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► **To cite this version:**

J.H. van Vleck. Some recent progress in the theory of magnetism for non-migratory models. *Journal de Physique et le Radium*, 1959, 20 (2-3), pp.124-135. 10.1051/jphysrad:01959002002-3012400 . jpa-00236001

HAL Id: jpa-00236001

<https://hal.science/jpa-00236001>

Submitted on 4 Feb 2008

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SOME RECENT PROGRESS IN THE THEORY OF MAGNETISM FOR NON-MIGRATORY MODELS

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Résumé. — Dans le présent article il n'est question uniquement que de modèles où les électrons magnétiques n'émigrent pas d'un atome à un autre. La première partie passe en revue les progrès accomplis depuis 1950 par les différents chercheurs qui ont calculé le « point de Curie » avec le modèle d'Heisenberg, et ont déterminé le comportement de la susceptibilité au-dessus de ce point. Au cours de ces dernières années, les calculs ont été grandement améliorés en ajoutant des termes supplémentaires aux développements limités dans le cas de la méthode de développement en série, et en étendant cette méthode et celle de « Bethe-Peierls-Weiss » à de plus grandes valeurs de spin. De plus, la théorie de « B-P-W » a été appliquée au ferrimagnétisme et spécialement à l'antiferromagnétisme où elle donne à la fois le point de Néel et la valeur maximum correspondante de la susceptibilité. La dite approximation à couplage constant de Kasteleijn et Van Kranendonk est une méthode relativement simple ; appliquée aux réseaux à trois dimensions elle donne des résultats remarquablement satisfaisants. La deuxième partie passe en revue de récents développements des calculs entrepris en vue de déterminer l'aimantation à très basse température par la méthode des ondes de spin. La troisième partie intéresse l'anisotropie ferromagnétique. Ici il est nécessaire de généraliser le modèle d'Heisenberg aux interactions spin-orbite, car autrement il n'en résulterait aucune anisotropie. Une démonstration générale est donnée du fait qu'avec le couplage quadripolaire, la constante K_1 d'anisotropie cubique doit varier comme la dixième puissance de l'aimantation aux basses températures. Un modèle monoatomique d'anisotropie peut être utilisé pour les ferrites, mais dans le cas de substances ferromagnétiques dont les spins de chaque atome ont pour valeur $3/2$ ou moins, il est nécessaire d'inclure le couplage entre atomes pour obtenir une anisotropie appréciable. La variation thermique de l'anisotropie magnétique du nickel reste un mystère. Par contre, la théorie du champ cristallin permet d'expliquer l'anisotropie particulièrement grande des ferrites à faible teneur de cobalt.

Abstract. — The present paper is concerned entirely with models in which the magnetic electrons do not migrate from atom to atom. Part I reviews the progress made since 1950 by various workers in calculating the Curie point for the Heisenberg model and the behavior of the susceptibility above it. The calculations have been greatly improved in recent years by including more terms in the series method, and in extending both this method and that of Bethe-Peierls-Weiss to higher values of the spins. Furthermore, the B-P-W theory has been applied to ferrimagnetism, and especially to antiferromagnetism where it gives both the Néel point and the corresponding maximum value of the susceptibility. The so-called constant coupling approximation of Kasteleijn and Van Kranendonk is a relatively simple method which gives surprisingly good results for three-dimensional lattices. Part II reviews recent developments in the calculation of the magnetization at very low temperatures by the method of spin waves. Part III is concerned with ferromagnetic anisotropy. Here it is necessary to generalize the Heisenberg model by including spin-orbit interaction, since otherwise no anisotropy results. A general proof is given that with quadrupole type coupling, the cubic anisotropy constant K_1 should vary as the tenth power of the magnetization at low temperatures. In ferrites a "one-atom" model of the anisotropy can be used, but in ferromagnetic materials where the spins of the individual atoms are $3/2$ or less it, is necessary to include coupling between atoms to obtain appreciable anisotropy. The temperature variation of the magnetic anisotropy of nickel is still a mystery. On the other hand, crystalline field theory furnishes an explanation of the unusually large anisotropy of dilute cobalt ferrites.

The present report does not pretend to be a comprehensive survey of the theory of magnetism. In the first place, it only is concerned with new developments since the conference on magnetism held in Grenoble in 1950. Secondly, it will be confined to theories or calculations based on models in which the electrons are non-migratory. In a broad sense all such models are of the Heitler-London or Heisenberg type, but in many cases include complications caused by directional valence and spin-orbit interaction not included in the conventional Heisenberg theory.

We will assume that the reader is familiar with the main models of this type as of 1950, the original calculation of Heisenberg, the Bethe-Peierls-Weiss method of calculation in the vicinity of the Curie point, the Bloch spin wave theory at low temperatures, anisotropic exchange as a cause of anisotropy, and of course Néel's pioneer work on antiferromagnetism and ferrimagnetism.

It is desirable to confine our attention to non-migratory models for several reasons. With this restriction, there is less danger of the report being too diffuse and general, and we escape, in parti-

cular, discussing the role, if any, of the 4s electrons as middlemen, or entering into the perennial controversy as to whether the non-migratory or whether the band model with itinerant electrons is the better. It seems to be consensus of opinion today that the Heisenberg model is a good approximation for many conducting ferromagnetics. The last decade, moreover, has witnessed a tremendous growth in the importance attached to ferrites and to antiferromagnetics, and these are usually materials which are non-conducting, and for which it is a good approximation to regard the electrons responsible for magnetism as bound each to particular atoms.

The topics which we will discuss are (I) calculations at relatively high temperatures, near or above the Curie point ; (II) spin wave theory and particulary ; (III) models of ferro- or ferrimagnetic anisotropy.

I. Calculations in the vicinity of the Curie point.

— SERIES DEVELOPMENT FOR FERROMAGNETICS. — The susceptibility above the Curie point may be developed in a series

$$\chi = \frac{Ng^2 \beta^2 S(S + 1)}{3kT} \sum_{n=0}^{\infty} \frac{a_n}{t^n}, \quad (1)$$

where $t = kT/J$, with J the exchange integral. In 1950, only the coefficients through a_4 had been calculated, even for the simple lattices (simple, f-c, b-c cubic, hexagonal and quadratic layer lattices) and these only for spins of $1/2$. The extension to arbitrary spin was made in 1955 by Brown and Luttinger [1]. The values of a_5 were computed by Brown [1] in 1956 for body-centered and simple cubic lattices, and also for the quadratic layer lattice. The calculations of Brown and Luttinger, and of Brown, are closely paralleled by those of Rushbrook and Wood [2], made independently and practically simultaneously. The agreement between the two computations is gratifying.

Rushbrook and Wood, however, report a " very small " error in Brown's value of a_5 for $S > 1/2$. The value of a_6 for $S = 1/2$ has been recently calculated by Domb and Sykes [2].

From the series (1), the Curie temperature may be determined in either one of two ways. One, the customary procedure, is find T_c from the value of t which makes $(1/\chi_n) = 0$, where χ_n denotes the n th approximation in (1). This is the procedure used in connection with table I. Another criterion is to determine the Curie temperature from the value of t for which the series (1) converge, i.e., $a_n t/a_{n-1} = 1$. Brown and also Rushbrook and Wood show that for space gratings it makes very little difference which criterion is used. For the surfaces gratings, however, the spread between the results which the two criteria is quite appreciable.

BETHE-PEIRLS-WEISS METHOD. — The so-called B-P-W method, wherein interactions within a cluster are included rigorously, and those with other atoms by a molecular field determined by a consistency condition, has been extended to spins greater than $1/2$, by Brown and Luttinger in their important paper already mentioned [1]. The equations become quite complicated, and the aid of modern computing machines has to be invoked to effect the calculations.

The improvements that have taken place since 1950 in the series and B-P-W methods are not to be regarded as simply minor extensions in numerical accuracy. They have clarified a major question of principle. For awhile it looked like the convergence of the series method was chaotic. The situation was improved in 1950 when Zehler detected some numerical errors in the early calculations of Opechowski. It has now become clear that the convergence of the series method is quite satisfactory, and agrees rather gratifyingly with the results of the B-P-W method, as shown in table I.

TABLE I
CALCULATED VALUES OF kT_c/J

LATTICE	SPIN	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	B.-P.-W.	CONSTANT COUP. APPROX.
—	—	—	—	—	—	—	—	—
s. c.	$\frac{1}{2}$	3.0	(abs.)	2.00	1.93	1.83	1.85	1.82
	$\frac{5}{2}$	35.0	26.7	27.8	25.8	26.6	28	27.9
b. c. c.	$\frac{1}{2}$	4.0	2.0	2.95	2.39	2.79	2.91	2.88
	$\frac{5}{2}$	46.7	39.1	39.8	37.1	37.8	40	39.8
f. c. c.	$\frac{1}{2}$	6.0	4.74	4.26	4.24	4.26	?	4.93
	$\frac{5}{2}$	70.0	63.0	60.2	58.7	?	?	?

For brevity, we give only results for $S = 1/2$ and $S = 5/2$; for other values of S , the original papers should be consulted. The value of n in each case is that at which the series (1) is terminated. The insertion of a question mark as an entry means that the calculation for this particular case has not yet been properly made. We can safely say that the Curie point for the three-dimensional Heisenberg model can now be predicted with reasonable precision for arbitrary values of S . The uncertainty is minor compared to the various deviations from the idealized models caused by the actual physical situation (spin-orbit perturbations, allotropic modifications, electron migration, etc.). We should, however, note that for surface gratings the series and B-P-W methods do not agree, as the former predicts that the quadratic and hexagonal layer gratings should have a Curie point and hence be ferromagnetic, while the latter agrees with the spin wave theory in predicting that these gratings should be incapable of ferromagnetism. Fortunately, the three rather than two dimensional cases are those of actual physical interest.

We may remark, incidentally, that the new calculations have brought to light a numerical error in the original computations of Weiss for the particular case of the body centered lattice with $S = 1$. The writer has always been suspicious of Weiss' result in this particular instance, as the Curie point which Weiss found (viz., $T_c/J = 6.66$) was not intermediate between the values (viz., 10.7 and 8.3) furnished respectively by the first and second (gaussian) approximations $n = 1, 2$ of the series method. In general, one expects the correct value to be bounded by these two limits, inasmuch as the fluctuations in energy for states of given total crystalline spin which tend to suppress ferromagnetic alignment are respectively neglected and grossly overestimated in these two approximations. With the new value 8.7 obtained by Brown and Luttinger, this difficulty disappears.

THE CONSTANT COUPLING APPROXIMATION. — Most of our preceding discussion has centered around the work of Brown and Luttinger or Rushbrook and Wood which involved more refined and hence more laborious computation than previously. In the opposite direction, a simpler method of determining Curie points with fairly good precision for spatial lattices has been recently developed by Kasteleijn and Van Kranendonk [3] and in somewhat different form independently by Oguchi [4]. Their idea is essentially to treat a system of only two atoms, rather than a larger cluster as in B-P-W. The two atoms are joined by an exchange potential $-2JS_1 \cdot S_2$, and they call their model the „constant coupling approximation” because the coefficient of $S_1 \cdot S_2$ is not a variational parameter. Coupling with other atoms is replaced by a mole-

cular field. The partition function with this model is readily written down. There are two parameters to be determined, viz., the constant of proportionality in the molecular field and the magnetization M of the crystal. These two parameters are determined by a consistency requirement, that the mean magnetization of the pair differ from that of the whole crystal of N atoms by factor $2/N$, and by the fact that $M/g\beta$ is the value of the magnetic quantum number M_z of the whole crystal which maximizes the free energy F . It is well known that in large ensembles the partition function has a large maximum, so that instead of summing over all values of M_z it suffices to use the single value of M_z determined by the condition $\partial F/\partial M_z = 0$. The number of complexions, or statistical weight is very sensitive to M_z , and so affects the entropy term in the free energy $U-TS$. The analytical difficulties are appreciably less with the constant coupling than with the B-P-W method while the numerical values of the Curie point are almost as good as with the latter, as reference to the last column of Table I shows. We should, however, stress that though the constant coupling approximation gives good results for the simple and body-centered cubic lattices, it does not represent a really refined model, since the results depend only on the number of nearest neighbors. It hence does not take account of the cyclic groupings which make different gratings with the same number of neighbors behave differently. Thus the constant coupling approximation predicts ferromagnetic properties for the hexagonal surface grating, though spin wave and B-P-W calculations make it pretty clear that this should not be the case. The failings of the constant coupling approximation are apt to be particularly pronounced when nearest neighbors of a given atom are also neighbors of each other, for then there are short-range cyclic coordinations which are not taken into account. This fact presumably explains why the constant coupling model gives poorer results for the face-centered than for the simple or body-centered cubic gratings (cf. Table I).

ANTIFERROMAGNETISM. — The series method apparently cannot feasibly be used to determine the Néel point in antiferromagnetic materials, This question has been examined in some detail by Brown and Luttinger [1]. The Néel point is characterized by a maximum rather an infinity in the susceptibility, and so is harder to locate. Furthermore since the series alternate in sign, there is no simple way of determining when they do not converge.

It is, however, possible to compute the Néel point with the B-P-W method. The first paper applying this method to antiferromagnetic media was one by Li [5], in 1951. He treated only spins of $1/2$,

and the extension to spins ≤ 3 was made by Brown and Luttinger. In a forthcoming paper J. S. Smart calculates the susceptibility at the Néel point, and finds good agreement with experiment. The constant coupling approximation can also be applied to antiferromagnetism, as has been done by Kasteleijn and Van Kranendonk in their second paper [6].

Before leaving the discussion of antiferromagnetics we may mention an interesting paper by Miss O'Brien [7] on this subject at very low temperatures, — namely chrome methyl alum which has a Néel point around .02 °K. She shows that the usual credos that dipolar coupling cannot produce a transition temperature in a cubic compound, and that the Ising model does not correspond to a physically real situation, are not true in this material. The dipolar terms do not average out because of a peculiar staggering of crystalline field axis, and the Ising model is applicable because the crystalline field suppresses two components of the atoms magnetic moment, so that the latter is essentially a scalar rather than vector quantity. The Néel point computed on the basis of pure dipolar, and not exchange coupling agrees with experiment practically within the rather large experimental error (25 % or so).

FERRIMAGNETISM. — In 1956 the B-P-W method was extended to ferrimagnetic media by J. S. Smart [8], though only for somewhat special cases. He assumed, to simplify the analysis, that each lattice has a spin $1/2$, that each spin in lattice A is coupled only to n_b nearest-neighbors of atoms B , and each spins of B to n_a of A . The Curie or Néel temperatures which he computes are materially lower than those calculated by Néel with the conventional molecular field method. Such differences are not surprising, for the latter method has an accuracy comparable with only the first approximation $n = 1$ of the series method. The B-P-W and molecular field methods do not always agree as to whether ferrimagnetism should even occur. For the cases that he investigated, Smart concludes that ferrimagnetism can occur only if $n_a \cdot n_b > 5(n_a + n_b)/2$, whereas there is no condition of this character in the molecular field method. As a check on the accuracy of Smart's work, it may be noted that, according to the sign of J , his formulas reduce to those of Weiss or Li in the special case $n_a = n_b$.

Smart deduces curves for $1/\chi$ vs. T above the Néel temperature which are pronouncedly different than those furnished by the molecular field theory. More complete comparison with experiment is highly desirable, although the restriction to $S = 1/2$ makes the theory perhaps too special to make this possible.

In concluding this section, we may remark that

the theory for non-conducting ferromagnetic, anti-ferromagnetic, and possibly ferrimagnetic materials has now reached a sufficient degree of refinement that theory and experiment should be compared more carefully than has previously been done anent the curves $1/\chi$ vs. T above the Curie point. Some theoretical insight should thereby be obtained regarding the causes of the observed deviations from linearity, and the distinction between the ferromagnetic and paramagnetic Curie points.

II. Spin waves. — Numerous articles have appeared in the past few years on the bearing of spin wave theory on line width and relaxation phenomena in ferromagnetic resonance, interaction with conduction electrons, etc. Also, Herring and Kittel have made important contributions in showing that the applicability of spin wave theory is considerably more general than that of the Heisenberg model. These questions, however, we consider beyond the scope of the present report, and confine our attention to spin wave theory insofar as it affects the calculation of specific heat and susceptibility for the Heisenberg model. So we will discuss the developments in spin wave theory only in rather cursory fashion.

The advances in spin wave theory insofar as we are concerned fall mainly into two categories — refinements in the theory for the ordinary ferromagnetic case, and generalization or extension to include antiferromagnetism and ferrimagnetism.

HIGHER APPROXIMATIONS IN THE FERROMAGNETIC CASE. — It is well known that the conventional spin wave theory is not rigorous because only the problem of one reversed spin is solved exactly, and it is assumed that the eigenvalues for n reversed spins can be compounded additively from those associated with single reversals. Numerous attempts have been made to correct for this oversimplification.

The latest and presumably most reliable is that of Dyson [9]. He finds that when the corrections for the interaction between two reversed spins are included, the development of the expression for the saturation magnetization in the vicinity of $T = 0$ takes the form

$$M = M_0[1 - aT^{3/2} - bT^{5/2} + \dots] \quad (2)$$

instead of the conventional

$$M = M_0[1 - a'T^{3/2}] \quad (3)$$

Dyson's result is in disagreement with the earlier results of other workers, who did not agree among themselves, as Néel pointed out in 1954 [10]. It had previously been claimed [11] that the leading correction term to (3) was proportional to T^2 or $T^{7/4}$. It is fortunate that Dyson finds instead

there is a small term in $T^{5/2}$. For practical purposes, the effect of the correction is negligible, as Dyson shows that inclusion of the b term affects the value of $M - M_0$ by less than 5 percent even at half the Curie temperature.

THEORY FOR ANTIFERRO- AND FERRIMAGNETIC MEDIA. — A considerable number of papers have been published by Kaplan, Anderson, Kubo and others [12] since 1950 extending spin wave theory to antiferromagnetic and ferrimagnetic materials. Most of these articles have been concerned primarily with magnetic resonance. We will confine our attention to some recent work of Kouvel and Brooks [13] in which the behavior of the magnetic moment and specific heat at low temperatures is investigated, both theoretically and experimentally.

We will here quote the rather expressive formulas which Kouvel and Brooks derive for the saturation magnetization and specific heat of a ferrimagnetic material at low temperatures :

$$M = M_0 \left[1 - \frac{0.117}{|S_1 - S_2|} \left\{ \frac{kT|S_1 - S_2|}{4|J|S_1 S_2} \right\}^{3/2} \right] \quad (4)$$

$$C_v = 0.113 Nk \left\{ \frac{|S_1 - S_2|}{4|J|S_1 S_2} \right\}^{3/2} (kT)^{3/2}. \quad (5)$$

Here J is the exchange integral assumed to be negative, and S_1, S_2 are the spins of the two sublattices. We have assumed that the magnetic atoms form a simple cubic lattice (NaCl type) ; the numerical factors for other cubic lattices have different values than 0.117 and 0.113.

The antiferromagnetic case requires special treatment, as the expression (5) vanishes. Kouvel and Brooks show that for a simple cubic antiferromagnetic lattice, the formula for the specific heat becomes

$$C_v = 13.7 Nk(kT/12|J|S)^3. \quad (6)$$

The specific heats for antiferromagnetics and ferrimagnetics are thus markedly different, being proportional to T^3 and $T^{3/2}$ respectively. A true antiferromagnetic has no saturation moment, so it is meaningless to talk about how (4) is modified in the antiferromagnetic case. However, for a material having $S_1 = S_2$ but $g_1 \neq g_2$, ferri- as regards magnetic moment, but antiferro as regards angular momentum, it can be shown that the saturation magnetization should behave in the fashion

$$M = M_0(1 - aT^3 + \dots). \quad (7)$$

It would be interesting if behavior of this type could be found experimentally.

The proportionality of the specific heat to $T^{3/2}$ for ordinary ferrimagnetics is verified in the measurements of Kouvel [14] on the specific heat of magnetite. This is a striking confirmation of spin wave theory except that the computed and obser-

ved proportionality factors multiplying $T^{3/2}$ do not agree. Kouvel notes that in antiferromagnetics, the magnetic T^3 term in C_v may be considerably larger than the ordinary Debye vibrational term of this type and so may be detectable.

III. Ferro- and ferrimagnetic anisotropy. — We will discuss the subject of anisotropy in some detail, as it plays a central role theoretically in the understanding of spin-orbit perturbations of crystalline energy levels and it is a matter of great importance in connection with technological applications, notably in the ferrites. We will confine our attention to cubic crystals, as this is the commonest case, and perhaps the most interesting.

OCTOPOLAR POTENTIALS. — The logical starting point for the discussion of cubic anisotropy in a material whose magnetism arises primarily from spin is an effective potential or spin Hamiltonian of the type

$$V = a \{ S_x^4 + S_y^4 + S_z^4 \} + C, \quad (8)$$

where a is a constant and

$$C = -\frac{3}{5} a \left[S^2(S+1)^2 - \frac{1}{3} S(S+1) \right]. \quad (9)$$

The constant C is included to make V average to zero when all Zeeman components are weighted equally. Although the C term has no bearing on the amount of anisotropy, its inclusion somewhat facilitates the discussion, as then the matrix elements of (8) have the structure of those of a spherical harmonic of cubic symmetry and degree $n = 4$. So we may term (8) an octopolar potential. It is the potential of lowest degree that gives any deviations of cubic from central symmetry, i.e., from complete isotropy.

Suppose now that the material is magnetized along a direction specified by direction cosines $\alpha_1, \alpha_2, \alpha_3$ relative to the principal cubic axes. The effect of the exchange forces producing the ferromagnetism we may represent, semi-theoretically, semi-empirically, by introducing a very powerful molecular field which space quantizes S along the direction $\alpha_1, \alpha_2, \alpha_3$, which we can take as the z' axis. Then the eigenvalues of S_z are $M_s = -S, \dots, +S$. We therefore transform (8) from x, y, z to the x', y', z' system. Since (8) is small compared to the exchange potential responsible for the molecular field, we may safely drop all terms non-diagonal in M_s , i.e., retain only the part of the transformed potential which is symmetric about the z' axis. (There must be complete symmetry about this axis since it is the only direction of outstanding polarization in the unperturbed system.) The expectation value of this part of (8) is readily shown to have the form

$$\langle V \rangle = K_1(\alpha_1^2 \alpha_2^2 + \alpha_3^2 \alpha_1^2 + \alpha_2^2 \alpha_3^2) + \langle V_0 \rangle \quad (10)$$

where $\langle V_0 \rangle$ is independent of the direction cosines, and K_1 , the anisotropy coefficient, is

$$K_1 = -2a \left\langle \frac{35}{8} M_s^4 - \frac{15}{4} M_s^2 (S^2 + S - \frac{5}{6}) + \frac{3}{8} S(S-1)(S+1)(S+2) \right\rangle. \quad (11)$$

The idea of using an octopolar potential (8) to explain ferromagnetic anisotropy was first due to Bloch and Gentile [15]. However, the model strikes something of a snag when one tries to apply it to ferromagnetic metals. Namely there is no splitting, and hence no anisotropy from an octopolar potential unless $S \geq 2$. One can demonstrate this result abstractly by group theory, or more elementarily, simply by noting that the expression (11) vanishes for any possible choice of M_s , $S \leq 3/2$. Actually the common ferromagnetic metals have a mean value of S per atom considerably less than two. So, unless one assumes some sort of fluctuation effect in the spins per atom, the one-atom octopolar model is incapable of explaining ferromagnetic anisotropy in such cases.

QUADRUPOLE-QUADRUPOLE COUPLING. — To escape this difficulty, the writer in 1937 developed a quantum-mechanical treatment [16] of quadrupole-quadrupole coupling between atoms, — a model which has already been considered classically in one phenomenological form or another by various authors, notably Akulov [17]. In the quadrupole-quadrupole model, the anisotropy is considered to arise from the coupling between atoms rather than from the anisotropy in the crystalline field acting on a single atom. The simplest potential of the quadrupole-quadrupole type is

$$V_{qq} = A(\mathbf{S}_i \cdot \mathbf{r}_{ij})^2 (\mathbf{S}_j \cdot \mathbf{r}_{ij})^2, \quad (12)$$

where r_{ij} is the radius vector connecting atoms i and j . A coupling of the type (12) arises from the interaction of spin-orbit coupling and exchange energy, when the perturbation development is pushed far enough to include terms of the fourth order in the spin-orbit coupling, and the exchange energy between the two atoms is included in the unperturbed energy and is dependent on how the orbital angular momentum in excited states is aligned relative to the line joining the two atoms. Coupling of this type is one form of what is called "anisotropic exchange", although the term is most commonly used for the particular case of a lower order effect of pseudodipolar structure which we will discuss later. Even the effect of the octopolar splitting is called anisotropic exchange by the Japanese writers; the usage is a purely semantic question. The octopolar member makes the energy in the molecular field, which is essentially exchange energy, a function of direction. Practically every model of anisotropy is caused by

anisotropic exchange in the general sense of the word. The spin-orbit coupling makes the exchange energy anisotropic because it makes the spin conscious of the dependence of inter-atomic energy (including that portrayed by molecular fields) on how the orbital wave functions are oriented. An elaborate attempt to trace the origin of anisotropy in interatomic forces has been made by Carr [18]; even crystalline potentials ultimately are of inter-atomic origin.

At first sight the octopolar and quadrupolar mechanisms seem quite different, but actually this is not the case. The quadrupole-quadrupole interaction can be regarded, as far as anisotropy is concerned, as simply octopolar coupling in which the unit of structure whose spin is involved in (8) is a "molecule" of two atoms (i.e., any pair of two nearest-neighbors rather than a single atom). One sees immediately why there can be cubic anisotropy from q - q coupling between atoms of spin unity of greater, since then the resultant spin can be two and so give splitting in the octopolar effect (8). If the spins are only $1/2$, however, the q - q mechanism is inoperative for anisotropy, as the collective spin of the pair cannot exceed unity. It seems fairly evident that if

$$\mathbf{S}_j = \mathbf{S}_i = \frac{1}{2} \mathbf{S},$$

the expression (12) becomes a biquadratic form in the components of \mathbf{S} which will be similar to (8) after averaging over all pairs if the vectors r_{ij} are distributed equally in certain preferred directions differing from each other only by a cubic "covering" operation.

The argument can be described more exactly as follows. Any wave function for a pair of atoms can be expressed in the form

$$\Psi = \sum_{S, M_s} C_{SM_s} \Psi_{SM_s}, \quad (13)$$

where S and M_s denote eigenstates of the pair's collective spin S and its component in the direction of the molecular field. The expectation value of the q - q coupling (12) then acquires the form

$$\langle V_{qq} \rangle = \sum_{S, S', M_s} \langle SM_s | V_{qq} | S' M_s \rangle \langle SM_s | \rho | S' M_s \rangle, \quad (14)$$

where

$$\langle SM_s | \rho | S' M_s \rangle = C_{SM_s} C_{S' M_s}'.$$

The elements of (14) non-diagonal in M_s have been dropped, as can safely be done for the same reasons of symmetry as explained in connection with the passage from Eq. (8) to (10). The state of the system need not necessarily be capable of description by a wave function, i.e., can be a "mixture" in the von Neumann sense, in which case ρ is to be interpreted as a density matrix. (The real reason for our ability to neglect the elements of V_{qq} non-diagonal in M_s is that the corresponding off-diagonal elements of ρ vanish because there is no statistical correlation between different values of M_s if the direction of outstanding magnetization is the same as the direction of quantization). The elements $\langle SM_s | V_{qq} | SM_s \rangle$ in (14) are of precisely the same structure as those averaged in (11), except for a proportionality factor dependent on S . This

fact can be demonstrated by group theory, or otherwise. The non-diagonal elements in S are of subordinate importance, and are absent entirely if the two constituent atoms have spins of 1, as then only the maximum value of S viz., $S = 2$, can contribute to the anisotropy. Since the distribution among the various values of S is a function of temperature, the variation of susceptibility with temperature can be different for the q - q model than for the pure octopole potential which involves only one S .

TEMPERATURE DEPENDENCE OF ANISOTROPY RESULTING FROM AN OCTOPOLAR POTENTIAL. THE TENTH POWER LAW. — One of the greatest successes of theory is that one can show that an octopolar potential (8) leads to a relation between the anisotropy constant K_1 and the saturation intensity of magnetization M of the form

$$K_1/K_{10} = (M/M_0)^{10} \quad (15)$$

where the zero subscript denotes values at $T = 0$. The result (15) is, of course, really a connection between K_1 and M , but we discuss (15) under the heading of temperature dependence because it enables one to compute the variation of K , with T if that of M is known, either experimentally or theoretically.

The relation (15) can be derived very generally. Existing proofs [19, 20] give rather too much the impression that they hinge on somewhat special assumptions, e.g., classical limits, spin wave models, etc., depending on the kind of analysis. It therefore seems worth while to give here a proof which is general and simple. At $T = 0$ the only inhabited state is, of course, that of maximum spin in the direction of magnetization i.e., $M_s = S$. If the temperature is raised somewhat, the state $M_s = S - 1$ will also begin to be populated. Let us denote by $1 - y$ and y the fractional populations of the states $M_s = S$ and $M_s = S - 1$ in (11). If $f(M_s)$ denote the expression (11) regarded as a function of M_s , the anisotropy constant at low temperature should be given by

$$\frac{K_1}{K_{10}} = \frac{(1 - y)f(S) + yf(S - 1)}{f(S)}. \quad (16)$$

where K_{10} is the value of K_1 at $T = 0$.

Using the formula (11) to evaluate f , one finds immediately $f(S - 1) = (1 - 10/S)f(S)$ and so

$$\frac{K_1}{K_{10}} = 1 - \frac{10}{S}y. \quad (17)$$

The saturation intensity of magnetization is proportional to M_s , and hence

$$M = M_0 \left\{ (1 - y) + \frac{(S - 1)}{S}y \right\} = M_0 \left\{ 1 - \frac{y}{S} \right\}. \quad (18)$$

Comparison of (17) and (18) suggests at first sight a linear relation

$$\frac{K_{10} - K_1}{K_{10}} = \frac{10(M_0 - M)}{M_0}. \quad (19)$$

However, we must remember that the anisotropy vanishes at the Curie point. An extrapolative formula which meets this condition and which agrees with (19) in the low temperature domain, where the anisotropy is appreciable is clearly the relation (15).

So far we have used quantum mechanics. In classical theory treated by Zener [19] the anisotropy coefficient K_1 is proportional to the zonal harmonic

$$P_4(\cos \theta) = \left\{ \frac{35}{8} \cos^4 \theta - \frac{15}{4} \cos^2 \theta + \frac{3}{8} \right\} \quad (20)$$

where θ is the angle between the spin vector S and the direction of magnetization (cf., Eq. (11)), where in the classical limit $M_s/S \sim \cos \theta$ and only the terms of highest degree in M_s , S need be retained). The anisotropy is proportional to the average of (20). At low temperatures, the deviations of $\cos \theta$ from unity are small, and so

$$P_4(\cos \theta) \sim (1 - 5\theta^2) \quad (21)$$

and

$$K_1 = K_{10} [1 - 5 \langle \theta^2 \rangle_{AV}]$$

since $\cos \theta = 1$ at $T = 0$. The magnetization is proportional to $\cos \theta$ and so at low temperatures

$$M = M_0 \left(1 - \frac{1}{2} \langle \theta^2 \rangle \right). \quad (22)$$

Hence we are again led to a relation of the form (19) which extrapolates to (15) when the proper behavior at the Curie temperature is included. Zener is able to derive (15) exactly rather than by extrapolation, but the classical diffusion model which he uses is physically admissible only at low temperatures, where (19) is valid.

TEMPERATURE VARIATION FOR QUADRUPOLE-QUADRUPOLE COUPLING. — If the spins of the two adjacent atoms are parallel, then only the state of maximum collective spin for the two atoms contributes to the density matrix, and the temperature variation of the anisotropy will be precisely the same as with the octopole potential. In the spin wave picture, at low temperatures two adjacent elementary magnets are practically parallel, so that this assumption is warranted, and the tenth power law is valid. Originally the writer [16] obtained a sixth power law, as he assumed that the averages for adjacent atoms could be computed independently. Then the anisotropy coming from (12) is proportional to

$$\begin{aligned} \langle [P_2(\cos \theta)]^2 \rangle &\sim \langle 3M_{s_i}^2 - S_i(S_i + 1) \rangle^2 \\ &\sim C(1 - 6yS_i^{-1} + \dots) \end{aligned}$$

instead of $C(1 - 10S_i^{-1}y)$ if the populations of $M_s = S_i - 1$, S_i are y , $1 - y$. Keffer [20] first pointed out clearly the cause for this difference. Actually, from the spin wave model, or otherwise, we know that there is a high degree of correlation

between neighboring spins in the region where anisotropy is important. Until recently, it was generally believed that the tenth power law was strikingly confirmed experimentally in iron, but new or revised experimental data seem to indicate that at low temperatures a lower power, perhaps 5 is required. Carr suggests that the discrepancy may be caused by thermal expansion, neglected in the usual theory.

We can trace the difference between the correlated and uncorrelated models a little further. The uncorrelated model is equivalent to using Wigner coefficients to compute the values of C in (13), and then averaging over different values of M_{s1}, M_{s2} thus resolved into the S, M_s system of representation. The state $M_s = S - 1$ makes a contribution to K_1 of opposite sign to that of S , and of much larger absolute magnitude. This is the basic reason why such a high power of M/M_0 as the tenth appears in the expression for K_1 . For example, for $S = 2$ the values of the bracketed factor in (11), are respectively $3/2, -6, +9$ for $M_s = 2, 1, 0$. With uncorrelated atoms, reducing M_s may reduce S , and the repercussion on the anisotropy is less drastic than if M_s is changed but S kept unaltered. Consider, as a particular case, two spins of magnitude 1 with quadrupole-quadrupole coupling. Only the state $S = 2$ contributes to (14), as already mentioned. However, if M_s is reduced from 2 to 1 corresponding to the two possibilities 0, 1 and 1, 0 in individual spacial quantization, half the time the system will be in a state $S = 1$ rather than $S = 2$, in accord with the fact that the Wignerian resolution of $0, 1 + 1, 0$ involves $S = 1$ and $S = 2$ equally. This means that 50 % of the time the reduction in M_s simply "washes out" the anisotropy. Hence instead of $K_1 = K_{10}[(1 - y) - 4y]$ we have

$$K = K_{10}[(1 - y) - 2y] = K_0(1 - 6y/S)$$

giving us the sixth rather than tenth power law (cf., Eqs. (17) and (18)).

We must by all means mention that Akulov [17] obtained the tenth power law as far back as 1936. He used a classical calculation more or less equivalent to that involved in our Eqs. (20) and (21). He ostensibly assumed that all magnets in the crystal were parallel and precessed together around the direction of the field. This picture is not correct, and so at one time the writer criticized Akulov's calculation. However, since the quadrupole-quadrupole forces are of short range, it is sufficient to assume that adjacent spins are substantially parallel. The spin wave picture shows that this is the case at low temperatures, for the spin waves can be regarded as a sort of corkscrew precession of the spin distribution. So one can now easily understand why Akulov's calculation led to the correct result, and only requires a minor difference in interpretation to be physically admissible.

HIGHER ORDER HARMONICS. — To explain the higher order anisotropy $K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2$ it is necessary to introduce terms of the sixth order in the spins, whose transformation properties correspond to those of a spherical harmonic of the sixth rather than fourth degree. Still higher order terms are in principle possible. If we consider the anisotropy associated with poles of the $2n$ th degree, and denote by $K^{(2n)}$ the corresponding anisotropy, the generalization of (15) is

$$(K^{(2n)}/K^{(2n)_0}) = (M/M_0)^{\frac{n(n+1)}{2}} \tag{23}$$

a result first given by Zener for a classical model. It is necessary that n be even, and that $S \geq n/2$ to get a non-vanishing anisotropy.

The anisotropy coefficients $K^{(2n)}$ satisfying equation (23) are not to be confused with the conventional higher order anisotropy coefficients of the experimentalists, as the angular dependence is different except in the case $n = 4$; for instance, $K^{(12)}$ is a linear combination of K_1 and K_2 .

To prove (23) classically, we need only note that the expansion of $P_n(\cos \theta)$ about $\theta = 0$ is

$$P_n(\cos \theta) = P_n(1) \left[1 - \frac{1}{4} n(n+1) \theta^2 + \dots \right] \tag{24}$$

as one sees from the differential equation

$$\frac{1}{\sin \theta} \cdot \frac{d}{d\theta} \left[\sin \theta \frac{dP_n}{d\theta} \right] + n(n+1) P_n = 0$$

of zonal harmonics. When (21) is replaced by (24), we obtain (23) in place of (15).

The same result also holds true in quantum mechanics, as is most readily demonstrated by the Kramers symbolic method [21]. The transformation properties of P_n are those of $\xi^n \eta^n/n!$ in his symbolism. His elegant application of spinor analysis shows that the diagonal matrix elements $\langle SM|V^{2n}|SM \rangle$ of a potential corresponding to poles of the $2n$ th degree (whose transformation properties under rotation are similar to those of P_n) are proportional to $(S + M)!(S - M)!$ times the coefficient of

$$A^{*S+M} A^{S+M} B^{*S-M} B^{S-M} a^n b^n$$

in the expression

$$[AA^* + BB^*]^{2S-n} [aA^* + bB^*]^n [aB - Ab]^n$$

Consequently one has

$$\begin{aligned} \langle S - 1|V^{(2n)}|S - 1 \rangle \\ = \left[1 - \frac{n(n+1)}{2S} \right] \langle S|V^{(2n)}|S \rangle \end{aligned}$$

whence (23) follows in the same fashion as did (15) from (16) and (17).

HIGHER ORDER EFFECTS OF TERMS OF LESS THAN CUBIC SYMMETRY. — Coupling of dipolar or pseudo-dipolar structure

$$C[\mathbf{S}_i \cdot \mathbf{S}_j - 3r_{ij}^{-2}(\mathbf{S}_i \cdot \mathbf{r}_{ij})(\mathbf{S}_j \cdot \mathbf{r}_{ij})] \tag{25}$$

is well known generally to average to zero if there is cubic symmetry. However if one consider second order effects, i.e., the perturbing influence of the part of (25) which is non-diagonal in the exchange or molecular field energy, an anisotropic member of cubic structure can be obtained, as has been shown by various writers [16, 22]. In an interesting recent paper, Wolf [23] has called attention to a similar situation in connection with a one-atom spin-Hamiltonian with axial symmetry, i.e.,

$$V = aS_z^2$$

or more generally (rhombic symmetry),

$$V = a_1 S_x^2 + a_2 S_y^2 + a_3 S_z^2. \quad (26)$$

In the first approximation the effect of (26) is independent of direction if there is cubic symmetry. However, in the second approximation (26) will contribute to the anisotropy in the order a^2/J or, equivalently $a^2/g\beta H_{ex}$ where J is the exchange integral and H_{ex} is the exchange field.

The theory for the second order effects mentioned in the preceding paragraph has the merit that it gives a contribution to K_1 whose sign is unambiguous for a given lattice arrangement. According to unpublished work of Keffer, it gives the tenth power law (15) like the octopolar model if the corresponding approximations are made in both cases.

THE STRANGE CASE OF NICKEL. — This metal has an anisotropy which varies approximately as the fiftieth power of the magnetization at low temperatures. No proper explanation of this behavior has been devised. Since nickel has a magnetic moment of less than a Bohr magneton per atom, it is natural to try and attribute its magnetization to the higher order effect of pseudo-dipolar coupling, as this is the only mechanism which gives anisotropy from a pair of atoms when $S = 1/2$. The resulting anisotropy, though of proper sign at low temperatures, has nothing like fast enough variation with temperature. A possibility to be considered is an octopolar potential from clusters of four atoms each with spins $1/2$, or transient pairs each with spin 1, so that the collective spin is 2. However, such models, none too likely in the first place, give the tenth rather than fiftieth power. We will not pursue this subject further especially since nickel is a conductor and so not a good substance anyway to test calculations based essentially on the Heisenberg model.

FERRITES. — On the other hand, the ferrites should be a good proving ground. The Mn^{++} , Fe^{+++} and Fe^{++} ions all have spins of 2 or greater. So one can try applying the one-atom

octopolar model with much better justification than in metals. This has been done by Yosida and Tachiki [24] and by Wolf [23]. A difficulty is that the ferrites are composed of two or more kinds of magnetic ions, and one must segregate the contributions of individual ions to the observed total anisotropy. To facilitate this resolution, Yosida and Tachiki calculate first of all the amount of anisotropy to be expected from the nickel ions. They find that it accounts for only a small percentage of the measured anisotropy of nickel ferrites, and so attribute the anisotropy primarily to other ions in these compounds. This conclusion is probably correct, for the anisotropy of nickel ions is low on two counts; its ground orbital state is non-degenerate in a cubic field, and its spin quantum number is $S = 1$, so that it is incapable of splitting in an octopolar potential of type (8). It should not however, be inferred that a one-atom model of type $S < 2$ is incapable of generating any anisotropy, for even without such a splitting, the polarizability in the exchange field need not be centrosymmetric, as Yosida and Tachiki show. They also essay a calculation of the anisotropy contributed by the ferrous ion Fe^{++} . It is surprising that the anisotropy is not much larger than it is in comparison with ferric and manganic ions, for Fe^{+++} and Mn^{++} have 6S ground levels, whereas the orbital degeneracy of the ground state of the Fe^{++} ion is lifted only in virtue of the non-cubic part of the crystalline field. Yosida and Tachiki assume, in accord with crystallographic evidence, that this part of the field is mainly of trigonal symmetry, which can split the cubic Γ_5 orbital triplet into a doublet and singlet. The only moderate anisotropy of the ferrous ion shows unequivocally that the singlet is deepest. By assuming a fairly large trigonal splitting, determined from the observed g -factor, these workers compute an anisotropy coefficient K_1 of the proper order of magnitude and sign. This is a difficult and tricky calculation, even as regards the question of sign. Yosida and Tachiki properly include besides the usual $A.L.S$ term, a spin-orbit coupling of the form

$$\rho \left[(\mathbf{L} \cdot \mathbf{S})^2 + \frac{1}{2} (\mathbf{L} \cdot \mathbf{S}) - \frac{1}{3} L(L+1) S(S+1) \right] \quad (27)$$

which results from spin-spin interaction inside the ion. The potential (27), though much smaller than the conventional spin-orbit term, can be quite important in creating cubic anisotropy, as it can do so in the second rather than fourth order. It is much easier to obtain a positive than a negative K_1 . Both the fourth order effect of $AL.S$ and the second order effect of (27) give a positive K_1 . Though they do not mention this fact explicitly, Yosida and Tachiki are able to obtain a negative K_1 from the manifold Γ_5 only because of a cross-effect involving $AL.S$ to the second power

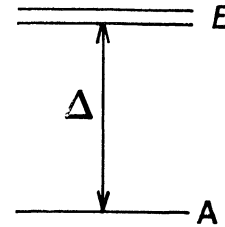
and (27) to the first. The constants ρ and A have to be just right to make the cross term preponderant. There are other effects besides those considered by Yosida and Tachiki which might modify the results; viz., the polarization by the exchange field, and various two-atom effects, such as pseudo-dipolar or quadrupole-quadrupole couplings. Wolf points out that the misplacing of a few ions in tetrahedral rather than octohedral sites may profoundly influence the anisotropy; because of inversion of the Stark pattern, a misplaced nickel iron, for instance, can become very strongly anisotropic like cobalt. In the case of the Mn^{++} and Fe^{+++} , Yosida and Tachiki do not attempt to compute the absolute magnitude of the anisotropy constants theoretically, but instead wisely take these from the experimental data on anisotropy and magnetic resonance. The anisotropy of the Fe^{+++} ions is apparently of opposite sign on the two kinds of sites, and considerably larger in magnitude than for the Mn^{++} ions.

Yosida and Tachiki study in some detail the temperature variation of the anisotropy of the Fe^{+++} and Mn^{++} ions on the basis of the one-atom octopolar model (8). They find good agreement with experiment, using Eqs. (10) and (11) with the distribution of values of M_s as a function of T determined by means of a molecular field model. They also find that this model represents quite well the dependence of magnetization on temperature. This is rather surprising as spin-waves should work better than Brillouin functions at very low temperature but they focus their attention primarily on somewhat higher temperatures. They find, in agreement with experiment, that the magnetization at medium temperatures (around a third to a half the Curie point), the anisotropy is somewhat higher than given by the tenth power law (15). This is not too surprising, for (15) is an extrapolative bridge between (19) at very low temperatures and proper behavior at the Curie point. At very low temperatures, the calculations with any octopolar model must of necessity agree with (15) or (19), but at medium temperatures the anisotropies which Yosida and Tachiki compute should be more reliable than those furnished by the connection formula (15).

THE GREAT ANISOTROPY OF THE COBALT FERRITES. — The cobalt ferrites have an anisotropy ten to a hundred times larger than the other ferrites. This fact has generally been regarded as something of a mystery, though various writers [23, 24] have suggested that it might somehow be attributed to a degenerate basic orbital state. Yosida and Tachiki give the impression that cobalt is a more complicated ion to treat than the others. Actually it may be easier, as anisotropy enters as a lower order effect. One can show [25] that the

splitting of the cubic orbital triplet Γ_4 into a doublet E and a singlet A by a trigonal field along the [111] axis, which presumably is the dominant non-cubic correction, should be of the form.

$$\Delta = a_1 \langle r_{3a}^2 \rangle_{AV} + a_2 \langle r_{3a}^4 \rangle_{AV}$$



and that furthermore the constants a_1 , a_2 should have values in Co^{++} respectively $-1/10$ and $-3/2$ those in Fe^{++} , provided the crystalline potential, i.e. the configuration of the surrounding atoms is the same. Hence, for most values of a_1 , a_2 , the splitting Δ should change sign in passing from Fe^{++} to Co^{++} . The comparatively small measured anisotropy of the ferrous ions requires that the A level be lowest in Fe^{++} . One can expect that then the orbitally degenerate E pair is deepest in Co^{++} , and if so an enormous anisotropy results. It can be further shown that then the direction of easy magnetization is [100], in agreement with experiment. The unusual anisotropy of the cobalt ferrites is hence qualitatively understandable. Furthermore, in a recent publication, J. C. Slonczewski [26] has a considerable measure of quantitative success in accounting for the magnitude and temperature variation of the anisotropies of ferrites containing small concentrations of cobalt, on the assumption that the E levels are deepest and that Δ is very large compared to the spin-orbit constant. With this model, the formula for the anisotropic part of the energy at $T = 0$ is very simple. If the crystalline field is not powerful enough to destroy Π coupling, the angular momentum of an E state about the trigonal axis t is $+\frac{3}{2}(h/2\pi)$. As $S = 3/2$ the spin-

orbit energy is $-\frac{9}{4}|\text{Acos}(M, t)|$ and is directionally dependent. If the magnetization M is along the [100] direction, $|\text{cos}(M, t)| = 1/\sqrt{3}$ while for [111], this cosine factor is unity for one-fourth and $1/3$ for three fourths of the ions. If the gaseous value 180 cm^{-1} is employed for the spin-orbit constant A , the computed anisotropy $E(111) - E(100)$ per cobalt ion is 30 cm^{-1} , about twice that observed for small concentrations of cobalt. The agreement as regards order of magnitude is quite satisfactory in view of the approximations made. This calculation gives only the part of the anisotropy which is linear in the concentration of cobalt. At higher concentrations there

are deviations from linearity which are presumably due to interactions between cobalt ions, for which an adequate theory has not yet been developed.

The writer wishes to express his thanks to the staff of the University of Hawaii for the use of their journals and library facilities, which made possible the writing of the present report.

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DISCUSSION

Mr. Kikuchi (Comment). — The results of the constant coupling approximation had been obtained before van Kranendonk and Kasteleijn as follows :

(1) YVON (J.), *Cahiers de Physique*, 1943.

(2) KIKUCHI (R.) and BUSSEIRON-KENKYU (in *Japanese*, 1951) reported at the Durham meeting of *American Physical Society*, 1953.

(3) NAKAMURA (T.) and BUSSEIRON-KENKYU (in *Japanese*, 1953). The first two people used different method from van Kranendonk's but Nakamura's method is exactly the same as the constant coupling method. Kikuchi's paper has appeared in English in the latest issue of *Annals of Physics*.

Mr. Nagamiya. — I might add : Nakamura has shown by his method that the susceptibility of an antiferromagnet with spin $1/2$ shows a maximum at a temperature which is slightly higher than the Néel temperature.

Mr. Vonsovskij. — What is the shape of the dispersion relation for spin waves in ferrimagnetic substances with equal spins on the sublattices ($|S_1| = |S_2|$) and $g_1 \neq g_2$? Our recent calculations (Turov, Irkhin and Vonsovskij) give a linear dispersion formula, and lead to a T^2 law for the magnetization, whereas you obtain a T^3 law.

Mr. Van Vleck. — According to the theory of Kouvel and Brooks, the energy of the lowest energy spin waves is proportional to the wave number k , and the deviations of the saturation magnetization from its maximum value are proportional to T^3 .

Mr. Riste. — Concerning the dispersion relation in ferrites, I may call to your attention a paper by KAPLAN (T. A.) (in *Phys. Rev.*, 1958, **109**, 182.) where he claims to have found a mistake in the calculation by Vonsovskij and Sedov when they obtained a linear relation. When introducing a correction Kaplan finds that V. and S.'s calculation also gives a quadratic law. Neutron scattering experiments by BROCKHOUSE (published in *Phys. Rev.*) and by RISTE, BLINOWSKI and JANIK (to be published in *Phys. Chem. Solids*) are in agreement with the quadratic law.

Mr. Wohlfarth (adds the following remarks). — The $T^{3/2}$ law holds almost up to the Curie point in Gd. This would agree with Dyson's calculations.

It is not certain that the $(M/M_0)^{10}$ power law for the variation of K_1 in iron is completely substantiated by experiment, because of experimental errors. Another exponent might also fit the measurements.

It would be interest to calculate K for CoPt and FePt, which are tetragonal, and have exceedingly high K values.

Mr. Kittel. — Prof. Van Vleck and I have extended the theory of the temperature dependence of anisotropy to include the magnetoelastic terms in the free energy. We are then able to discuss the temperature dependence of magnetostriction. We find that the "five constant" fit to the magnetoelastic energy of a cubic crystal, where expressed properly in terms of spherical harmonics, gives one contribution varying with temperature as $(M/M_0)^3$ and one contribution varying as $(M/M_0)^{10}$.

Mr. Jacobs. — The magnetocrystalline anisotropy constants of Fe at 77 °K usually used in recent graphs of (K/K_0) vs (M/M_0) comes from Dr. Bozorth' textbook. More recently, in the Handbook of the American Inst. of Physics, Dr. Bozorth reports a lower value. An identical value is obtained in current work by Dr. C. D. GRAHAM (*Gen. Elec.*, U. S. A.). The use of these values in the above graph suggests a lower value of power law dependency, e.g. perhaps 4 instead of 10.

Mr. Dreyfus. — Les interactions dipolaires magnétiques ont pour effet d'affecter considérablement la forme de la relation de dispersion des ondes de spin. Ceci a été montré par Holstein et Primakoff et plus récemment par Kittel. J'ai calculé l'influence de ces interactions sur les propriétés thermodynamiques. Le résultat est le suivant : pour l'aimantation la loi en $T^{3/2}$ est changée en T^2 . Pour la chaleur spécifique la loi est changée de $T^{3/2}$ en $T^{5/2}$. Ces effets ne sont sensibles qu'en dessous d'une température dépendant de l'intensité d'aimantation (pour le fer de l'ordre de 1 à 2 °K, pour les ferrites de l'ordre de 10 fois moins). A des températures encore plus basses, les modes « magnétostatiques » deviennent seuls importants et les propriétés thermodynamiques dépendent alors de la forme de l'échantillon.

Mr. Pearson. — I should like to ask Prof. Van Vleck if he could offer some explanation of the anomalous temperature variation of anisotropy energy in magnetic (Fe_3O_4) above its transition point.

Mr. Van Vleck. — I know of no explanation.

Mr. Smit. — The degeneracy of the lowest state of cobalt and iron ions in ferrites is determined by the sign of the trigonal field which is superimposed upon the octahedral field. This trigonal field is according to Vonsovskij, due to the non cubical surrounding of the cobalt ion by metal ions. This predicts the correct sign for Co in magnetite. On the other hand the displacement of the oxygen ions, described by the so-called n parameter (n ideal = 0.375) also induces a trigonal field, which for $n > 0.375$ is just opposite to that of the metal ions, because it concentrates negative charge around one body diagonal instead of positive charge. Simple calculations, disregarding the polarisation of the oxygen ions, show that the effect of the n parameter is more important than the effect of the metal ions for $n \approx > 0.380$. In ferrites with a large n parameter, as for instance Mn ferrite ($n = 0.385$) and in ferrites with much zinc, one should therefore expect the role of ferrous ions and of cobalt ions to be interchanged. Experimental evidence for this to occur this may be present in cobalt substituted Mn ferrite, in which the effect of Co is more than 10 times as small as in magnetite, and in mixed crystals of Fe_3O_4 and MnFe_2O_4 for low concentration of magnetite, in which, after Dr. R. W. Pearson, the anisotropy arising from the extra ferrous ions appears to be positive.

Mr. Nagamiya (remark). — One must be careful in calculating the crystalline field. It represents a combined effect of point charges, space charges, electron transfer, and the exchange of electrons. It is dangerous to draw a definite conclusion from a simple calculation.