum_0^\infty (n+2)E_n=\bar{V}. \tag{8}$$

To extract the anisotropy constants, let the E_n and $\bar{V}$ be expanded in powers of the direction cosines of magnetization. For cubic crystals,

$$E_n=K_{n0}+K_{n1}(\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2)+K_{n2}\alpha_1^2\alpha_2^2\alpha_3^2+\cdots, \tag{9}$$

$$\bar{V}=V_0+V_1(\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2)+V_2\alpha_1^2\alpha_2^2\alpha_3^2+\cdots. \tag{10}$$

It is apparent, however, that K_{n1} must be zero for $n<4$ since the spin-orbit interaction is linear in spin and, therefore, terms to the fourth order in α will appear first in fourth-order perturbation. Likewise K_{n2} is zero for $n<6$. Thus, at absolute zero, where the free energy F becomes the energy E,

$$K_1=\sum_{n=4}^\infty K_{n1}, \tag{11}$$

$$K_2=\sum_{n=6}^\infty K_{n2}, \tag{12}$$

and from (8)

$$\sum_{n=4}^\infty (n+2)K_{n1}=V_1, \tag{13}$$

$$\sum_{n=6}^\infty (n+2)K_{n2}=V_2. \tag{14}$$

Assuming that the perturbation expansion converges fast enough so that terms beyond the first nonvanishing term may be dropped,[10] one obtains from (11) and (13)

$$K_1\simeq K_{41}\simeq V_1/6, \tag{15}$$

and similarly

$$K_2\simeq K_{61}\simeq V_2/8. \tag{16}$$

It is apparent from Eqs. (15) and (16) that the spin-orbit perturbation has a much greater effect on the potential energy than it has upon the total energy.

By means of the last two equations, the problem of calculating the anisotropy constants is converted from a calculation of the energy E to that of calculating the potential energy $\bar{V}$. The advantage lies in the fact that the physical principles of the effect of spin-orbit coupling on $\bar{V}$ are more clear, and some rather simple methods can be used to approximate it, as discussed in the following section. Although a straightforward method exists for directly calculating the spin-orbit effect on the energy E (perturbation theory), in practice the method is exceedingly tedious in high orders, since the problem of obtaining and summing over the unperturbed eigenfunctions exists.

It may be noted that in place of (15) and (16) one equally well could have related the anisotropy constants to terms in the kinetic energy or to the mean value of the spin-orbit interaction. These last two, however, are sensitive to details of the wave function, whereas the Coulomb energy comes only from the square of the absolute magnitude of the wave function, or the charge density distribution.

Finally, it is necessary to consider the formulas analogous to (15) and (16) for the case of hexagonal symmetry. Since second- and fourth-order perturbations would be required here,

$$K_1\simeq V_1/4, \tag{17}$$

$$K_2\simeq V_2/6, \tag{18}$$

where V_1 and V_2 are now the terms in $\bar{V}$ multiplying the functions of hexagonal symmetry as in (2).

CALCULATION OF THE COULOMB ENERGY

Consider a charge density

$$\sigma(\mathbf{r})=\rho(\mathbf{r})-\sum\nolimits_n Z_n\delta(\mathbf{r}-\mathbf{R}_n), \tag{19}$$

where $\rho(\mathbf{r})$ is the electronic charge density, $\mathbf{R}_n$ the position of the nth nucleus, eZ_n the nuclear charge, and δ the Dirac delta function. The Coulomb energy is given then by

$$\bar{V}=\frac{e^2}{2}\int\int\frac{\sigma(\mathbf{r})\sigma(\mathbf{r}')d\tau d\tau'}{|\mathbf{r}-\mathbf{r}'|}+\frac{e^2}{2}\int\int\frac{[\rho(\mathbf{r},\mathbf{r}')-\rho(\mathbf{r})\rho(\mathbf{r}')]d\tau d\tau'}{|\mathbf{r}-\mathbf{r}'|}-\frac{e^2}{2}\sum_n Z_n^2\int\frac{\delta(\mathbf{r}-\mathbf{R}_n)d\tau}{|\mathbf{r}-\mathbf{R}_n|}, \tag{20}$$

as may be verified by substituting for σ from (19). The function $\rho(\mathbf{r},\mathbf{r}')$ is the probability of finding electrons at $\mathbf{r}$ and $\mathbf{r}'$. For charge neutrality the integral of $\sigma(\mathbf{r})$

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[10] If the next order terms are small, but not negligible, one must write, for example,

$$K_1=K_{41}+K_{61},\quad V_1=6K_{41}+8K_{61}=6K_1(1+K_{61}/3K_1)$$

and only a small error is incurred by using (15) even in this case.

over a unit polyhedron is zero, and thus the potential at $\mathbf{r}$,

$$P(\mathbf{r})=-e\int\frac{\sigma(\mathbf{r}')d\tau'}{|\mathbf{r}-\mathbf{r}'|},\tag{21}$$

has lattice periodicity. The same is true of the second term on the right-hand side of (20) since at large separations $\rho(\mathbf{r},\mathbf{r}')\rightarrow\rho(\mathbf{r})\rho(\mathbf{r}')$. Thus, for a lattice containing N equivalent polyhedra,

$$\begin{aligned}\bar{V}=&\frac{Ne^2}{2}\int_0 d\tau\int\frac{\sigma(\mathbf{r})\sigma(\mathbf{r}')d\tau'}{|\mathbf{r}-\mathbf{r}'|}\\&+\frac{Ne^2}{2}\int_0 d\tau\int\frac{[\rho(\mathbf{r},\mathbf{r}')-\rho(\mathbf{r})\rho(\mathbf{r}')]d\tau'}{|\mathbf{r}-\mathbf{r}'|}\\&-\frac{Ne^2}{2}Z_0^2\int\frac{\delta(\mathbf{r})d\tau}{r},\end{aligned}\tag{22}$$

where the subscript 0 refers to the polyhedron surrounding the nucleus at the origin. If the polyhedra are not all equivalent, then a suitable average can be taken.

The last term on the right in (22) is a constant of no interest, which simply serves to subtract out a corresponding "self-energy" term in the first expression.

It will be assumed also, that the second term on the right in (22) may be ignored. Although this term, which contains the "exchange" energy, is not a negligible contribution to the Coulomb energy, it, nevertheless, is expected to contribute only a fractional amount to the anisotropy and will not affect the result in a decisive way.

To calculate the remaining term in (22), imagine the charge density divided into two parts, one, σ_0, independent of magnetization and a smaller part, σ_α, which depends on the direction of magnetization. The latter obviously comes from the orbital moment which is fastened to the spin through spin-orbit coupling. The nuclear charge is assigned to σ_0 and σ_α so that both integrate to zero over the unit polyhedron. Thus,

$$\begin{aligned}&\frac{Ne^2}{2}\int_0\int\frac{\sigma(\mathbf{r})\sigma(\mathbf{r}')d\tau d\tau'}{|\mathbf{r}-\mathbf{r}'|}\\&=\frac{Ne^2}{2}\int_0\int\frac{\sigma_0(\mathbf{r})\sigma_0(\mathbf{r}')d\tau d\tau'}{|\mathbf{r}-\mathbf{r}'|}\\&\quad+Ne^2\int_0\int\frac{\sigma_\alpha(\mathbf{r})\sigma_0(\mathbf{r}')d\tau d\tau'}{|\mathbf{r}-\mathbf{r}'|}\\&\quad+\frac{Ne^2}{2}\int_0\int\frac{\sigma_\alpha(\mathbf{r})\sigma_\alpha(\mathbf{r}')d\tau d\tau'}{|\mathbf{r}-\mathbf{r}'|}\\&=\text{const}-Ne\int_0\sigma_\alpha(\mathbf{r})P_0(\mathbf{r})d\tau\\&\quad+\frac{Ne^2}{2}\int_0\int\frac{\sigma_\alpha(\mathbf{r})\sigma_\alpha(\mathbf{r}')d\tau d\tau'}{|\mathbf{r}-\mathbf{r}'|},\end{aligned}\tag{23}$$

where P_0 is the crystalline potential of an unmagnetized crystal, which, expanded about the nucleus at the origin, has the form

$$\begin{aligned}P_0(\mathbf{r})=B_0(r)+B_1(r)(x^2y^2+x^2z^2+y^2z^2)\\+B_2(r)x^2y^2z^2+\cdots\end{aligned}\tag{24}$$

for cubic symmetry, and

$$P_0(\mathbf{r})=C_0(r)+C_1(r)z^2+C_2(r)z^4+\cdots\tag{25}$$

for the hexagonal.

The charge density σ_α must exhibit certain symmetries in x, y, z, and α_1, α_2, α_3, depending upon the crystal lattice. For the present, the simplest type of function of interest, namely, one having cylindrical symmetry about the direction of magnetization, will be assumed. Then in polar coordinates with the polar axis rotated into the direction of magnetization, σ_α in each polyhedron is described by $\sigma_\alpha(r,\theta)$, where θ is the polar angle. One may think of this function, which is independent of crystal symmetry and independent of α_1, α_2, α_3 when expressed in the above coordinate system, as a first approximation in an expansion about these axes.

Physically, the assumption here is similar to that discussed by Kittel and Galt,[11] except the Coulomb rather than the exchange energy is of interest. Integrals of the type $\int_0\sigma_\alpha(r,\theta)P_0(\mathbf{r})d\tau$ have been worked out by Zener.[1] Upon replacing the unit polyhedron by an equivalent sphere and transforming P_0 to the new coordinate system, one obtains with (24) and (25)

$$\begin{aligned}&\int_0\sigma_\alpha(r,\theta)P_0(\mathbf{r})d\tau\\&=\text{const}+(\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2)\int_0\sigma_\alpha(r,\theta)\\&\quad\times\left\{\left[B_1(r)r^4+\frac{B_2(r)r^6}{11}\right]\mathcal{P}_4(\cos\theta)\right.\\&\quad\left.-\frac{B_2(r)r^6}{11}\mathcal{P}_6(\cos\theta)+\cdots\right\}d\tau+\alpha_1^2\alpha_2^2\alpha_3^2\int_0\sigma_\alpha(r,\theta)\\&\quad\times\{B_2(r)r^6\mathcal{P}_6(\cos\theta)+\cdots\}d\tau\end{aligned}\tag{26}$$

for cubic symmetry, or

$$\begin{aligned}&\int_0\sigma_\alpha(r,\theta)P_0(\mathbf{r})d\tau\\&=\text{const}+\alpha_3^2\int_0\sigma_\alpha(r,\theta)\{[C_1(r)r^2+(6/7)C_2(r)r^4]\\&\quad\times\mathcal{P}_2(\cos\theta)-(6/7)C_2(r)r^4\mathcal{P}_4(\cos\theta)+\cdots\}d\tau\\&\quad+\alpha_3^4\int_0\sigma_\alpha(r,\theta)\{C_2(r)r^4\mathcal{P}_4(\cos\theta)+\cdots\}d\tau\end{aligned}\tag{27}$$

for the hexagonal case. The $\mathcal{P}_n$'s are Legendre polynomials.

In Appendix I, the last integral on the right in (23)

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[11] C. Kittel and J. K. Galt, in *Solid State Physics* (Academic Press, Inc., New York, 1956), Vol. 3, p. 466.

is performed by means of a multipole-type expansion. The result of this calculation is

$$\int_0\int\frac{\sigma_\alpha(\mathbf{r})\sigma_\alpha(\mathbf{r}')d\tau d\tau'}{|\mathbf{r}-\mathbf{r}'|}$$
$$=\text{const}-30(\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2)$$
$$\times\biggl\{S_{40}\biggl[\int_0\sigma_\alpha(r,\theta)r^2\mathcal{P}_2(\cos\theta)d\tau\biggr]^2$$
$$+\frac{21}{2}S_{60}\int_0\sigma_\alpha(r,\theta)r^2\mathcal{P}_2(\cos\theta)d\tau$$
$$\times\int_0\sigma_\alpha(r,\theta)r^4\mathcal{P}_4(\cos\theta)d\tau+\cdots\biggr\}$$
$$+3465\alpha_1^2\alpha_2^2\alpha_3^2S_{60}\int_0\sigma_\alpha(r,\theta)r^2\mathcal{P}_2(\cos\theta)d\tau$$
$$\times\int_0\sigma_\alpha(r,\theta)r^4\mathcal{P}_4(\cos\theta)d\tau+\cdots,\quad(28)$$

and

$$\int_0\int\frac{\sigma_\alpha(\mathbf{r})\sigma_\alpha(\mathbf{r}')d\tau d\tau'}{|\mathbf{r}-\mathbf{r}'|}=\text{const}-6S_{40}\left(10\alpha_3^2-\frac{35}{3}\alpha_3^4\right)$$
$$\times\biggl[\int_0\sigma_\alpha(r,\theta)r^2\mathcal{P}_2(\cos\theta)d\tau\biggr]^2+\cdots,\quad(29)$$

for the cubic and hexagonal cases, respectively. The constants S_{40} and S_{60} are lattice sums that have been evaluated by McKeehan[12] and are given in the Appendix I.

In all the last four equations, the charge density σ_α now may be replaced with the electronic density ρ_α since the constant part of σ_α integrates to zero in all cases.

ANISOTROPY CONSTANTS

If v is the atomic volume, then from (15), (16), (26), and (28) the cubic anisotropy constants per unit volume are

$$K_1=\frac{-e}{6v}\int_0\rho_\alpha(r,\theta)\biggl\{\biggl[B_1(r)r^4+\frac{B_2(r)r^6}{11}\biggr]\mathcal{P}_4(\cos\theta)$$
$$-\frac{B_2(r)r^6}{11}\mathcal{P}_6(\cos\theta)+\cdots\biggr\}d\tau$$
$$-\frac{15e^2}{6v}\biggl\{S_{40}\biggl[\int_0\rho_\alpha(r,\theta)r^2\mathcal{P}_2(\cos\theta)d\tau\biggr]^2$$
$$+\frac{21}{2}S_{60}\int_0\rho_\alpha(r,\theta)r^2\mathcal{P}_2(\cos\theta)d\tau$$
$$\times\int_0\rho_\alpha(r,\theta)r^4\mathcal{P}_4(\cos\theta)d\tau+\cdots\biggr\},\quad(30)$$

$$K_2=\frac{-e}{8v}\int_0\rho_\alpha(r,\theta)B_2(r)r^6\mathcal{P}_6(\cos\theta)d\tau+\cdots$$
$$+\frac{3465e^2}{16v}S_{60}\int_0\rho_\alpha(r,\theta)r^2\mathcal{P}_2(\cos\theta)d\tau$$
$$\times\int_0\rho_\alpha(r,\theta)r^4\mathcal{P}_4(\cos\theta)d\tau+\cdots,\quad(31)$$

and from (17), (18), (27), and (29) the hexagonal constants are

$$K_1=\frac{e}{4v}\int_0\rho_\alpha(r,\theta)\{[C_1(r)r^2+(6/7)C_2(r)r^4]\mathcal{P}_2(\cos\theta)$$
$$+(8/7)C_2(r)r^4\mathcal{P}_4(\cos\theta)+\cdots\}d\tau$$
$$\times\frac{-10e^2}{v}S_{40}\biggl[\int_0\rho_\alpha(r,\theta)r^2\mathcal{P}_2(\cos\theta)d\tau\biggr]^2+\cdots,\quad(32)$$

$$K_2=-\frac{e}{6v}\int_0\rho_\alpha(r,\theta)C_2(r)r^4\mathcal{P}_4(\cos\theta)d\tau+\cdots$$
$$+\frac{35e^2}{6v}S_{40}\biggl[\int_0\rho_\alpha(r,\theta)r^2\mathcal{P}_2(\cos\theta)d\tau\biggr]^2+\cdots.\quad(33)$$

Insofar as the second-order constants are correct with the terms given, the first-order constants may be written

$$K_1=-\frac{e}{6v}\int_0\rho_\alpha(r,\theta)\biggl[B_1(r)r^4+\frac{B_2(r)r^6}{11}\biggr]\mathcal{P}_4(\cos\theta)d\tau$$
$$-\frac{5e^2}{2v}S_{40}\biggl[\int_0\rho_\alpha(r,\theta)r^2\mathcal{P}_2(\cos\theta)d\tau\biggr]^2-\frac{4}{33}K_2+\cdots,\quad(34)$$

and

$$K_1=\frac{e}{4v}\int_0\rho_\alpha(r,\theta)[C_1(r)r^2+(6/7)C_2(r)r^4]$$
$$\times\mathcal{P}_2(\cos\theta)d\tau-(12/7)K_2+\cdots,\quad(35)$$

for the cubic and hexagonal cases, respectively. The cubic case serves to illustrate that the series rapidly converges, since K_2 is small compared with K_1. The K_2 term in (35), however, is not entirely negligible for hexagonal cobalt.

The parameters B_1, B_2, C_1, and C_2 which describe the crystalline potential within a polyhedron are estimated in Appendix II. This potential may be thought of as arising firstly from an internal contribution due to crystal symmetry, if any, in the charge distribution about the enclosed lattice point; and secondly from external contributions due to the arrangement of neighbors around the given polyhedron. The latter is calculated by using an ion-core approximation with the conduction electrons assumed to be uniformly spread out. Tentatively, only this second part of the potential will be considered.

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[12] L. W. McKeehan, Phys. Rev. **52**, 18 (1937); **52**, 527 (1937); **43**, 1025 (1933).

TABLE I. Anistropy constants at absolute zero of temperature in ergs/cc.

	K_1	K_2
Fe	5.7×10^5 [a]	9×10^4 [b]
Ni	-7.5×10^5 [a]	4×10^5 [b]
Co	8.4×10^6 [c]	2.4×10^6 [c]

[a] Taken from curves in R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951), pp. 568, 569.

[b] H. Sato and B. S. Chandrasekhar, J. Phys. Chem. Solids 1, 228, 1957).

[c] Average of values given by W. Sucksmith and J. E. Thompson, Proc. Roy. Soc. (London) **A225**, 362 (1954).

When one uses the results of Appendix II, the anisotropy constants for cubic nickel and iron are

$$K_1 \simeq \frac{5}{6}\frac{e^2S_{40}}{v}(Z_cD-3A^2), \tag{36}$$

$$K_2 \simeq \frac{3465}{16}\frac{e^2S_{60}}{v}AD, \tag{37}$$

and for hexagonal cobalt

$$K_1 \simeq \frac{e^2S_{22}}{4v}Z_cA-\frac{12}{7}K_2, \tag{38}$$

$$K_2 \simeq \frac{35}{18}\frac{e^2S_{40}}{v}(3A^2-Z_cD), \tag{39}$$

where Z_c is the effective charge on an ion core, and A and D are multipole moments defined by $A=\int_0\rho_\alpha(r,\theta)r^2\times\mathcal{P}_2(\cos\theta)d\tau$ and $D=\int_0\rho_\alpha(r,\theta)r^4\mathcal{P}_4(\cos\theta)d\tau$. The $\mathcal{P}_6(\cos\theta)$ term in the expression (31) for K_2 is neglected because, in the first transition group of elements, ρ_α comes largely from $3d$ wave functions, which lead to no $\mathcal{P}_6$ component.

In Table I the measured values of these anisotropy constants are tabulated. Using these measurements, one finds that A in equations (36) through (39) must have the respective values 3.4, 24, and -2.4, all times 10^{-19}, for Fe, Co, and Ni. Likewise the constant D must take the respective values 2, 200, and 10 times 10^{-37}. In solving for A and D a value of $Z_c=\frac{1}{2}$ was assumed, as this is approximately the number of conduction electrons of Ni and Co. This value of Z_c for Fe is questionable, but the constants are quite insensitive to Z_c in this case.

It now can be shown by a direct calculation that the numbers obtained above are reasonable values for the integrals A and D. The charge density $\rho_\alpha(r,\theta)$ may be expected to have a radial dependence, $R^2(r)$, mainly appropriate to $3d$ wave functions. Since any dependence of ρ_α on azimuthal angle has been neglected,

$$\rho_\alpha \sim R^2(r)(\lambda^2\cos^2\theta+\lambda^4\cos^4\theta+\cdots), \tag{40}$$

where it is recognized from central symmetry that ρ_α is an even function of $\cos\theta$. Powers of $\cos\theta$ higher than the fourth are probably quite small since they cannot arise from d functions. The parameter λ measures the spin-orbit coupling and the power of λ is the order to which perturbation theory must be carried to obtain a particular term in (40). Since the term $\cos^2\theta$ transforms to the crystal axes as a quadratic in the direction cosines of magnetization, the principal part of this term would therefore come from second order in the spin-orbit coupling. Likewise $\cos^4\theta$ transforms as a fourth-order function in the direction cosines and thus comes from fourth-order perturbation.

To obtain a measure of λ, one may consider the orbital angular momentum, which quenched in the zeroth approximation, initially appears in first-order perturbation theory (for a specific calculation see Fletcher[7]). Therefore, in units of $\hbar$, $\langle M\rangle\sim\lambda$ where $\langle M\rangle$ is the expectation value of the orbital momentum along the spin direction.

Thus, from (40), $A\sim\langle r^2\rangle\langle M\rangle^2$ and $D\sim\langle r^4\rangle\langle M\rangle^4$. Using Hartree functions, one finds that $\langle r^2\rangle$ in a unit polyhedron has the approximate value 4×10^{-17} cm^2, and from spectroscopic splitting factors and gyromagnetic ratio measurements $\langle M\rangle^2\sim10^{-2}$ for the materials under consideration. Thus, $A\sim4\times10^{-19}$ and since $\langle r^4\rangle\sim4\times10^{-33}$, $D\sim4\times10^{-37}$, which, except in one case, is of the general order of magnitude needed to give the measured anisotropy constants. However, in an analysis of this type, nothing can be said about the sign of A and D.

PHYSICAL INTERPRETATION OF ANISOTROPY

One now may examine the principal mechanisms of anisotropy as given by (36) through (39). Those terms containing a Z_c arise from the interaction between the part of the charge cloud that is coupled to the spin, and the crystalline potential of a "normal" unmagnetized crystal. The remaining terms arise from interactions between charge clouds on different atoms.

The charge distribution is influenced by the spin through spin-orbit coupling, which induces an orbital momentum in the spin direction and, consequently, distorts the electronic distribution. For pictorial purposes, the electron density about a particular nucleus may be imagined as having a spheroidal shape with a principal axis in the direction of magnetization. If the spin direction is rotated, this charge distribution rotates with it. Thus, in a sufficiently inhomogeneous potential, which may arise from either of the two ways discussed above, anisotropy results.

The picture described above is, of course, not the only point of view that can be taken, since, in addition to the Coulomb energy, the kinetic energy and the spin-orbit energy itself are functions of the direction of magnetization. However, these energies all are related by the virial theorem and perturbation theory; thus, it is necessary to consider the mechanics of but one of them.

From the values of A and D, derived from the measured K_1 and K_2, it is concluded that the dominant part of K_1 in Ni and Co comes from the interaction of the charge distribution with the crystalline field. This is an interaction which is not considered by Van Vleck,[4] since his Hamiltonian just contains effective interactions between two spins on neighboring atoms; and the crystalline-field interaction is not susceptible to such phenomenological treatment.

One flaw in the calculation, here, is that the crystalline potential due to crystal symmetry in the charge has not been estimated. The present result is obtained on the approximation that ρ_0, the charge density of an "unmagnetized" material, has spherical symmetry about a lattice point, and that the potential comes from lattice sums over neighboring atoms. A check on the validity of this postulate seems possible in the case of cobalt since the hexagonal lattice sums are highly strain-dependent.[12]

Finally, the author would like to acknowledge some helpful discussions with Y. Yafet during the preparation of this paper.

APPENDIX I

By breaking the integral over the crystal into integrals over unit polyhedra, one may write

$$\int \frac{\sigma_\alpha(\mathbf{r}')d\tau'}{|\mathbf{r}-\mathbf{r}'|} = \sum_n \int_n \frac{\sigma_\alpha(\mathbf{r}')d\tau'}{|\mathbf{r}-\mathbf{r}'|} = \sum_n \int_0 \frac{\sigma_\alpha(\mathbf{r}'+\mathbf{R}_n)d\tau'}{|\mathbf{r}-\mathbf{r}'-\mathbf{R}_n|}$$
$$= \sum_n \int_0 \frac{\sigma_\alpha(\mathbf{r}')d\tau'}{|\mathbf{r}-\mathbf{r}'-\mathbf{R}_n|}, \quad (41)$$

when the polyhedra are all alike. Then

$$\int_0\int \frac{\sigma_\alpha(\mathbf{r})\sigma_\alpha(\mathbf{r}')d\tau d\tau'}{|\mathbf{r}-\mathbf{r}'|} = \int_0\int_0 \frac{\sigma_\alpha(\mathbf{r})\sigma_\alpha(\mathbf{r}')d\tau d\tau'}{|\mathbf{r}-\mathbf{r}'|}$$
$$+\sum_{n\neq 0}\int_0\int_0 \frac{\sigma_\alpha(\mathbf{r})\sigma_\alpha(\mathbf{r}')d\tau d\tau'}{|\mathbf{r}-\mathbf{r}'-\mathbf{R}_n|}, \quad (42)$$

and the denominator of the last term on the right may now be expanded in powers of r and r'.

Strictly speaking, this expansion does not converge in the outer extremities of the unit polyhedron. However, it is recognized that the radial distribution of σ_α is determined largely by the unfilled-inner-core electrons and, therefore, is very small in these outer extremities, which effectively removes the divergence difficulty.

The Coulomb interaction between two charge distributions about different centers has been considered by Carlson and Rushbrooke.[13] Using their results, and again assuming symmetrical charge distribution in the plane perpendicular to the magnetization, one obtains

$$\frac{Ne^2}{2}\int_0\int \frac{\sigma_\alpha(\mathbf{r})\sigma_\alpha(\mathbf{r}')d\tau d\tau'}{|\mathbf{r}-\mathbf{r}'|}$$
$$= \text{const} + \frac{Ne^2}{2}\sum_{l=0}^{\infty}\sum_{l'=0}^{\infty}(-1)^{l'}\frac{(l+l')!}{l!l'!}S_{l+l'}\int_0 \sigma_\alpha(\mathbf{r})r^l$$
$$\times \mathcal{P}_l(\cos\theta)d\tau \int_0 \sigma_\alpha(\mathbf{r})r^{l'}\mathcal{P}_{l'}(\cos\theta)d\tau, \quad (43)$$

where the polar angle is measured relative to the direction of magnetization and $S_{l+l'}$ is a lattice sum evaluated by McKeehan.[12] In particular, for cubic materials

$$S_4 = S_{40}[1-5(\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2)]$$

and

$$S_6 = S_{60}[1-(21/2)(\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2)$$
$$+(231/2)\alpha_1^2\alpha_2^2\alpha_3^2];$$

in hexagonal crystals $S_2 = S_{20}+S_{22}\alpha_3^2$ and

$$S_4 = S_{40}[1-10\alpha_3^2+(35/3)\alpha_3^4].$$

For face-centered cubic crystals $S_{40}=-7.53/a^5$, $S_{60}=-26.63/a^7$; for body-centered cubic $S_{40}=-3.11/a^5$, $S_{60}=5.45/a^7$; and for ideal hexagonal close-packed crystals $S_{22}=0.0051/a^3$, $S_{40}=0.34/a^5$, where a is the cube edge of the unit cell in cubic materials and the edge length of the base of the unit cell in the close-packed hexagonal. For cobalt with a c/a of 1.624, $S_{22}=0.035/a^3$.

APPENDIX II

If the S-band electrons are uniformly smeared out, they contribute nothing to the cubic or hexagonal potential. If eZ_c is the charge of each ion core, then

$$P_0 = M(r)+eZ_c\sum_n \frac{1}{|\mathbf{r}-\mathbf{R}_n|}$$
$$= N(r)+eZ_c\sum_{n\neq 0}\sum_l \frac{r^l}{R_n^{l+1}}\mathcal{P}_l(\cos(\mathbf{r},\mathbf{R}_n)), \quad (44)$$

where $\mathcal{P}_l$ is a Legendre polynomial. The lattice sums are again those evaluated by McKeehan.[12] Up to terms including $\mathcal{P}_6$, one obtains

$$P_0 = F(r)-eZ_c[5S_{40}+(21/2)S_{60}r^2]$$
$$\times(x^2y^2+x^2z^2+y^2z^2)+eZ_c(231/2)S_{60}x^2y^2z^2 \quad (45)$$

for cubic symmetry, and

$$P_0 = G(r)+eZ_c(S_{22}-10S_{40}r^2)z^2+eZ_c(35/3)S_{40}z^4 \quad (46)$$

for hexagonal, where the S_{l0} are given in Appendix I.

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[13] B. C. Carlson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc. 46, 626 (1950).