These results indicate essentially no divergence along the periphery of a characteristic ring. The presence of asterism, however, shows that there is distortion present in the crystals. The only distortions that could produce peripheral widening of spots would be those arising from the bending of crystals about axes parallel to the incident x-ray beam. Since no divergence appeared, the results indicate that the axes of bending were fairly well confined to the plane of the sheet.

DECEMBER 1, 1937 PHYSICAL REVIEW VOLUME 52

On the Anisotropy of Cubic Ferromagnetic Crystals

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(Received October 18, 1937)

It is shown that the dependence of the intensity of magnetization on direction in cubic single crystals probably results from the interplay between orbital valence and spin-orbit interaction. Because of the spin-orbit coupling, the spin vectors responsible for the ferromagnetism feel slightly the anisotropic electrostatic forces which connect the orbital angular momenta of different atoms and whose bonding effect is called orbital valence. In consequence there is apparent dipole-dipole coupling between the spins of different atoms with a constant of proportionality about fifty times larger than results from pure magnetic forces between spins. The same mechanism also gives rise to apparent quadrupole-quadrupole coupling, but it is shown very generally that the latter is possible only if the spin quantum numbers of the atoms are greater than $\frac{1}{2}$. Although dipole-dipole coupling is well known not to contribute to cubic anisotropy when the elementary magnets are all parallel, there is an appreciable contribution in the second approximation of perturbation theory in which complete parallelism is not assumed. The perturbation calculations can be carried through for both the dipole or quadrupole models, provided a Weiss molecular field is used to portray exchange interaction. Both lead to a constant K_1 of about the observed order of magnitude in the expression $F_0+K_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2)+K_2\alpha_1^2\alpha_2^2\alpha_3^2$ for the free energy. The temperature variation of K_1 is given correctly in so far as K_1 vanishes much more rapidly than the intensity of magnetization near the Curie point, but the calculations are not sufficiently refined to give quantitative details of the temperature dependence, such as, for example, the different behavior of iron and nickel. The empirical values of K_2 seem somewhat larger than one would expect provisionally from dimensional considerations, but higher order calculations are needed before this point can be definitely settled. Our model is admittedly somewhat phenomenological, but in our opinion comes closer to physical reality than others in the literature, which are criticized. An explanation is given of why the so-called lattice sums in magnetostriction have larger magnitude, and sometimes different sign, than computed for pure magnetic coupling between the spins. In the final section a brief discussion is included on the anisotropy of hexagonal crystals.

Part I. Descriptive Survey and Critique

1. Introduction

It is well known that even in cubic crystals there is some ferromagnetic anisotropy, i.e., the ease of magnetization is dependent on the choice of axes. The magnetization curves for the 100, 010, and 001 axes are of course completely equivalent because of the cubic symmetry, but the latter does not require a similar behavior for the 100, 110, and 111 directions, and it is indeed found that nickel is more readily magnetized along the 111 than the 100 axis, while the reverse is true of iron. The empirical results are best expressed in terms of a free energy function F. It is shown in the literature[1] that the observed anisotropy is explicable in terms of a free energy of the form

$$F=F_0+F_1+F_2, \tag{1}$$

where F_0 is purely isotropic, but where F_1 and F_2 involve the direction cosines α_1, α_2, α_3 of the field relative to the principal cubic axes in the fashion

$$F_1=K_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2), \tag{2}$$

$$F_2=K_2\alpha_1^2\alpha_2^2\alpha_3^2. \tag{3}$$

We suppose the field powerful enough so that

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[1] For an excellent resumé of this part of the subject, and references, see. R. M. Bozorth, J. App. Phys. **8**, 575 (1937), Phys. Rev. **50**, 1076 (1936), also Stoner, *Magnetism and Matter*, pp. 385–401.

it is unnecessary to distinguish between the direction of the applied field and that of local magnetization.

The selection of the best values of K_1, K_2 to represent the experimental magnetization curves is not an easy task, and constitutes the so-called subject of technical magnetization.[1] However, it is not the part of the problem with which we shall be concerned. Rather, we shall confine our attention to the theoretical explanation of the existence of nonvanishing constants K_1, K_2 of the proper order of magnitude, in other words, the origin of the anisotropy on the basis of atomic theory.

The forces between atoms which are primarily responsible for ferromagnetism are the exchange interactions. However, they are well known not to lead to any anisotropy,[2] provided the atoms are considered to be effectively in *s* states. To explain the fact that the susceptibilities do depend somewhat on direction, it is necessary to superpose some other coupling on the large exchange forces. The most obvious type of such other interaction is that represented by the mutual energy of two dipoles.

2. Dipole-dipole coupling

The conventional treatment of this coupling is one in which all the elementary dipoles are regarded as mutually parallel. It has often been pointed out that under these circumstances, dipole-dipole forces[3] are unable to give any anisotropy in cubic crystals. The reason is quite simple. The mutual potential energy of a collection of parallel dipoles transforms like a quadratic form under a rotation of axes. The distinction between complete isotropy and cubic symmetry can be represented by a form of no lower order than the fourth, i.e., the expression (2). A quadratic form, on the other hand, yields either perfect isotropy (equal coefficients of α_1^2, α_2^2, and α_3^2), or no more than rhombic or perhaps axial symmetry.

However, when the dipoles are not all perfectly parallel, it is no longer true that dipole-dipole coupling is incapable of yielding any anisotropy. Instead, it will be shown in Section 10, that when a perturbation calculation is carried to the second order, there is a dependence on direction except in the case of complete parallelism. The latter case is, of course, an ideal one not achieved practically except at $T=0$. It is obviously necessary to carry the perturbation calculation to the second rather than first approximation, since a quadratic form can simulate a biquadratic one only when raised to the second power.

3. Quadrupole-quadrupole coupling—the necessity of $S > \frac{1}{2}$ for this

The most frequently employed model of cubic anisotropy is that wherein each magnet is somehow supposed to carry with it a quadrupole moment.[4] A dependence on direction of the form (2) is then achieved even when the quadrupoles are all perfectly parallel. Irrespective of the question of the mechanism responsible for the quadrupole-quadrupole coupling, there is a fundamental difficulty with all quadrupole models as applied to nickel. Quite possibly, here the spin of each elementary magnet is $\frac{1}{2}$,—at least this is the value which gives the best interpretation of the variation of the magnetization of nickel with temperature.[5] However, the most general potential coupling together two spins of quantum number $\frac{1}{2}$ and symmetrical in them is

$$\begin{aligned} V= V_0-2J(S_{x_i}S_{x_j}+S_{y_i}S_{y_j}+S_{z_i}S_{z_j}) \\ +C(2S_{z_i}S_{z_j}-S_{x_i}S_{x_j}-S_{y_i}S_{y_j})+D(S_{x_i}S_{x_j}-S_{y_i}S_{y_j}) \\ +E(S_{x_i}S_{y_j}+S_{x_j}S_{y_i})+F(S_{x_i}S_{z_j}+S_{x_j}S_{z_i}) \\ +G(S_{y_i}S_{z_j}+S_{z_j}S_{y_i}), \quad (4) \end{aligned}$$

inasmuch as any polynomial in S_{x_i}, S_{y_i}, S_{y_i} can be expressed as identically equal to a linear form $a_0+a_1S_{x_i}+a_2S_{y_i}+a_3S_{z_i}$ because with $S=\frac{1}{2}$ the matrices S_{x_i}, S_{y_i}, $\cdots$, S_{z_j} are all of the second rank, and so satisfy simple algebraic equations

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[2] The so-called Dirac vector model shows that the exchange forces between equivalent electrons are formally equivalent to a coupling energy of the form $-\frac{1}{2}Jn_in_j-2J\mathbf{S}_i\cdot\mathbf{S}_j$ between the spins, where J is the exchange integral and n_i, n_j are the number of electrons outside closed shells in atoms i, j. (See P. A. M. Dirac, Proc. Roy. Soc. **A123**, 714 (1929), or J. H. Van Vleck, Phys. Rev. **45**, 405 (1934).) The additive constant $-\frac{1}{2}Jn_in_j$ is unimportant for present purposes and hence omitted in our Eqs. (9) and (45). The dot product $\mathbf{S}_i\cdot\mathbf{S}_j$ is clearly invariant under rotation, and so cannot lead to anisotropy.

[3] Cf., for instance, R. Becker, Zeits. f. Physik **62**, 253 (1930), or Mahajani, reference 4.

[4] G. S. Mahajani, Phil. Trans. Roy. Soc. **228**, 63 (1929); N. S. Akulov, Zeits. f. Physik **57** 249; **59** 254 (1929); R. Gans and E. Czerlinsky, Ann. d. Physik **16**, 625 (1933).

[5] Cf. F. Tyler, Phil. Mag. **9**, 1026 (1930); E. Stoner, Phil. Mag. **10**, 27 (1930).

which permit the degree to be depressed, e.g.

$$S_{x_i}^2=\tfrac{1}{4},\quad S_{x_i}^3=\tfrac{1}{4}S_{x_i},\quad S_{x_i}S_{y_i}+S_{y_i}S_{x_i}=0,$$
$$S_{x_i}S_{y_i}-S_{y_i}S_{x_i}=iS_{z_i},\quad (S=\tfrac{1}{2}).\qquad (5)$$

We throughout suppose our angular momentum vectors to be expressed as multiples of the Bohr unit $h/2\pi$. If we take the z axis as that of the radius vector r_{ij} joining magnets i and j, the coefficients D, E, F, G will vanish if the interaction is invariant with respect to rotation about r_{ij}. We will henceforth therefore neglect the corresponding part of (4). (Even if these terms did not vanish, (4) would be essentially a second order rather than quadrupole-quadrupole proposition.) The first term of (4) is a trivial constant, while the J term is merely the Heisenberg isotropic coupling. The factor -2 is included in its definition in order to make the coefficient J identical with the conventional exchange integral.[2] The C term is of the dipole-dipole type as far as the dependence on spin-alignment is concerned. We thus see that with spins of $\frac{1}{2}$ (one uncompensated electron per atom), dipole-dipole coupling is the most general type of nonisotropic interaction. The constant of proportionality C need not, however, have the value

$$C=g^2\beta^2/r_{ij}^3,\quad (\beta=he/4\pi mc)\qquad (6)$$

characteristic of the mutual energy of two magnets separated by a distance r_{ij}. Here β is the Bohr magneton, and g is the Landé factor,[6] equal to two for spins. We throughout use the term "dipole-dipole" as allowing an arbitrary proportionality factor. When C is to be restricted to (6), we shall speak of "true magnetic coupling."

As a specific example of this theorem that spins of $\frac{1}{2}$ cannot generate quadrupole coupling, let us consider the simplest type of quadrupole-quadrupole potential, *viz.*

$$V=V_0+\gamma S_{z_i}^2S_{z_j}^2.\qquad (7)$$

When we utilize the first relation of (5), the right side of (7) reduces to a trivial constant $V_0+\frac{1}{16}\gamma$. Eq. (7) is, of course, not the most general expression quadratic in each of the spin components, but for our purposes is sufficiently typical of the workings of quadrupole-quadrupole interaction provided we take the z axis to be the line joining the two atoms. Then (7) is a quite general form which is invariant under rotations about this line and whose mean value is nonvanishing in the first approximation.

If the anisotropy of nickel is to be explained otherwise than with essentially dipole-dipole coupling, it is necessary that the carriers of the magnetic moment in nickel have spins of 1 or greater. A model of this type has indeed been proposed by Wolff and by Mott and Jones from other evidence[7] but we find it rather difficult to believe that the atomic spin have such a large value in nickel. At the absolute zero, the value of the saturation magnetization of nickel is 0.6 Bohr magnetons per atom. Presumably this behavior means that 60 percent of the nickel ions are in the magnetic configuration d^9 and 40 percent in the nonmagnetic configuration d^{10}, with 0.6 conduction electrons per atom in $4s$ bands which are wide enough so that the magnetism of their spins is annihilated because of the Pauli principle. With Mott's model, there would be 30 percent of the ions in d^8, 70 percent in d^{10}, with still 0.6 conduction electrons per atom. Since very much greater energy is required to ionize an atom twice rather than once, it is hard to see why the ions should prefer to be in d^8 rather than d^9. At the same time, we are not unmindful of the fact that Mott and Jones have listed certain arguments favoring a spin $S=1$ for nickel. Possibly the difficulty regarding the high ionization energy of d^8 is overcome by some of the $4s$ conduction electrons being sucked in towards the d^8 ions, so that the mean charge cloud around these ions corresponds to considerably less than twofold ionization.

In the case of iron, there appears to be no

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[6] As we are dealing with media where practically all the magnetism comes from spin, the g factor can immediately be equated to 2. However, we prefer to carry an undetermined g factor because the calculations in Part II may have some future application to other problems in which the angular momentum vectors of the different atoms coupled together do not arise solely from spin. The analysis in Part II is immediately adapted to such problems merely by replacing the spin vector **S** by the total angular momentum **J**, and the spin quantum number S by the inner quantum number J.

[7] A. Wolf, Zeits. f. Physik **70**, 519 (1931); also especially N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys*, pp. 224–227. Attempts to deduce the configuration of the nickel ions from the formula $\chi=Ng^2\beta^2(S^2+S)/3k(T-T_c)$ for the susceptibility above the Curie point are in our opinion inconclusive, since this formula is valid theoretically only if $T\gg T_c$ whereas in practice it is used in regions where T is not much greater than T_0.

objection to granting a spin of unity, or perhaps even $\frac{3}{2}$, as the Fe atom has two electrons less than Ni, and so is further from a completed *d* shell. The most general potential coupling together two spins of unit quantum number is a polynomial of the second degree in S_{xi}, S_{yi}, S_{zi}, and also of this degree in S_{xj}, S_{yj}, S_{zj}. The proof is based on the fact that S_{xi}, S_{yi}, S_{zi} are three-rowed matrices when $S=1$, and is similar to that used in establishing that (4) is the most general potential with dipole-dipole coupling. Consequently, the most general interaction between two spins of unit quantum number consists of quadrupole-quadrupole and lower order (dipole-dipole, dipole-quadrupole) terms, inasmuch as dipoles and quadrupoles are respectively linear and quadratic in vectorial properties. If the spins or quadrupole axes are all parallel, the most general dependence on direction is of the form (2). This is true even when the spins are not all parallel, provided only a first-order perturbation calculation is made, as will be shown in sections 11–12. The additional term (3) would require apparent hexapole-hexapole coupling. This can mean that either (*a*) the spin is greater than unity, or else that (*b*) the elementary magnets are not perfectly parallel. In case (*b*) the angular dependence (3) is yielded if the perturbation calculation is carried to a sufficiently high approximation, *viz.* the second order with dipole-quadrupole coupling, or the third order with dipole-dipole interaction. That these are the proper orders can be seen from the powers to which the direction cosines are raised, on remembering that each spin transforms like a vector.

4. Origin of the coupling terms

So far we have introduced the interaction between atoms more or less *ad hoc*, and we must now inquire into its physical causes. One possibility is that we have to do with *bona fide* magnetic coupling, so that the constant C in (4) has the form (6). The resulting value of K_1 is, however, too small by a factor 10^3 (see fine print, Section 6).

In our opinion, the most likely explanation of the origin of the anisotropic terms is to be found in the concept of *orbital valence*. By the latter term, we mean the fact that the mutual electrostatic energy of two atoms depends on the way their orbital angular momenta as well as on the way their spins are aligned. The orbital coupling involves in general not merely the orientation of the orbital angular momentum vectors relative to each other, but also their orientation relative to the axis joining the two atoms. The latter ingredient, on the other hand, does not appear in the Heisenberg exchange interaction, which is formally equivalent to isotropic spin-spin coupling. Expressed in formulas, the energy of orbital valence is of the form $f(\mathbf{L}_i\cdot\mathbf{L}_j, L_{zi}, L_{zj})$ whereas the exchange energy is $F(\mathbf{S}_i\cdot\mathbf{S}_j)$. Here $\mathbf{L}_i$ is the angular momentum vector of atom i, and the z axis is supposed that joining the two atoms. In other words, orbital valence is anisotropic, but exchange energy is isotropic because $\mathbf{S}_i\cdot\mathbf{S}_j$ is unaffected if similar rotations are given to $\mathbf{S}_i$ and $\mathbf{S}_j$. Since practically all the ferromagnetism arises from the spin, anisotropy in the orbital moment may at first sight seem to be of little consequence. However, the effect of spin-orbit coupling is not entirely negligible even when the orbital moment is largely quenched, and so the energy will not be entirely independent of how the spins are oriented relative to the figure axis. The situation may be likened to that in the spectra of diatomic molecules, where the energies of Σ_1, Σ_0, Σ_{-1}, the three components of a "p type triplet," are not quite the same even though a Σ state has zero mean orbital angular momentum.[8] If only one orbital state need be considered for each atom, the most general potential representing the dependence of energy on spin alignment is given by a function of the form (4) in case the spin of each atom is $\frac{1}{2}$. If the spin of each atom is 1, we must add to (4) some quadrupole-quadrupole terms, analogous to (7), and also perhaps some quadrupole-dipole coupling, linear in one spin and quadratic in the other. Similarly with $S=\frac{3}{2}$ hexapole terms must be included. These results are consequences of the limited rank of the spin matrices, which make polynomials of low degree the most general function, as explained in Section 3. Thus the superposition of spin-orbit coupling and orbital valence leads directly to potentials which simulate true magnetic dipole-dipole or quadrupole-quadrupole coupling, except for the

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[8] M. H. Hebb, Phys. Rev. **49**, 617 (1936).

proportionality factor, but have in reality an entirely different origin.

The one weak point in the argument is that actually more than one orbital state surely does come into play for each atom. In reality, the orbital as well as spin vectors probably readjust themselves considerably when the temperature is varied. We do not wish to enter into any detail as to what the orbital states look like, since this would require us to delve into the intricate question of just how the orbital angular momentum is destroyed or "quenched," a subject imperfectly understood at present. The mechanism of quenching is probably not the same as the crystalline potential operative in paramagnetic salts.[9] If it were, the g factor should be different for different cubic ferromagnetic materials, due to inversion of the Stark pattern. Namely, in a cubic field, sometimes a degenerate and sometimes a nondegenerate orbital state is deepest, depending upon the number of electrons. The g factor should be much nearer 2 in the latter than in the former event. The inversion of the Stark pattern[10] explains, for instance, why the paramagnetic salt cobalt chloride has a g factor 1.54 as compared with 1.95 for chromic chloride. The g factors for ferromagnetic metals, on the other hand, are always remarkably near 1.9 (except for the freak case of pyrrhotite), showing that the quenching mechanism cannot be the same as the crystalline fields acting in paramagnetic salts. It is, of course, not surprising that the quenching machinery should be completely different in conducting metals than in nonconducting ionic salts. In the case of the ferromagnetic metals the quenching mechanism is probably the coupling between the orbital angular momentum vectors of different atoms, of antiferromagnetic sign as suggested by Sommerfeld and Bethe.[11] The coupling is not so strong but that a large number of orbital states are inhabited at room temperatures. The behavior is then exceedingly complicated, as rigorously the whole crystal rather than one atom ought to be treated as a single quantum mechanical unit. Another way of stating the difficulty is that the factors C and γ in (4) or (7) are matrices in the orbital quantum numbers rather than ordinary numbers. Since we treat them as ordinary numbers (which would be rigorous were there only one orbital state), our use of a potential such as (4) or (7) to represent the interplay between orbital valence and spin-orbit interaction must be regarded as somewhat phenomenological. In consequence it is possible that the constants C and γ should be regarded as functions of the temperature. They represent, so to speak, the mean effect of the interplay, which can vary with temperature because the Boltzmann distribution among the orbital states varies with T.

5. Representation of exchange coupling by means of a molecular field

A further approximation is necessary before the calculation can be started. Even when the orbital problem has been simplified by use of (4) or (7), there is still the ordinary Heisenberg exchange coupling, which must be included in the unperturbed part of the energy, as the isotropic ferromagnetic action is much larger than the small perturbations causing anisotropy. However, the determination of the characteristic values of the exchange energy $-2\Sigma_{j>i}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$ for the entire crystal is well known to be a hopeless task. We therefore resort to the usual artifice of regarding the exchange energy as equivalent to a molecular or inner field proportional to the intensity of magnetization. The constant of proportionality κ may, if desired, be a function of T. This use of a Weiss field is, again, somewhat phenomenological, but has been shown to have a quantal basis in Heisenberg's theory of ferromagnetism. Namely, he shows that an inner field with the constant of proportionality independent of temperature results if identity of energy is assumed for all states with the same resultant crystalline field.[12] Empirically, this approximation is quite a good one. In fact, Weiss[13] used his inner field model with great success long before the advent of quantum mechanics to explain the variation of the saturation intensity with tem-

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[9] For a survey of work on the influence of the crystalline field on paramagnetic susceptibilities, see Chapter X of Stoner's *Magnetism and Matter*, especially p. 292 ff.

[10] J. H. Van Vleck, Phys. Rev. **41**, 208 (1932).

[11] A. Sommerfeld and H. A. Bethe, *Handbuch der Physik*, second edition, Vol. 24/2, p. 613.

[12] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928); presentation in terms of the vector model in Chapter XII of J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*.

[13] For a resumé of the original Weiss theory and its relation to the more modern Heisenberg quantum-mechanical model, see Stoner, *Magnetism and Matter*, pp. 350–361.

perature. This simple model with κ independent of T works better than the more refined model in which a Gaussian distribution is assumed. Partial theoretical explanations of why this is so have been given along different lines by Fay[14] and by Opechowski.[15]

We thus base our calculations in Part II on a Hamiltonian function of the form

$$\begin{aligned}\mathcal{H}= & -g\beta\kappa\mathbf{I}\cdot\Sigma_i\mathbf{S}_i\\ & +\sum_{j>i}C_{ij}[\mathbf{S}_i\cdot\mathbf{S}_j-3r_{ij}^{-2}(\mathbf{S}_i\cdot\mathbf{r}_{ij})(\mathbf{S}_j\cdot\mathbf{r}_{ij})]\\ & +\sum_{j>i}\gamma_{ij}r_{ij}^{-4}(\mathbf{S}_i\cdot\mathbf{r}_{ij})^2(\mathbf{S}_j\cdot\mathbf{r}_{ij})^2,\end{aligned}\tag{8}$$

where I is the intensity of magnetization. We shall see that a nonvanishing anisotropy constant K_1 is obtained when the C and γ terms are regarded as perturbations, and the development is carried to the second approximation in C or first approximation in γ. It is to be emphasized that (8) is to be regarded as a substitute for the more exact secular problem, which would involve a Hamiltonian of the form

$$\begin{aligned}\mathcal{H}= & -2\Sigma_{j>i}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j+A\Sigma_i\mathbf{L}_i\cdot\mathbf{S}_i\\ & +\Sigma_{j>i}f_{ij}(\mathbf{L}_i\cdot\mathbf{L}_j,\ \mathbf{L}_i\cdot\mathbf{r}_{ij},\ \mathbf{L}_j\cdot\mathbf{r}_{ij})\end{aligned}\tag{9}$$

where f_{ij} is some polynomial function.[16] The first or molecular field term of (8) replaces the exchange or first member of (9). The remainder of (8) is regarded as representing the constraints on the spin which would be obtained if the interplay between the second and third, i.e., spin-orbit and orbital valence terms of (9) could be treated exactly.

It would, of course, be desirable if the calculations could be based directly on (9) rather than (8) but the labor involved appears prohibitive. Even if (9) is simplified by replacing the first member by an inner field, the partition function would have to be developed to at least the fifth order for any anisotropy to appear. This order is required because cubic anisotropy is achieved only if the spin-orbit parameter A is raised to at least the fourth power; also the f term must be utilized at least once in the expansion, giving an additional power. The anisotropy exists only in virtue of f_{ij} because here $\mathbf{L}_i$ and $\mathbf{L}_j$ are coupled to $\mathbf{r}_{ij}$ as well as simply to each other whereas the rest of (9) is isotropic. If f_{ij} is linear in $\mathbf{L}_i\cdot\mathbf{r}_{ij}$ and $\mathbf{L}_j\cdot\mathbf{r}_{ij}$ it would have to be raised to the fourth power to make the direction cosines appear in the fashion (2), and then an eighth-order development would be required.[17] Such a procedure obviously is out of the question. Even if the eighth order computation could be made, the approximation would not be a particularly good one, inasmuch as f_{ij} and A are of the same order of magnitude as kT, so that series expansion of the partion function does not converge adequately. The fact that any development has to be carried a long way means, of course, many powers of T in the denominator, and so it is qualitatively understandable why the temperature dependence may be more rapid than can be depicted by our model (8) if C and γ are regarded as constant with respect to T. We believe, however, that with C and γ functions of temperature, our model (8) has a fairly general significance as a phenomenological approximation. In particular, it need not be confined to the Heitler-London method, since the orbital states may not necessarily be anchored to each atom, but instead can be of the itinerant Bloch-Slater variety.

6. Results of calculations based on the Hamiltonian (8)

The model embodied in the Hamiltonian function (8) is not too difficult to handle analytically, and can be tested by reckoning out the constants K_1 and K_2. The mathematical detail is presented in Part II, and at this stage we shall simply summarize the conclusions. The three possible checks are on the sign, magnitude, and temperature variation of K_1 and K_2.

Sign of K_1.—There is no feasible way of determining the sign of K_1 if it is due to the quadrupole-quadrupole or last part of (8). If, however, K_1 is due to dipole-dipole or second

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[14] C. H. Fay, Proc. Nat. Acad. Sci. **21**, 537 (1935).

[15] W. Opechowski, Physica **4**, 181 (1937).

[16] Part of f_{ij} in (9) may be linear in $\mathbf{S}_i\cdot\mathbf{S}_j$ since the exchange integrals themselves depend on how the orbital angular momentum vectors are aligned when the atoms are not in s states. In other words orbital valence affects the exchange as well as Coulomb energy. This complication is of no particular interest to us, for the validity of (8) as a substitute for (9) is not much influenced by whether f_{ij} involves $\mathbf{S}_i\cdot\mathbf{S}_j$.

[17] It is to be emphasized that consideration of transformation properties show that three distinct quantities must each be raised to at least the fourth power. The necessity of this power of A is seen by imagining the $\mathbf{S}_i$ to rotate with the $\mathbf{L}_i$ held fast; that of $\mathbf{L}_i\cdot\mathbf{r}_{ij}$ by rotating $\mathbf{L}_i$ relative to the crystal; that of H^4 by rotating the external field.

member of (8), then K_1 is negative for a face or body-centered lattice, and positive for a simple cubic one. The reason why the sign can be determined in one case but not in the other is the following. It does not appear practical to determine the sign of either C or γ in (8), as detailed specification of atomic wave functions would be necessary. Now K_1 is linear in γ, but involves C only through its square, since dipole-dipole effects enter only in the second approximation (cf. Eqs. (30) and (44)). Hence the dipole-dipole contribution to K_1 is of determinate sign even though there is ambiguity in C itself. The dipole-dipole coupling gives a K_1 of the proper sign for nickel, since the latter has a face-centered lattice and negative K_1. This agreement is gratifying, inasmuch as nickel is the material which is most likely to have $S=\frac{1}{2}$, and we saw in Section 3 that with $S=\frac{1}{2}$, the quadrupole contribution to K_1 vanishes so that only the dipole explanation can be used. When we come to iron, the observed sign (positive with a body-centered lattice), does not check with the dipole-dipole model, but is not inconsistent with $S>\frac{1}{2}$ and quadrupole-quadrupole coupling. It is probable that iron has a spin of at least unity. If so, here, both causes of K_1 enter simultaneously. The right sign is possible only if the quadrupole effect is more important than the dipole one. It is not clear theoretically why this should be the case, as in the next paragraph we estimate very crudely the two effects to be of the same rough order of magnitude when they are both present. It is thus impossible to tell *a priori* which should be the larger, and so the best that can be done is to appeal to the empirical evidence.

Order of magnitude of K_1.—The constant K_1 should be of the order $A^4/10kT_ch^2\nu^2$, or thereabouts, per atom if due to dipole-dipole interaction, and of the order $A^4/h^3\nu^3$ if due to the quadrupole-quadrupole effect. The basis of these estimates is set forth in fine print below. Here A is the usual spin-orbit constant, T_c is the Curie temperature, and ν is a quantity of the order of magnitude of the separation of energy levels caused by interaction of the orbit with the crystalline field (or alternatively, of the coupling energy between the angular momentum vectors of adjacent atoms, something presumably of the same order of magnitude). A reasonable estimate is perhaps[18] $A^2/h\nu=10$ cm^{-1}, $\nu=10^4$ cm^{-1}, $kT_c\sim10^3$ cm. If so, then when due to either effect, K_1 is of the order 10^{-2} cm^{-1} per atom or 10^5 ergs/cm^3. It is not surprising that both the dipole and quadrupole mechanisms should lead to the same order of magnitude for K_1, as there is little distinction between them from the standpoint of the more fundamental equation (9) although they appear differently in (8). This estimate $K_1\sim10^5$ is of the order of the experimental values. Namely iron has $K_1=6\times10^5$ at room temperatures, while nickel has $K_1=-3\times10^4$ at this temperature, but about -3×10^6 at liquid hydrogen.[19] Thus with the model which we propose, there is no difficulty in understanding the existence of anisotropies as large as are observed.

To derive the above estimates of K_1, we first note that the calculations of Section 10 show that the constant K_1 is of the order $C^2/10kT_c$ per atom if ascribed to dipole-dipole coupling. The factor 10 does not follow from dimensional considerations, but is included because the purely numerical factor involved in Table I of Section 10 is rather small. The quantity C is the constant of proportionality in the second member of (8). It should be of the same order of magnitude $A^2/h\nu$ as the spin-orbit splitting in a molecular state devoid of mean angular momentum (cf. Hebb's calculations[8] on ρ type tripling in $^3\Sigma$ states). The splitting is of this order rather than simply A because it disappears in the first approximation for such a state. If the dipole-dipole constant C arose primarily from a pure magnetic interaction rather than spin-orbit coupling, C would be of the order of magnitude. 2 cm^{-1} given by (6) with $r_{ij}^{-3}\sim10^{23}$ rather than $C\sim A^2/h\nu\sim10$ cm^{-1}, and K_1 would be too small by a factor about 10^{-3}.

If K_1 is due to our quadrupole-quadrupole coupling, it should be of the same order of magnitude as γ (cf. Section

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[18] The expression $C\sim A^2/h\nu$ should be of the same order of magnitude as the constant term in the width of a ρ type triplet in band spectra. This term is 1.99 cm^{-1} for the oxygen molecule (R. Schlapp, Phys. Rev. **51**, 342 (1937)), and an extra power of at least ten seems in order in extrapolating to heavy elements like nickel. The quantity C can also be gauged by $^3\Pi_0{}^+-{}^3\Pi_0{}^-$ intervals in molecular spectra, with similar results. Another quite different method of estimation is furnished by considering the multiplet splitting in the configuration d^5 of say Cr II, which is again about 10 cm^{-1} (cf. page 162 of Bacher and Goudsmit's tables). This splitting is of the order $A^2/h\nu_1$, where ν_1 is the coupling energy between l vectors of the same atom rather than of different atoms and is probably somewhat greater than our ν. So, if anything, 10 cm^{-1} is an underestimate of C, and hence it is not too surprising that $|K_1|$ should sometimes reach almost 10^7 ergs/cm^3, as appears to be the case for nickel at very low temperatures.

[19] The experimental values of K_1 quoted here and in the tables of Part II are taken from Bozorth, reference 1, and are based ultimately largely on Japanese work on magnetization curves; Honda, Masumoto, Kaya, and Shirakawa, Sci. Rep. Tohoku Univ. **17**, 111 (1928); **24**, 391 (1935).

11, especially Table III) and γ is of the order $A^4/h^3\nu^3$. At first sight it might seem that γ should be of the same order of magnitude $A^2/h\nu$ as C, but to obtain a splitting like (7) which involves the spins all told to the fourth degree, it is necessary that the perturbing potential be raised to the fourth power, which involves a fourth rather than second order perturbation calculation. (In this connection, the third term of (9) is to be regarded as the unperturbed energy, and the second member $\Sigma_i A\mathbf{l}_i \cdot \mathbf{s}_i$, summed over two atoms, is to be treated as the perturbing potential.)

Temperature variation of K_1.—As regards the dependence of K_1 on T, our model proves correct only in a rough qualitative way in that it does indeed predict that the anisotropy should fade out much more rapidly than does the intensity of magnetization itself when the temperature is raised towards the Curie point. However, the predicted variation with temperature is still not as drastic as is found experimentally. In the case of iron, the observed anisotropy varies approximately as I^{10} near the Curie point,[20] whereas the computed values given in Table III simulate more nearly I^6 or I^5. Here we use the quadrupole-quadrupole calculations in order not to be in conflict on the sign of K_1. In the case of nickel, K_1 is actually over fifty times larger at 17° than at 293°K, whereas according to our calculations K_1 should increase but very little in numerical magnitude when T is reduced below room temperatures. This statement is true regardless of whether the dipole or quadrupole model is used, since either one gives qualitatively about the same variation with T (cf. Tables I and III of Part II). For the latter reason, no explanation is obtained of why it is that dK_1/dT is very much larger in absolute value at low temperatures for nickel than for iron, so that the absolute zero is approached in a quite different way for the two materials.

We believe that the failure of the models based on the Hamiltonian function (8) to give the proper quantitative temperature dependence should not be regarded as too serious a difficulty, since (8) presupposes a somewhat phenomenological treatment of the orbital part of the problem. In fact, we mentioned at the end of Section 5 that (8) might not give a rapid enough variation with T. As stressed in Section 5, C and γ ought really to be regarded as undetermined functions of the temperature, rather than as constants as we have taken them to be in obtaining the theoretical predictions mentioned in the preceding paragraph. Another, but probably less important source of error, is the use of the Weiss inner field as a method of depicting the workings of exchange interactions between the spins. Additional leeway is obviously obtained if the proportionality factor κ in the molecular field is regarded as a function of temperature, rather than constant, as we take it to be. To examine how serious are the deficiencies of the Weiss field approximation, we give in Section 12 an alternative method of calculation of the quadrupole-quadrupole effect in which the exchange interactions in the pair under consideration are taken into account rigorously and only the effect of outside atoms represented by means of the molecular field. The difference between this perhaps improved method of calculation and the original one given in Section 11 is unimportant (cf. Table III). Unfortunately, it does not appear feasible to carry out the computations with the Bloch "spin-wave" type of approximation which is particularly suitable for low temperatures.

Magnitude of K_2.—We have not carried the perturbation calculations to a high enough order to permit saying anything on either the sign or temperature variation of K_2. Dimensional considerations, such as those given in fine print above, suggest that K_2 would differ from K_1 by a factor $A^2/h^2\nu^2$ or perhaps $A^2/h\nu kT_c$ and hence be about 10^{-3} to 10^{-2} as great as K_1. Actually K_2 is comparable with K_1. For instance, K_2 almost equals K_1 in iron above 500°K, while K_2 is about 30 percent of K_1 in nickel at 123°K. This difficulty is not merely one characteristic of the particular model (8) which we use, since with any type of calculation the spin-orbit parameter must be raised to the sixth rather than fourth power to generate an angular dependence of the form (3) rather than (2). As suggested to me by Dr. Bozorth, part of the apparent discrepancy may be associated with the different size of the angular factors in (2) and (3). The maximum of $\alpha_1^2\alpha_2^2\alpha_3^2$ is only 1/27, as compared with $\frac{1}{3}$ for $\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2$, while the difference in mean value is even greater, *viz.* a factor 21. Whether the dimensional considerations on magnitudes relate more exactly to the expressions (2)

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

and (3) inclusive or exclusive of the directional factors cannot be determined without a rather laborious explicit calculation of K_2. Of course one must bear in mind that because of the small angular factor mentioned above, the constant K_2 is not easy to measure with precision, and so the experimental values may not be very accurate. However, the observed magnetization curves are so complicated that it is scarcely conceivable that they can always be depicted by a dominant fourth order form F_1 without the admixture of comparable F_2 terms. In fact in some cases appreciable higher harmonics F_3 and F_4 may be required.

In nickel, K_1 apparently changes sign at about 420°K. To be sure, this is in a region where the anisotropy is so small that the experimental data may not be reliable. If the change in sign is real, it would perhaps indicate that excited states of nickel can have $S>\frac{1}{2}$ and so manifest quadrupole coupling even though the normal states, which determine the sign at low temperatures, have $S=\frac{1}{2}$ and so only the dipole effect. Another more likely possibility is that the higher order perturbation terms are for some reason abnormally important, as they would need to be to generate a K_2 much larger than K_1, such as is apparently shown in nickel at high temperature. These terms will make some contribution to the angular structure (2) as well as (3).

7. Relation to other models of ferromagnetic anisotropy in the literature

Bloch and Gentile's theory and the one atom model.—A large number of papers have already been written on the same subject as the present article, *viz.* the origin of the anisotropy constants K_1, K_2 in atomic theory, but usually in our opinion on the basis of models which cannot be regarded as a close or satisfactory approximation to physical reality. Considerable resemblance, however, appears at times between the preceding discussion and that given by Bloch and Gentile.[21] This statement is particularly true regarding the way in which the constants enter dimensionally, and the idea that cubic anisotropy exists primarily in virtue of spin-orbit interaction, but only after the spin-orbit parameter is raised to the fourth power. In a certain sense, all our calculations in Part II may be regarded as simply an attempt to put their general scheme of things on a firmer and more tangible basis. Nevertheless, there is one respect in which our approach seems to differ from theirs in principle. Their explanation for ferromagnetic anisotropy appears to be the interplay between spin-orbit interaction and the quantization of a single atom in a crystalline field. It is perhaps not entirely fair to make this statement definitely, as their paper is couched in such general language that it is impossible to extract from it exactly the type of orbital quantization which is implied. However, they do talk of the "*s* state of an atom," "excitation of one atom," etc. and so would seem to imply that each orbit can be quantized in a crystalline field. Such a picture we shall call the "one-atom model," as it would imply that magnetic anisotropy can be deduced from a secular problem involving only one atom, provided exchange is represented by an inner field. In other words, the Bloch-Gentile Hamiltonian function differs from ours in that the last, or orbital valence term of (8), is replaced by the sum $\Sigma_i V_i$ of the individual crystalline potentials of the separate atoms. However, we advance in the next paragraph reasons for believing that such a model is incapable of yielding any appreciable anisotropy. We maintain that the coupling between orbital angular momentum vectors of different atoms is a vital ingredient, rather than the interaction of a single vector with the crystalline field.

The reason why the one-atom model cannot give appreciable cubic anisotropy is the degeneracy whereby many levels coincide in a cubic field. If we have a nonmagnetic, nondegenerate orbital level (type Γ_1 or Γ_2 in Bethe's[22] notation) in a cubic field, and add the spin, then group theory shows that the resulting levels are completely degenerate[23] so long as the spin quantum number S is less than 2, as is altogether probable.

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[21] F. Bloch and G. Gentile, Zeits. f. Physik 70, 395 (1931).

[22] H. Bethe, Ann. d. Physik 3, 133 (1929).

[23] The appropriate relations in the language of group theory are the following formulas for the reduction of the "direct products" of the spin and orbital representations:

$$\Gamma_6\times\Gamma_1=\Gamma_6,\quad \Gamma_6\times\Gamma_2=\Gamma_7,\quad \Gamma_4\times\Gamma_1=\Gamma_4,$$
$$\Gamma_4\times\Gamma_2=\Gamma_5,\quad \Gamma_8\times\Gamma_1=\Gamma_8\times\Gamma_2=\Gamma_8$$

inasmuch as $S=\frac{1}{2}$, 1, $\frac{3}{2}$ have the cubic transformation properties of Γ_6, Γ_4, Γ_8 respectively. There is no splitting when the reduced product contains only one irreducible representation, as in the above cases.

This result is intimately connected with the fact that the most general polynomial in the spin vector is an expression of the first, second, or third degree according as S equals $\frac{1}{2}$, 1, or $\frac{3}{2}$, whereas cubic anisotropy requires the fourth degree. In consequence of this fact, the atom will be isotropically bound as long as one considers only matrix elements of the Zeeman energy (i.e., energy of the atom in the Weiss molecular field) connecting the different components of the ground level. As soon as one includes matrix Zeeman components joining the ground state and excited orbital levels based on other representations than Γ_1 or Γ_2, cubic anisotropy can appear. However, as shown in fine print below, a very high order perturbation development is required, and the resulting value of K_1 is too small to be significant.

In Section 6 we saw that a K_1 of about the right order of magnitude is obtained if K_1 is dimensionally of the structure $[A^4/h^2\nu^2 10kT_c]\varphi$ or $[A^4/h^3\nu^3]\varphi$. Here φ is a function only of the dimensionless argument $g\beta\kappa I/kT$. ($10f$ or f_1+f_2 in our later Eqs. (32), (38) are examples of essentially φ functions.) Any portion of the free energy leading to the angular structure (2) must involve the spin-orbit parameter A and the molecular field $H=\kappa I$ each to at least the fourth power. The requisite fourth power of κI was previously tacitly contained in φ which was not mentioned in Section 6 as φ is of the order of magnitude unity. However, the appearance of the argument $g\beta\kappa I/kT$ is as a rule possible only in virtue of nonisotropic "low frequency" matrix elements connecting energy levels split by intervals small compared with kT. When the Zeeman components leading to anisotropy join normal and excited states, the dimensionless factor[24] usually becomes instead $\kappa I/h\nu$, and K_1 is of the order $A^4\kappa^4 I^4/h^7\nu^7$ or perhaps $A^4\kappa^4 I^4/h^6\nu^6 kT_c$, and then K_1 would be about 10^2 ergs/cm^3 rather than the observed 10^5 to 10^6.

If there is a spin of unity or greater, and if the ground orbital state of the atom happens to be Γ_3, the orbital level is degenerate but by exception nonmagnetic. Then there is no difficulty with g-factors. Also the introduction of the spin causes a small splitting of the ground level (as embodied in the group theory relation $\Gamma_3\times\Gamma_4=\Gamma_4+\Gamma_5$, if $S=1$, or $\Gamma_3\times\Gamma_8=\Gamma_6+\Gamma_7+\Gamma_8$ if $S=\frac{3}{2}$), so that the desired small lifting of the degenerary is available. Conceivably this situation is part of the explanation of the anisotropy of iron. It will not work for nickel if the latter has $S=\frac{1}{2}$, as the formula $\Gamma_3\times\Gamma_6=\Gamma_8$ shows that the degeneracy persists even after insertion of the spin. However, we doubt if it is an accurate picture of things to use the crystalline field mechanism in conductors, as explained in Section 4. So it is rather academic to discuss at length any specific details of the one atom model.

Powell's model.—In an interesting paper, Powell[25] secures the desired angular structure (2) by introducing an anisotropic Weiss field. The dissymmetry in the latter is somehow to be associated with the effects of spin-orbit interaction, and should perhaps be regarded as a phenomenological substitute for the last two terms of (9). However, the relation of Powell's model to the actual workings of spin-orbit coupling is apparently such a remote and heuristic one that it cannot yet be regarded as a real explanation of ferromagnetic anisotropy.

Akulov's calculation of the temperature variation of K_1.—There are numerous papers by Mahajani, Akulov and others[4] based on rather arbitrary quadrupole-quadrupole models, but as far as we know, in only one of them, by Akulov,[20] is any attempt made to compute theoretically the temperature dependence of K_1. His results are in better agreement with experiment than ours, as he finds the anisotropy varying as the tenth power of the intensity of magnetization near the Curie point. However, he regards the spins of adjacent atoms as all parallel, and all precessing together about the axis of resultant magnetization. According to statistical mechanics, the elementary magnets tend less and less to be mutually parallel as the temperature is raised, and it is hard to believe that the assumption of complete parallelism is a better approximation to the true workings of exchange coupling than is the Weiss molecular field. The latter, to be sure, probably does not take sufficient cognizance of the tendency of magnets to coagulate locally into parallel clusters, but the modified calculation

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[24] Powers of kT in the denominator of the free energy or partition function arise in general from perturbing matrix elements involving energy changes $h\Delta\nu$ small compared to kT, because kT replaces $h\Delta\nu$ in the perturbation denominators when terms are paired in appropriate fashion (cf. K. F. Niessen, Phys. Rev. **34**, 253 (1929); J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Section 46). Hence a small splitting of the ground state by the crystalline field is necessary. (For formal purposes a zero splitting can be regarded as a small splitting, but in the cases under consideration zero splitting gives essentially the same transformation properties as free rotation and so does not cause anisotropy.) In the text we have listed one power of $1/kT$ in K_1 as possible even when the ground level does not split, because sufficiently high perturbation calculations involving the interaction with excited states may ultimately lead to anisotropic low frequency matrix elements.

[25] F. C. Powell, Proc. Roy. Soc. **130**, 167 (1930); with R. H. Fowler, Proc. Camb. Phil. Soc. **27**, 280 (1931). An anisotropic Weiss field is also suggested by Mahajani, reference 4.

given in Section 12 appears to indicate that the temperature dependence is probably not greatly modified by this tendency, although the latter admittedly works in the right direction.

Bozorth and McKeehan's model.—Practically all the papers using quadrupole-quadrupole coupling are open to the objection that they introduce this mechanism more or less *ad hoc* without supplying any basis in atomic theory. An attempt to circumvent this difficulty has been given in a recent article by Bozorth and McKeehan.[26] They neatly point out that spin dipoles can give rise to quadrupole and still higher order moments when it is remembered that the spin is not anchored to the nucleus but instead travels around with the electron. Thus on taking the time average, i.e., matrix elements diagonal in the electronic orbital quantum numbers, there is a dipole of finite extent, which will introduce quadrupole moments as long as there is a correlation between the direction of the electronic spin and the directions of anisotropy in the "time exposure" electronic charge cloud. Also it is necessary that the spin quantum number S be $>\frac{1}{2}$, since (4) is the most general potential when $S=\frac{1}{2}$. With complete correlation and with pure magnetic interaction the constant K_1 would then be of the order of magnitude $R^2g^2\beta^2/r_{ij}^5$, where R is the atomic radius. If we take $R^2/r^2\sim 1/10$, $r_{ij}^3=10^{-23}$ the resulting value of the constant K_1 is indeed of the order of magnitude observed experimentally. For this reason they suggest that true magnetic coupling (6) is sufficient to explain anisotropy, and dismiss the possibility of the electrostatic interaction between the charge clouds of different atoms, represented essentially by the last term of (9), as of uncertain magnitude and unnecessary. However, in our opinion, the correlation between spin and orbital alignment is slight, i.e., the electronic charge cloud does not orient very much with the spin, since the observed g factors of nearly 2 indicate that the orbital angular momentum is largely quenched and decoupled from the spin. So with pure magnetic interaction, the anisotropy would be too weak by a factor 1000 or so. The loss in magnitude is recovered when the Bozorth-McKeehan model is so amended that the primary coupling between different atoms is electrostatic, as seems inevitable since the orbital valence terms are surely much larger than the pure magnetic ones. (For the latter reason, incidentally, the anisotropy would be much too large were there anything like complete correlation between spin and orbital orientation.) With this modification, there is at least a vague resemblance between the Bozorth-McKeehan model and our use of the quadrupole potential (7) for $S>\frac{1}{2}$, though the approaches are entirely different. The gist of the matter is that enough fo the orbital anisotropy "sticks" to the spins to create apparent quadrupole forces between them.

8. Magnetostriction

It is not our main purpose to discuss magnetostriction, but we can note in passing how our theory has some bearing on this subject. There is a considerable literature on magnetostriction,[27] the essence of which is that it is possible to understand many of the phenomena, especially those concerned with spatial variation, if one assumes that besides the ordinary elastic energy, there is the energy of a dipole lattice which is strained due to the magnetic field, and which so loses its perfect cubic spacing. However, there is the difficulty usually stated in the form that the theoretical so-called "lattice sums" do not have the proper value, being sometimes too small, sometimes even of the wrong sign. Another way of saying the same thing is that empirically the constant of proportionality C in the dipole-dipole potential (4) (or rather its derivatives with respect to r_{ij}) does not have the value (6) corresponding to pure magnetic coupling. Fortunately in Section 4 it was shown that most of C probably does not arise from this cause, but rather from the interplay between orbital valence and spin-orbit interaction, so that C has an order of magnitude $A^2/h\nu$ about fifty times larger than (6). (As a matter of fact, even the pure exchange coupling gives rise to magnetostriction, but the resulting contribution is isotropic, and we shall consider only the spatial variation.) Hence it is clear why the so-called lattice sums should usually turn out considerably larger than given by

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[26] R. M. Bozorth and L. W. McKeehan, Phys. Rev. **51**, 216 (1937); L. W. McKeehan, Phys. Rev. **52**, 18 (1937).

[27] N. S. Akulov, Zeits. f. Physik **52**, 389 (1928); **59**, 254 (1930); **69**, 78 (1931); Becker, reference 3; R. Gans and J. v. Harlem, Ann. d. Physik **16**, 162 (1933); W. Heisenberg, Zeits. f. Physik **69**, 287 (1931); F. C. Powell, Proc. Camb. Phil. Soc. **27**, 561 (1931).

(6), and not necessarily with the sign demanded by (6). According to Powell [27, 28] the anomaly in iron amounts to a factor 13, in sufficient agreement as regards order of magnitude with our rough estimate 50. Quantitative comparison of the values of C obtained from the anisotropy in the intensity of magnetization and from magnetostriction immediately suggests itself, but is not very feasible, since the former involves C itself, while the latter depends on the derivatives with respect to r_{ij}.

One thing which the magnetostriction data clearly show is that the first order dipole energy is larger than the quadrupole. In cubic systems we have seen that as far as anisotropy is concerned, the dipole energy appears only in the second order and cannot be resolved from the quadrupole contribution, as both effects enter additively when $S>\frac{1}{2}$. With magnetostriction, however, it is different. The dipole-dipole effects can come into play in the first order because the strain makes the crystal cease to be cubic. The magnetostriction data show that in (8) the constant C is certainly larger than γ. Namely, if one assumed that the magnetic energy of strain were of the order $\gamma\delta l/l$ rather than $C\delta l/l$, where l and δl are respectively the lattice spacing and strain therein, the magnetostriction would not be as large as the observed by a factor about 100. Also it is doubtful if its angular dependence would be correct, because strain of quadrupole lattices would lead to different spatial behavior than would that of dipole ones. Since C is thus so much larger than γ, it is once again hard to see why K_2 is as large as is observed, for from crude dimensional considerations one would expect the ratio of K_2 to K_1 to be about the same as that of γ to C.

It is possible that the "one-atom model" has some importance and relevance for magnetostriction even though it does not for ferromagnetic anisotropy. When a cubic crystal becomes strained, it acquires only tetragonal symmetry, and the bottom states can split, provided $S>\frac{1}{2}$. So under strain the one-atom crystalline potential can materially hamper the free alignment of the spins, and conceivably it might be possible to explain magnetostriction with this mechanism instead of the coupling (8) or (9). No doubt the two effects, crystalline potential and orbital valence, are superposed in reality.

Part II. Mathematical Analysis

9. Preliminary details

We now proceed to the mathematical calculation of the partition function $Z=\Sigma_\lambda e^{-W_\lambda/kT}$ for our model. Once this has been computed, the free energy is supplied immediately by the relation $F=-kT\log Z$. Our Hamiltonian function is

$$\mathcal{H}=-g\beta H\Sigma_i S_{zi}+\Sigma_{j>i}w_{ij}, \tag{10}$$

where i, j refer to the various atoms of the crystal, w_{ij} is in the interaction energy between atoms i, j, and H is supposed directed along the z axis. The total effective field H is composed of the external field H_{ext} and the Weiss internal field, which is supposed to depict the ordinary exchange interaction as explained in section 5, and which is presumably proportional to the intensity of magnetization I, so that

$$H=H_{\text{ext}}+\kappa I. \tag{11}$$

For the purposes of the present paper, only the second term of (11) is of importance, but by taking H to be solely the external field, it is easily possible to adapt the calculation of section 10 to two other entirely different problems, *viz.* the adiabatic demagnetization of titanium alum, and the Gaussian fluctuations in the Heisenberg theory of ferromagnetism, as we shall show in two later papers.

Let us now regard the first member of (10) as the unperturbed system. A system of representation can then be used in which each atom is space-quantized separately, the corresponding characteristic

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[28] Akulov and Becker, reference 27, obtained factors 2 and 5 respectively rather than 13, but Powell showed that this apparent discrepancy was because they used different boundary conditions or demagnetization corrections, not appropriate to the shape of the specimens usually employed experimentally.

value of S_{zi} being denoted by m_i. The unperturbed energy is then

$$W_0 = -g\beta H \Sigma_i m_i. \tag{12}$$

The second part of (10) is the perturbing potential.

10. Second-order effect of dipole-dipole coupling

Equation (8) shows that the interaction energy w_{ij} contains both dipole and quadrupole terms (provided $S > \frac{1}{2}$). However, the two terms contribute additively to K_1 to the approximation under consideration (second order in C, first in γ), and so may be treated separately. The consideration of the quadrupole part will therefore be reserved until Section 11. In the present case of dipole-dipole coupling, the interaction is thus

$$w_{ij} = \sum_{q,q'=x,y,z} a_{ij}^{qq'} S_{qi} S_{qj'} \quad (a_{ij}^{qq'} = a_{ij}^{q'q}). \tag{13}$$

For the sake of increased generality, needed in connection with other problems, a quadratic form has been used in (13) which is somewhat less specialized than the second member of (8). In fact, except for a trivial additive constant, (13) has the same generality as all of (4).

The matrix elements of the perturbing potential may readily be computed with the aid of the well-known formulas

$$S_{zi}(m_i\,;m_i') = m_i\delta(m_i\,;m_i'), \quad (S_{xi} \mp iS_{yi})(m_i\,;m_i') = (S^2+S-m_i^2 \mp m_i)^{\frac{1}{2}}\delta(m_i \pm 1\,;m_i'), \tag{14}$$

where δ is the Kronecker delta, and S is the spin quantum number of the atom, which we suppose the same for all atoms, but which need not necessarily be $\frac{1}{2}$. Because (13) involves the product of only two spins, Σw_{ij} is never off-diagonal in more than two quantum numbers. A typical element is, for example

$$\Sigma_{j>i} w_{ij}(m_k m_l\,;m_k+1,\, m_l-1) = \tfrac{1}{4}(a_{kl}^{xx} + a_{kl}^{yy})(S^2+S-m_k^2-m_k)^{\frac{1}{2}}(S^2+S-m_l^2+m_l)^{\frac{1}{2}}. \tag{15}$$

Here we have listed only those quantum numbers which are different in the initial and final states. In the particular case (15), these two states involve the same energy, so that in the notation of a previous article,[29] the transition (15) is one of the type indicated by the superscript$^{=}$. Another example, not of this type, is

$$\Sigma_{j>i} w_{ij}(m_l\,;m_l-1) = \tfrac{1}{2}\Sigma_k(a_{kl}^{zx} - ia_{kl}^{zy})m_k(S^2+S-m_l^2+m_l)^{\frac{1}{2}}. \tag{16}$$

In this instance the energy change is $g\beta H$.

The partition function can now be calculated to terms in w_{ij}^2 inclusive by means of formulas (64), (65), (68–72) given in Section 6 of a previous paper,[29] which we shall call *l.c.* In fact the present calculation resembles in many ways that given in detail in sections 1–2 of *l.c.* However, there is the distinction that we there supposed the field strength small, so that we could stop with second powers thereof. In the present ferromagnetic case, the effective, inner field is not small, and saturation cannot be neglected. Cubic anisotropy first appears in the approximation H^4. So it is necessary to use a more general theory in which all powers of the field strength are retained. The requisite skeleton mathematical basis is supplied by Eqs. (64) etc. of Section 6 of *l.c.*, which have the desired generality, and serve as a starting point for the present calculation. The inclusion of a crystalline field, allowed in Section 6 of *l.c.* is, however, not necessary for present purposes. When the formulas of *l.c.* for the partition function are utilized, there are still sums over the various quantum numbers to be evaluated. Fortunately they can all be factored into sums over individual quantum numbers of the type

$$B_n = \sum_{m=-S}^{S} m^n e^{m\theta} / \sum e^{m\theta} \quad \text{with} \quad \theta = g\beta H/kT. \tag{17}$$

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[29] J. H. Van Vleck, J. Chem. Phys. 5, 320 (1937).

The function B_n defined by (17) may be evaluated explicitly by means of the relation

$$B_n=Q^{-1}d^nQ/d\theta^n \quad \text{where} \quad Q=\sum e^{m\theta}=e^{-S\theta}(1-e^{(2S+1)\theta})/(1-e^{\theta}).$$

With the aid of *l.c.*, one thus finally finds that

$$\begin{aligned} Z/Z_0=1&-\tfrac{1}{2}Nk^{-1}T^{-1}\Sigma_j a_{ij}{}^{zz}B_1{}^2+\tfrac{1}{2}NB_1{}^2B_2k^{-2}T^{-2}[(\Sigma_j a_{ij}{}^{zz})^2-\Sigma_j(a_{ij}{}^{zz})^2] \\ &+\tfrac{1}{8}Nk^{-2}T^{-2}B_1{}^4[(N-4)(\Sigma_j a_{ij}{}^{zz})^2+2\Sigma_j(a_{ij}{}^{zz})^2]+(NB_1{}^3/2kTg\beta H)[(\Sigma_j a_{ij}{}^{zx})^2+(\Sigma_j a_{ij}{}^{yz})^2 \\ &-\Sigma_j(a_{ij}{}^{zx})^2-\Sigma_j(a_{ij}{}^{yz})^2]+\tfrac{1}{4}NB_2{}^2k^{-2}T^{-2}\Sigma_j(a_{ij}{}^{zz})^2+\tfrac{1}{2}(NB_2B_1/kTg\beta H)[\Sigma_j(a_{ij}{}^{zx})^2+\Sigma_j(a_{ij}{}^{yz})^2] \\ &+\tfrac{1}{32}Nk^{-2}T^{-2}(S^2+S-B_2+B_1)(S^2+S-B_2-B_1)\Sigma_j(a_{ij}{}^{xx}+a_{ij}{}^{yy})^2 \\ &+\tfrac{1}{8}(NB_1/2kTg\beta H)(S^2+S-B_2)\Sigma_j[(a_{ij}{}^{xx}-a_{ij}{}^{yy})^2+4(a_{ij}{}^{xy})^2]. \end{aligned} \tag{18}$$

Here Z_0 is the partition function in the absence of the perturbing potential $\Sigma_{j>i}w_{ij}$. The contribution of the factor Z_0 to the free energy $F=-kT\log Z$ is simply the free energy corresponding to an ideal gas in a magnetic field, and consequently isotropic as far as the latter's orientation is concerned. This part of F is obviously of no interest for us. In writing (18), we have replaced $\Sigma_{j>i}$ by $\tfrac{1}{2}N\Sigma_j$. This is legitimate because the atoms are all alike in behavior in the cubic gratings we are considering.

Equation (18) involves the a_{ij} relative to a system of coordinate axes such that the applied field is always in the z direction. To study anisotropy, it is necessary to express the interaction energy w_{ij} in terms of similar constants A_{ij} for a system of axes fixed relative to the crystal, which are denoted by capital letters, i.e.,

$$w_{ij}=\Sigma_{q,\,q'=X,Y,Z}A_{ij}{}^{qq'}S_{qi}S_{qj}. \tag{19}$$

The reason that the results must be expressed in terms of the A's rather than the a's is, of course. that the A's are constants independent of the direction of the applied field, whereas the a's are not, Since w_{ij} must be invariant of the coordinate system, and since the S_i transform like vectors, comparison of (14) and (19) shows that the transformation relations connecting the a's and A's are

$$a_{ij}{}^{qq'}=\Sigma_{p,p'=XYZ}\,\lambda_{qp}\lambda_{q'p'}A_{ij}{}^{pp'}, \tag{20}$$

where the λ_{qp} are direction cosines. We now substitute (19) in (18). A large number of terms coalesce or drop out if we assume, as we do, that there is cubic symmetry. In virtue of the latter, sums like $\Sigma A^{XY}A^{YZ}$ in which a letter (here X or Z) appears only once, must vanish for there is nothing to distinguish between the positive and negative X (or Y or Z) directions. If such sums did not vanish they would not be invariant under the substitution $X=-X$, inasmuch as $A^{-XY}=-A^{XY}$. Also because of the parity of all coordinate axes in a cubic system, we must have

$$\Sigma_j(A_{ij}{}^{zz})^2=\Sigma_j(A_{ij}{}^{xx})^2, \quad \Sigma_j A_{ij}{}^{xx}A_{ij}{}^{yy}=\Sigma_j A_{ij}{}^{xx}A_{ij}{}^{zz}, \quad \text{etc.}$$

Similar relations also apply in the x, y, z system. They would not be true were the summation over j removed, as the interaction between any given pair of atoms certainly does not have cubic symmetry. With the summation, however, the full cubic symmetry of an atom's environment is manifested. Thus it is finally found that (18) becomes

$$\begin{aligned} Z/Z_0=1&-\tfrac{1}{2}Nk^{-1}T^{-1}\Omega_0B_1{}^2+\tfrac{1}{8}Nk^{-2}T^{-2}[B_1{}^4(N-4)+yB_1{}^2B_2]\Omega_0{}^2 \\ &+\tfrac{1}{5}Nk^{-2}T^{-2}[\tfrac{1}{4}B_1{}^4-\tfrac{1}{2}B_1{}^2B_2+\tfrac{1}{4}B_2{}^2+\tfrac{1}{16}(S^2+S-B_2)^2-\tfrac{1}{16}B_1{}^2+\tfrac{1}{8}(S^2+S-B_2)(B_1kT/g\beta H)]\Omega_1 \\ &+\tfrac{1}{5}Nk^{-2}T^{-2}(kT/g\beta H)[\tfrac{1}{4}B_1(S^2+S-B_2)-B_1{}^3+B_2B_1]\Omega_2 \\ &+\tfrac{1}{5}Nk^{-2}T^{-2}[\tfrac{1}{16}(S^2+S-B_2)^2-\tfrac{1}{16}B_1{}^2-\tfrac{1}{8}(S^2+S-B_2)(B_1kT/g\beta H)]\Omega_3 \\ &-Nk^{-2}T^{-2}[\tfrac{1}{2}B_1{}^4-B_1{}^2B_2+\tfrac{1}{2}B_2{}^2+\tfrac{1}{16}(S^2+S-B_2)^2-\tfrac{1}{16}B_1{}^2 \\ &\quad+\tfrac{1}{8}(kT/g\beta H)(S^2+S-B_2)B_1+(kT/g\beta H)(B_1{}^3-B_2B_1)]\Omega_4(\alpha_1{}^2\alpha_2{}^2+\alpha_1{}^2\alpha_3{}^2+\alpha_2{}^2\alpha_3{}^2-\tfrac{1}{5}), \end{aligned} \tag{21}$$

where $\Omega_0=\frac{1}{3}\Sigma_j(A_{ij}^{XX}+A_{ij}^{YY}+A_{ij}^{ZZ})$ and

$$\Omega_1=3b+2c+4d,\quad \Omega_2=b-c+3d,\quad \Omega_3=b+4c-2d,\quad \Omega_4=b-c-2d$$

$$b=\Sigma_j b_{ij}=\tfrac{1}{3}\Sigma_j\{(A_{ij}^{XX})^2+(A_{ij}^{YY})^2+(A_{ij}^{ZZ})^2\},\quad c=\tfrac{1}{3}\Sigma_j(A_{ij}^{XX}A_{ij}^{YY}+A_{ij}^{YY}A_{ij}^{ZZ}+A_{ij}^{ZZ}A_{ij}^{XX}),\tag{22}$$

$$d=\tfrac{1}{3}\Sigma_j\{(A_{ij}^{XY})^2+(A_{ij}^{YZ})^2+(A_{ij}^{ZX})^2\}.$$

In (21), the notation α_1, α_2, α_3 has been used in place of λ_{zX}, λ_{zY}, λ_{zZ}, respectively. The additive constant $-\frac{1}{5}$ is included in the angular factor in the last term of (21) in order to make this term average to zero, inasmuch as the mean or power value of (21) will be needed in a later paper.

Formula (21) is valid for any value of the spin. In the important special case $S=\frac{1}{2}$ one has

$$B_1=\tfrac{1}{2}\tanh\,(g\beta H/2kT),\qquad B_2=\tfrac{1}{4},\tag{23}$$

and the analytical form of (21) is really rather simple, merely a polynomial in B_1.

Demagnetization corrections.—In case the test body is not molded in the shape of a sphere, the boundary conditions do not in general exhibit cubic symmetry even though the crystal belongs to the cubic classification. Then it is not allowable to suppose that the part of the A's due to the pure magnetic coupling (6) satisfy the relation

$$\Sigma_j A_{ij}^{XX}=\Sigma_j A_{ij}^{YY}=\Sigma_j A_{ij}^{ZZ}.\tag{24}$$

Instead, because (5) varies only as the inverse cube of the distance, the way the specimen is molded makes itself felt in a complicated way, giving rise to the so-called demagnetization corrections. It is well known that a rigorous theory of the latter is feasible only if the body is cut in an ellipsoidal form. Otherwise the various atoms cannot be regarded as equivalent in their grating sums and it would not be allowable to replace $\Sigma_{j>i}$ by $\frac{1}{2}N\Sigma_j$, as presupposed in (18) and (21). For this reason (18) and (21) are not rigorous when the body is molded in a cube or some other nonspherical shape compatible with cubic symmetry even though the full validity of (24) is then restored. The expression (21) can be used not merely for a spherical specimen, but also for a body cut in an ellipsoid of revolution with axis parallel to the field, provided Ω_o is defined not as before (22) but as

$$\Omega_o=\Sigma_j a_{ij}^{zz}=-Ng^2\beta^2\Phi+\tfrac{1}{3}\Sigma_j(A_{ij(o)}^{XX}+A_{ij\,(o)}^{YY}+A_{ij\,(o)}^{ZZ}).\tag{25}$$

Here Φ is the demagnetization plus Lorentz factor fully explained in Section 4 of *l.c.* The value of Φ for a sphere is 0, while Φ equals $4\pi/3$ and $-8\pi/3$ respectively for very prolate and very oblate ellipsoids. The subscript (o) attached to A_{ij} in (25) means that the part of A_{ij} due to the pure magnetic coupling is to be omitted. On the other hand this part of A_{ij} should still be included in computing Ω_1, Ω_2, Ω_3, Ω_4. These expressions all involve the A_{ij}'s quadratically, so that in the sums (22) the pure magnetic coupling (6) gives rise only to inverse sixth powers and there is no trouble with boundary conditions regardless of shape. The orbital valence portion $A_{ij(o)}$ which we saw in Section 4 doubtless constitutes the bulk of A_{ij} does not introduce shape complications even in the linear relation (25) since $A_{ij(o)}$ varies much more rapidly with distance than the inverse cube and so satisfies (24). The demagnetization factor Φ makes no contribution to the anisotropy if the body is always cut in the same direction relative to the field. This is what appears to be done experimentally; e.g., three specimens are cut in the form of long rods along the 100, 110, and 111 axes respectively, and their magnetization curves measured separately. The demagnetization correction for a long rod is presumably about the same as for a very prolate ellipsoid. Anyway, these corrections are not very important for our present purposes, since the extreme range $-8\pi/3$ to $4\pi/3$ in the Φ factor is very small compared with the constant of proportionality $\kappa\sim 10^5$ of the Weiss molecular field.

Numerical checks.—There are three simple checks on the arithmetical correctness of (21) which should be mentioned, and which we have verified. One is that if the functions B_1, B_2 be expanded as Taylor's series in $\theta=Hg\beta/kT$, *viz.*

$$B_1=\tfrac{1}{3}\theta x-\theta^3(2x^2+x)/90,\quad B_2=\tfrac{1}{3}x+\theta^2(4x^2-3x)/90,\quad (x=S^2+S)\tag{26}$$

then the coefficient of Ω_4 in (21) vanishes unless one goes to the fourth power of H. This must be the case, for since H transforms like a vector, only terms in H^4 or higher can exhibit a dependence on the direction cosines of the form $\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2$. A term in H^2, for instance, could only give quadratic dependence and because of cubic symmetry, can only contribute to the constant part of Z. The second check is that the coefficient of Ω_4 also vanishes in the limit $H=\infty$, which corresponds to complete parallelism of the dipoles; here $B_1=\sqrt{B_2}=S$.

The third check is that the direction-independent part of (21) should reduce to (53) and the unnumbered equation after (55) of *l.c.* when the development is terminated with H^2, and when the potential w_{ij} is specialized to exchange plus true magnetic-dipole coupling so that w_{ij} has the form given in (13) of *l.c.* (The notation J rather than S was used in *l.c.* for the angular momentum vector and the exchange integral was denoted by K rather than J, while v_{ij} is the same as our $-2J_{ij}r_{ij}^3/g^2\beta^2$.) Then

$$\Omega_0=Ng^2\beta^2(-\Phi+z'v),\quad \Omega_1=N^2g^4\beta^4(2Q_0+5Q_1),\quad \Omega_2=\tfrac{1}{2}N^2g^4\beta^4\cdot 3Q,\quad \Omega_3=N^2g^4\beta^4(-Q_0+5Q_1),\tag{27}$$

where $Q_0 = 2N^{-2}\Sigma r_{ij}^{-6}$, $Q_1 = Q - Q_0 = 4N^{-2}g^{-4}\beta^{-4}\Sigma_j J_{ij}^2$, $z'v = -2Ng^{-2}\beta^{-2}\Sigma_j J_{ij}$. The first relation of (27) follows from (25). The easiest way to establish the rest of (27) is to note that Ω_1, Ω_2, Ω_3 are independent of the choice of coordinate axes. So it is allowable to place the z axis along r_{ij} for each term in the lattice sums involved in the definitions (22), even though a different choice of axes is then required for each term. With (27), Eq. (21) reduces properly to (53) of *l.c.* Incidentally, (53) and other relations of *l.c.* apply when the dipole-dipole coupling is due to orbital valence, rather than of true magnetic origin, provided $g^2\beta^2/r_{ij}^3$ be replaced by C_{ij} in definatory relations such as (8) or (18) of *l.c.*

The structure factor Ω_4 in the anisotropic part of the partition function (21–22) is conveniently expressed in terms of a set of axes ξ_j, η_j, ζ_j which are so selected that ζ_j always is along r_{ij}, and whose choice hence varies with each term j in the sum. Then

$$\Omega_4 = \sum_j [b_{ij}' - c_{ij}' - 2d_{ij}'][1 - 5(\lambda^2_{X\zeta_j}\lambda^2_{Y\zeta_j} + \lambda^2_{Y\zeta_j}\lambda_{Z\zeta_j}^2 + \lambda^2_{Z\zeta_j}\lambda^2_{X\zeta_j})], \tag{28}$$

where the λ's are direction cosines and where b_{ij}', c_{ij}', d_{ij}' are similar to b_{ij}, c_{ij}, d_{ij} except for being computed relative to the ξ_j, η_j, ζ_j rather than X, Y, Z axes. Thus b_{ij}', c_{ij}', d_{ij}' are defined by (22) except that ξ_j, η_j, ζ_j throughout replace X, Y, Z. The advantage of (28) is that it employs the simplest choice of axes for each individual pair of atoms in the sum.

If w_{ij} has the dipole-dipole form given by the second member of (8), the expression (28) becomes

$$\Omega_4 = 3\sum_j C_{ij}^2[1 - 5(\lambda^2_{X\zeta_j}\lambda^2_{Y\zeta_j} + \lambda^2_{Y\zeta_j}\lambda^2_{Z\zeta_j} + \lambda^2_{Z\zeta_j}\lambda^2_{X\zeta_j})]. \tag{29}$$

To determine sign behavior, no harm will be done if the summation in (29) is restricted to the immediate neighbors of the given atom i. In the first place C_{ij} varies rapidly with r_{ij}, as the inverse sixth power if caused by the true magnetic effect (6), and still more drastically if due to the interplay of orbital valence and spin-orbit interaction. Also, especially, as one gets very far from a given atom, the distribution approaches effectively more and more that of a continuum. As soon as the summation can be replaced by an integral over a sphere, it vanishes, as the bracketed factor in (29) integrates to zero. By restricting ourselves to the nearest neighbors we probably overestimate slightly the numerical value of the sum (29), since the sign of the angular factor in (29) for the next-to-nearest neighbors, which presumably contribute the next-most-important terms, is the opposite to that for the leading terms. Possibly, but not very likely, this fact explains why K_2 is as large as it is relative to K_1, for the cancellation of the first and second zones is not as complete in K_2 as in K_1. With the restriction to nearest neighbors, the values of (29) are as follows for the various lattices.

$$\begin{array}{lccc} & \text{simple} & \text{face-centered} & \text{body-centered} \\ \Omega_4 = & +18\,C^2, & -9\,C^2, & -16\,C^2, \end{array} \tag{30}$$

where C is the value of C_{ij} connecting adjacent atoms. To a sufficient approximation the free energy is

$$F = -kT\log Z = -kT\log Z_0 - kT(Z_1/Z_0) + kT(Z_1/Z_0)^2 - kT(Z_2/Z_0) + \cdots \tag{31}$$

if Z_1 and Z_2 denote respectively the parts of (21) of the first and second degree in the A_{ij}. Consequently the anisotropy constant K_1 in (2) has the value

$$K_1 = Nk^{-1}T^{-1}f(g\beta H/kT)\Omega_4, \tag{32}$$

where $f(g\beta H/kT)$ denotes the long factor inclosed by square brackets in the last or Ω_4 term of (21).

Before we can compute with (32), it is necessary to agree on how to select the effective field H. We shall neglect the applied field H_{ext} in comparison with the inner field, an approximation which is completely warranted for our purposes inasmuch as the factor of proportionality κ by which the intensity of magnetization is multiplied to get the effective Weiss field is so very large. It is, however, at the same time tacitly supposed that the external field is adequate to make the inner field coincide in direction with it, or in other words to produce saturation. Our computed values of the free energy thus relate to $-\int I dH_{\text{ext}}$ integrated out to a field H_{ext} adequate to produce saturation, but at the

Table I. *Anisotropy for dipole-dipole model with* $S=\frac{1}{2}$.

$g\beta\kappa I/kT$	∞	6	4	3.2	2.6	2	1.6	1.2	0.8
$I/I_0=\frac{1}{2}B_1$	1	0.996	0.96	0.92	0.86	0.76	0.66	0.54	0.38
T/T_c	0	.33	.48	.58	.66	.76	.825	.9	.95
K_1kT_c/NC^2 (calc.)	−.140	−.139	−.126	−.102	−.076	−.046	−.028	−.011	−.003
T (nickel)	0^{30}	210	305	365	420	480	525	570	605°K
K_1 (obs., nickel)	-3×10^6	-1.6×10^5	-3×10^4	-5×10^3	0	$+10^4$	$+10^4$	$+10^4$	$+10^4$ ergs/cm³

same time small compared with κI.[31] We shall assume that the factor of proportionality κ in the molecular field is independent of temperature. Then the Heisenberg theory[32] shows that

$$H=\kappa I=3kT_cI/I_0g\beta(S+1), \qquad T_c=2Jz(S^2+S)/3k, \tag{33}$$

where I/I_0 is the ratio $I/g\beta S$ of the saturation intensity of magnetization at the given temperature to the complete saturation at the absolute zero. T_c is the Curie temperature, z is the number of neighbors, and J is the exchange integral. In computing the tables we take $g=2$, as the difference between 2 and the experimental value 1.9 is inconsequential. In order to record dimensionless expressions, we give the theoretical values of K_1kT_c/NC^2 rather than of K_1 itself. To evaluate (21) it is necessary to determine the values of T to be correlated with each value of I. It proves unimportant whether one uses the experimental correlation or the theoretical one $I=g\beta B_1$ given by the Weiss-Heisenberg theory, since the latter reproduces the observed $I-T$ curves sufficiently well for our purposes.

In Section 6, it was shown that the values of NC^2/kT_c by which the calculated K_1kT_c/NC^2 must be multiplied through to yield the observed K_1 at room temperatures and lower are of a reasonable order of magnitude. If C^2 is regarded as constant with respect to T, the calculated variation of K_1 with T is not sufficiently rapid; reasons why this should be so are also discussed in Section 6. Comparison of Tables I and II show that the behavior of K_1 for $S=\frac{1}{2}$ and $S=1$ is very similar except for a constant proportionality factor. Hence it matters little what atomic spin is assumed in the present qualitative status of the theory. For possible significance of the small positive experimental values of K_1 at high temperatures, see the very end of Section 6.

11. First-order effect of quadrupole-quadrupole interaction

We now consider the case where the coupling between atoms is of the quadrupole rather than dipole type. Referred to axes fixed relative to the field, the interaction between two atoms is of the type form

$$w_{ij}=\Sigma_{q,q',q'',q'''=x,y,z}\,a_{ij}{}^{qq'q''q'''}S_{qi}S_{qi'}S_{qj''}S_{qj'''}, \tag{34}$$

which is, of course, biquadratic in the two spins, considered together, or quadratic in the individual spins, considered separately. Without loss of generality, we may suppose (34) symmetric not merely

Table II. *Anisotropy for dipole-dipole model with* $S=1$.

$g\beta\kappa I/kT$	∞	3	2	1.6	1.3	1	0.8	0.6	0.4
$I/I_0=B_1$	1	0.95	0.85	0.77	0.69	0.58	.48	.38	.26
T/T_c	0	.48	.64	.72	.79	.87	.91	.95	.97
K_1kT_c/NC^2 (calc.)	−.75	−.68	−.50	−.35	−.24	−.13	−.05	−.02	−.01

Values of K_1T_c/NC^2 given in Tables I and II are calculated for face-centered lattice; for body-centered and simple cubic lattices, they should be multiplied by 16/9 and −2, respectively.

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[30] The experimental values of K_1 given in Tables I and III are for $T=21$°K and $T=93$°K respectively rather than $T=0$. Extrapolation indicates that in nickel $|K_1|$ is probably much larger than 3×10^6 at the absolute zero.

[31] In very weak fields, the direction of the spontaneous magnetization no longer coincides with the applied field, and is distributed in accordance with a statistical theory developed by Heisenberg (reference 27, not to be confused with his better known exchange theory, reference 12, of ferromagnetism). Heisenberg's ideas have been applied by Bozorth to ferromagnetic anisotropy in weak fields, especially the difference in direction between the vectors **B** and **H**. (Phys. Rev. **42**, 882 (1932)). Such investigations, of course, do not aim to explain the atomic origin of the anisotropy.

[32] Cf., for instance, J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Chap. XII, Eqs. (34), (37) and (29).

as regards permutation of the two atoms, but also as regards permutation of indices relating to the same atom, whence

$$a_{ij}{}^{qq'q''q'''}=a_{ij}{}^{q''q'''qq'},\quad a_{ij}{}^{qq'q''q'''}=a^{q'qq''q'''}. \tag{35}$$

(If there were any unsymmetrical terms contrary to the second relation of (35), they could immediately be reduced to lower degree by the familiar relations $S_xS_y-S_yS_x=iS_z$, etc.)

We suppose, as before, that the exchange interaction can be represented by means of an inner field (33), and regard (34) as a perturbation. As often previously mentioned, with quadrupoles the perturbation calculation need by carried only to the first order to bring out the cubic anisotropy (2). To this approximation the free energy is then identical with the mean interaction energy; i.e.,

$$F=-kT\log Z_0+\textstyle\sum_{j>i}(w_{ij})_{\text{Av}}. \tag{36}$$

The average denoted by the subscript Av is, of course, proportional to the diagonal sum in the system of representation, described in Section 9, in which each spin is separately space-quantized.

We now pass from axes x, y, z fixed relative to the field to axes X, Y, Z fixed in the crystal, denoting by capital letters the coefficients corresponding to (34) in the X, Y, Z system. The transformation equations connecting the two sets of coefficients are

$$a_{ij}{}^{qq'q''q'''}=\Sigma_{QQ'Q''Q'''=X,Y,Z}\,\lambda_{qQ}\lambda_{q'Q'}\lambda_{q''Q''}\lambda_{q'''Q'''}A_{ij}{}^{QQ'Q''Q'''}. \tag{37}$$

In precisely the same way that (21) was obtained from (18), it is found on using the cubic symmetry of the lattice that (36) becomes

$$F=F_0+\Omega_5[f_1+f_2][\alpha_1{}^2\alpha_2{}^2+\alpha_2{}^2\alpha_3{}^2+\alpha_3{}^2\alpha_1{}^2], \tag{38}$$

where F_0 is a purely isotropic term and where

$$\Omega_5=-N\Sigma_j[A_{ij}{}^{ZZZZ}-A_{ij}{}^{XXYY}-2A_{ij}{}^{XYXY}]. \tag{39}$$

The expressions f_1 and f_2 appearing in (38) are dimensionless functions of the argument $g\beta H/kT$, defined by

$$f_1=(S_{x_i}{}^2S_{x_j}{}^2)_{\text{Av}}+(S_{y_i}{}^2S_{y_j}{}^2)_{\text{Av}}+(S_{z_i}{}^2S_{z_j}{}^2)_{\text{Av}}-(S_{x_i}{}^2S_{y_j}{}^2)_{\text{Av}}-(S_{y_i}{}^2S_{z_j}{}^2)_{\text{Av}}-(S_{z_i}{}^2S_{x_j}{}^2)_{\text{Av}} \tag{40}$$

$$\begin{aligned}f_2=-\tfrac{1}{2}[&(S_{x_i}S_{y_i}+S_{y_i}S_{x_i})(S_{x_j}S_{y_j}+S_{y_j}S_{x_j})+(S_{y_i}S_{z_i}+S_{z_i}S_{y_i})(S_{y_j}S_{z_j}+S_{z_j}S_{y_j})\\&+(S_{z_i}S_{x_i}+S_{x_i}S_{z_i})(S_{z_j}S_{x_j}+S_{x_j}S_{z_j})]_{\text{Av}}.\end{aligned} \tag{41}$$

Although Ω_5 is evaluated in the X, Y, Z system, the averages of the spin vectors involved in (40–41) relate to the x, y, z system. Since each atom is separately spaced quantized in the system of representation being used (cf. Section 9), the averages may be taken over atoms i and j separately. In virtue of (14) and (17), Eqs. (40–41) may be written

$$f_1=[\tfrac{1}{3}(S^2+S)-\tfrac{3}{2}B_2]^2,\qquad f_2=0, \tag{42}$$

with B_2 as in (17). If $S=\frac{1}{2}$, then $B_2=\frac{1}{4}$, and f_1 vanishes, in agreement with our statement in section 3 that a quadrupole model is capable of yielding anisotropy only if $S>\frac{1}{2}$. If the quadrupole interaction energy has the form given by the third member of (8), which is sufficiently general for our purposes, then in the same way that (29) was obtained, it is found that

$$\Omega_5=-N\Sigma_j\gamma_{ij}[1-5(\lambda^2{}_{X\zeta_j}\lambda^2{}_{Y\zeta_j}+\lambda^2{}_{Y\zeta_j}\lambda^2{}_{Z\zeta_j}+\lambda^2{}_{X\zeta_j}\lambda^2{}_{Z\zeta_j})], \tag{43}$$

where the ζ_j axis is directed along r_{ij}. If γ_{ij} has a nonvanishing value γ only between neighbors, (43) yields

$$\begin{array}{cccc} & \text{face-centered} & \text{body-centered} & \text{simple cubic}\\ \Omega_5/N & +3\gamma & +(16/3)\gamma & -6\gamma\end{array} \tag{44}$$

TABLE III. *Anisotropy for quadrupole-quadrupole model with* $S=1$.

$g\beta\kappa I/kT$	∞	4	3	2.5	2	1.6	1.3	1	0.8	0.6
$I/I_0=B_1$	1.0	0.98	0.95	0.91	0.85	0.77	0.69	0.58	.48	.38
T/T_c	0	.38	.48	.55	.64	.72	.79	.87	.91	.95
$K_1/N\gamma$ (calc.)	1.333	1.20	.98	.81	.56	.34	.20	.10	.04	.02
T (iron)	0^{32}	400	500	575	670	750	820	910	950	990°K
K_1 obs (iron)	$6\times 1C^5$	3.6×10^5	2.7×10^5	2×10^5	1.3×10^5	$.7\times 10^5$	$.4\times 10^5$	$.1\times 10^5$	0	0 ergs/cm^3
$K_1/N\gamma$ (sec. 12)	1.333	1.13	.89	.76	.47	.27	.16	.07	.03	.01

Values of $K_1/N\gamma$ in Table III are calculated for body-centered lattice; for face-centered and simple cubic lattices, they should be multiplied respectively by 9/16 and $-9/8$, respectively.

The numerical values of K_1/γ given by (38,) (42), (44) for various temperatures are shown in Table III for the case $S=1$.

Nothing can be said at present from pure theory concerning the sign of γ. For discussion of the relation of the calculated to observed values of K_1 see Section 6. The general lay of the land is about the same as in the dipole-dipole case; *viz.* the order of magnitude of γ required to fit the experimental data is reasonable, but the calculated temperature variation of K_1 is not rapid enough if γ is regarded as a constant. However, the discrepancy is not as great as in the case of nickel. For instance, the table shows that experiment gives a reduction in K_1 by a factor 50 in going from low temperatures to 910°K, and theory also yields a fairly large reduction factor, *viz.* 13, or 19 with the improved calculation given in the next section.

12. Alternative, perhaps improved calculation of first order quadrupole-quadrupole interaction

It is obviously only an approximation to represent the exchange coupling by a molecular field. It is therefore advisable to see if substantially the same results are obtained with somewhat different approximations. We therefore now describe a somewhat modified and slightly more intricate calculation, in which we take into account rigorously the exchange interaction between the two particular atoms i, j whose anisotropy we are computing, but we still employ an appropriately chosen Weiss field to represent the exchange coupling of atom i with all other atoms than j, or of j with all others but i. Instead of being separately space quantized the two atoms i, j have a quantum number $S'=0, 1, \cdots, 2S$ which quantizes their total resultant spin, and another quantum number $M'=-S', \cdots, S'$ which determines the spatial orientation of S'. The choice of the system of quantization thus is different for each pair of atoms in the sum, but this procedure is allowable, because we are at liberty to approximate to the mean value of each individual term in (36) in the best fashion possible. Although we are still using the artifice of an inner field to represent the interplay of an atom with all but one of its z neighbors, the present procedure probably constitutes an improvement over Section 11 as far as the calculation of the anisotropic interactions is concerned. The reason is that if we are computing the mean value of a given perturbing term w_{ij}, it seems more important to take into account rigorously the interaction between atoms i and j than that between atoms i or j and other atoms, since w_{ij} is particularly sensitive to the relative alignment of atoms i and j. With our amended model, Eqs. (38)–(41) are still applicable, but the averages over atoms i and j can no longer be computed independently, inasmuch as with our new system of quantization there is a correlation between the motions of atoms i and j. Consequently f_1 and f_2 no longer have the values (42). The matrix elements of S_{x_i}, etc. appropriate to the present system of representation may be found in the literature.[33] They are then multiplied out to form the expressions (40)–(41) with each state weighted with its appropriate Boltzmann factor $e^{-[W(S')-M'g\beta H]/kT}$. The mutual exchange energy $W(S')$ of atoms i, j has the value[2]

$$W(S')=-2J\mathbf{S}_i\cdot\mathbf{S}_j=-J[S'^2+S'-2S^2-2S], \tag{45}$$

where J is the exchange integral connecting i and j. Henceforth we shall consider only the special case $S=1$ of one quantum unit of spin per atom. Then

$$W(2)=-2J,\quad W(1)=2J,\quad W(2)=4J,$$

and it is found that

$$f_1+f_2=\tfrac{1}{2}[\cosh 2\theta-4\cosh\theta+3]/D, \tag{46}$$

where $\theta=g\beta H/kT$ and

$$D=(2\cosh 2\theta+2\cosh\theta+1)+(2\cosh\theta+1)e^{-4J/kT}+e^{-6J/kT}. \tag{47}$$

The result (46) may be easily deduced by the following argument instead of resorting to the rather laborious compounding of the matrix elements to compute the individual terms of (40)–(41) explicitly. All the cubic anisotropy must come from the different Zeeman components of the state $S'=2$, since the angular dependence (2) is impossible for a single system with resultant spin $S'=1$ or $S'=0$. (Cf. remarks under Bloch-Gentile theory in Section 7). In this connection

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[33] See, for example, Condon and Shortley, *The Theory of Atomic Spectra*, pp. 63–67.

atoms i and j are to be regarded together as a one unit, inasmuch as the interaction energy w_{ij} involves a dynamical system of two atoms. (Hence the spin of an individual atom, which is only a component part of the system, can still be only unity.) Furthermore, the contributions of the various Zeeman components of $S'=2$ to the anisotropy is easily seen to be independent of the sign of M'. Consequently f_1+f_2 must have the form $a \cosh 2\theta + b \cosh \theta + c$, where D is defined as in (47), and where a, b, c are independent of T, H, and J. The explicit values of a, b, c given in (46) follow immediately from the requirement that (46) must reduce to (42) when $J=0$.

The inner field must now be taken as

$$H=2J(z-1)I/I_0 g\beta \tag{48}$$

rather than as $2JzI/I_0 g\beta$, the usual Weiss-Heisenberg value, since one of the z interactions is taken into account rigorously rather than incorporated in this field. The formula for the ratio I/I_0 of the intensity of magnetization to its maximum value at $T=0$ is

$$I/I_0=\tfrac{1}{2}[(4 \sinh 2\theta + 2 \sinh \theta) + 2 \sinh \theta e^{-4J/kT}]/D. \tag{49}$$

The Curie temperature T_c is the temperature at which (48) has a double root in I at $I=0$, or what is the same, the temperature at which the susceptibility becomes infinite when a small external field is added to the right side of (48). Hence T_c is determined by the transcendental equation

$$kT_c=2J(z-1)(5+e^{-4J/kT_c})/(5+3e^{-4J/kT_c}+e^{-6J/kT_c}). \tag{50}$$

The Curie temperature given by (50) is almost identical with that $T_c=4zJ/3k$ (cf. Eq. (33) with $S=1$) given by the ordinary Heisenberg model, e.g. 10.4 as compared with 10.7 if $z=8$. Henceforth in applying formula (46) no appreciable harm will be done if we use the correlation of I/I_0 with T/T_c given by the conventional Weiss formula $I/I_0=B_1$, rather than by (49).[34] The values of $K_1/N\gamma$ computed from (46) are shown in the last line of Table III, Section 11. The difference between the new values and those originally computed in Section 11 is unimportant in the present status of the theory. For this reason it does not seem worth while to apply the present method to the second-order effect of dipole-dipole interaction, which would be more difficult.

13. Hexagonal crystals

We shall now in closing digress briefly on hexagonal instead of cubic lattices. It is found empirically that with a hexagonal structure, the dependence on the free energy on the angle φ between the applied field and the hexagonal axis is of the form

$$F=F_0+K' \sin^2 \varphi + K'' \sin^4 \varphi. \tag{51}$$

With our model, the constant K' results primarily from dipole-dipole interaction, which, owing to the loss of cubic symmetry, no longer vanishes in the first approximation. Instead, in exactly the same way that (38) was obtained, it is found on using (36), (19), (20), (14), (17) and the hexagonal symmetry that

$$F=F_0+\Omega_6 B_1{}^2 \sin^2 \varphi, \tag{52}$$

where

$$\Omega_6=-\tfrac{1}{2}N\Sigma_{j>i}[A_{ij}{}^{ZZ}-\tfrac{1}{2}(A_{ij}{}^{XX}+A_{ij}{}^{YY})], \tag{53}$$

with Z directed along the hexagonal axis. Since B_1 is the same as SI/I_0 the variation of $B_1{}^2$ with temperature can be found simply by squaring the values of I/I_0 given in Table I for $S=\frac{1}{2}$ or Table II for $S=1$. The theoretical variation with T is thus somewhat less rapid than in the case of fourth order or cubic anisotropy. (In Table II, the anisotropy was more nearly proportional to I^3). Experimentally the dependence on temperature is again greater than given by theory if Ω_6 is regarded as a constant. In fact in cobalt $K'+K''$ is even found to change sign at 550°K. The discrepancy must once more be attributed to the fact that Ω_6 is a function of temperature. As regards orders of magnitude one might at first thought expect Ω_6/N to be comparable with the constant C in (8). For instance, if the only important coupling is to six neighbors in the same equatorial plane as the given atom, (53) becomes $\Omega_6=-9NC/2$. In section 6 we estimated C to be of the order $A^2/h\nu \sim 10$ cm^{-1}. Then K' would be about 10^9 ergs/cm^3, whereas the experimental values are only of the order 10^7. As suggested

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[34] It is clearly to be understood that in using the formula $I/I_0=B_1$, the value (33) should be employed for H, as then this formula gives about the same $I-T$ curves as (49) with the field (48). The field (48) is still to be used in (46). The difference between the arguments (33) and (48), rather than the difference between the functional forms of (42) and (46), accounts for most of the divergence between the two sets of values of $K_1/N\gamma$ in Table III. The first line of Table III gives the field (33) instead of (48).

by Bloch and Gentile,[21] the explanation is probably that the arrangement of atoms in the hexagonal gratings does not deviate too greatly from cubic form. With strict cubic symmetry, the expression (53) would vanish, and with hexagonal the various members of (53) may nearly cancel, so that Ω_6 is considerably smaller than NC in magnitude. There is no corresponding cancellation in the fourth-order coefficient, which one should thus expect to be of about the same order 10^6 ergs/cm^3 as the cubic anisotropy coefficient K_2 in (1). This is indeed what is found experimentally in cobalt,[35] as at room temperatures K'' is 2.2×10^6 ergs/cm^3, or about one-half as large as $K'=5.1\times10^6$. The two terms of (51) are thus comparable even though they involve the spin-orbit parameter A to different powers (*viz.* the second and fourth).

It must be mentioned that the "one-atom model" of Bloch and Gentile described in Section 7 may have some significance for hexagonal crystals, since with only axial symmetry the crystalline field can lift the degeneracy if $S>\frac{1}{2}$. In fact the effective magneton number and g-factor can be different in different directions. Conceivably this fact has some connection with the anomalous behavior of pyrrhotite, which is ferromagnetic along certain axes but only paramagnetic along others.

The writer wishes to express his thanks to Dr. R. M. Bozorth and Professor F. Bitter for helpful comments.

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[35] These values of K', K'' are calculated in unpublished work of Bozorth, from the data of Honda and Masamuto, Sci. Rep. Tohoku Univ. **20**, 323 (1931). Gans obtained $K'=1.1\times10^6$, $K''=4.4\times10^6$ from previous work by Kaya, Sci. Rep. Tohoku Univ. **17**, 1157 (1928). Dr. Bozorth asks me to record the following errata in the discussion of cobalt in his recent paper (J. App. Phys. **8**, 575 (1937)). The statement on p. 585 that the higher power term K_2 in his formula $E=K_0+K_1S_1^2+K_2S_1^4$ is negligible is incorrect, as vanishing K_2 is not required by the absence of anisotropy in the plane perpendicular to the hexagonal axis. The ordinate of Fig. 18 is K_1+K_2 rather than K_1. Bozorth's K_0, K_1, K_2 for cobalt are the same as our $F_0+K'+K''$, $-K'-2K''$, and K'' respectively since his S_1^2 is $1-\sin^2\varphi$.

DECEMBER 1, 1937 PHYSICAL REVIEW VOLUME 52

On the Nature of Cosmic-Ray Particles

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(Received August 28, 1937)

VARIOUS authors[1] have taken the view that cosmic-ray particles consist of two or more kinds of corpuscles. According to Compton and Bethe, and Auger,[1] the soft component near sea level is thus composed of electrons and the penetrating one of protons. Assuming the theory of showers by Bhabha and Heitler[2] and by Oppenheimer and Carlson[3] to be correct, we ought to be able to distinguish cosmic-ray electrons from protons, if they exist at all, by observing whether or not the particles suffer a large loss of energy and often produce showers on colliding with a lead plate of a suitable thickness.

We carried out such experiments with a lead bar 1.5 cm thick mounted in the middle of a Wilson chamber 40 cm in diameter, which is placed in a magnetic field of about 17,000 oersteds. The operation of the chamber is actuated by the coincidence of two Geiger-Müller tube counters mounted above the chamber, the distance between the counters being about 50 cm. The results showed that at sea level near Tokyo (geomag. lat. 25.4°N) about 10 to 20 percent of cosmic-ray particles of energies, high enough to produce coincidence in the strong magnetic field and pass through the Wilson chamber, consist of electrons and positrons, the rest being heavy particles, since they do not produce showers nor suffer much loss of energy in passing through the lead bar. Among the latter, however, we were

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[1] A. H. Compton and H. A. Bethe, Nature **134**, 734 (1934); P. Auger, J. de phys. **6**, 226 (1935); C. D. Anderson and S. H. Neddermeyer, Int. Conf. on Physics, London **1**, 182 (1934); Phys. Rev. **50**, 268 (1936); J. Clay, Physica **3**, 338 (1936); L. Leprince-Ringuet, J. de phys. **7**, 70 (1936); J. Crussard and L. Leprince-Ringuet, Comptes rendus **204**, 240 (1937).

[2] H. J. Bhabha and W. Heitler, Proc. Roy. Soc. **A159**, 432 (1937).

[3] J. F. Carlson and J. R. Oppenheimer, Phys. Rev. **51**, 220 (1937).