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D. Ter Haar and M. E. Lines

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A SPIN-WAVE THEORY OF ANISOTROPIC ANTIFERROMAGNETICA

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This paper is a sequel to an earlier one (ter Haar & Lines 1962 referred to as A) in which we applied a molecular-field treatment to anisotropic antiferromagnetics. In the present paper we apply spin-wave theory to investigate the influence of anisotropy of nearest-neighbour interactions and of the occurrence of next-nearest-neighbour interactions on the stability of the types of order found in A.

After a brief introduction, face-centred cubic antiferromagnetics are considered in the second section. We find that there is no type of f.c.c. order which is stable for nearest-neighbour isotropic exchange interactions only. For the case of type 1 order with all spins along the direction of the unique cubic axis the order is stabilized by a small amount of anisotropy in the nearest-neighbour interaction. This is the only f.c.c. order which we found to be stable for nearest-neighbour interactions only. The influence of the more-remote-neighbour interactions is probably small for this case. For the case of type 1 order with all spins perpendicular to the unique cubic axis, we find that this type of order is only stable, provided interactions more remote than the nearest-neighbour ones occur. As far as type 2 order is concerned, the case where the preferred direction of order is in one of the ferromagnetically ordered planes turned out to be too complicated to be treated, but the case where the preferred direction is perpendicular to the ferromagnetic planes and the isotropic case can be treated. The orders in the latter cases are stable, provided the next-nearest-neighbour interactions are not too weak. If they are too weak, type 3A order is the stable one. Type 3A order with the spins oriented along the unique cubic axis is stable,

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provided there is a small amount of isotropic antiferromagnetic next-nearest-neighbour interaction present. Type 3A order with spins perpendicular to the unique cubic axis is stable only if we include second and third nearest-neighbour interactions of sufficient magnitude.

For most of these cases we have computed the spin-wave ground-state energy and the average value in this ground state of the total sublattice spin-component along the preferred direction; this value should be close to its maximum for the spin-wave treatment to be reliable. We observe that for all orders considered here there is a general rule: the order is not stable, if it is possible to single out a plane in the structure for which the average interactions between atoms within the plane and those outside is zero.

In §2 we discuss the body-centred tetragonal lattice. We find that type 1 order is stable, provided the isotropic next-nearest-neighbour exchange interaction is larger than the nearest-neighbour exchange interaction. If their ratio is less than $\frac{1}{2}$ the so-called rutile type diagonal order—or type 2 order—is stable whenever its existence is predicted by the molecular-field theory. In the latter case one must introduce four sets of spin-waves rather than the two sets occurring for the other types of order considered in the present paper.

In the last section we consider antiferromagnetic resonance. We find that the resonance frequency observed for MnO agrees rather better with the exchange interaction deduced from susceptibility measurements than with the value of this interaction deduced from mixed-salt paramagnetic-resonance measurements. For the case of MnF_2 we find a resonance wavelength of about 0·95 mm as against the experimental wavelength of 1·15 mm. We finally predict resonance frequencies of 15·0 and 19·1 cm^{-1} for $(NH_4)_2IrCl_6$ and K_2IrCl_6 if they should show type 1 order and of 10·6 and 13·5 cm^{-1}, if the order should be type 3A.

List of symbols

General

S_{ix}, etc.	The component in the direction x of the spin at the **i**th lattice site
x, y, z	A right-handed set of axes defined such that for any particular order z is the preferred direction of antiferromagnetic alinement
X, Y, Z	A right-handed set of axes defined along the principal cubic (or tetragonal) axes
A	The 3×3 matrix which transforms the co-ordinate system X, Y, Z into the system x, y, z
a_{ij}	The matrix elements of A
$\mathbf{j}\ \mathbf{j}'$	The vector position of an 'up' spin
$\mathbf{k}\ \mathbf{k}'$	The vector position of a 'down' spin
N	The number of sites in the entire lattice
S	The spin-quantum number
S_c	The classical total spin of an atom ($S_c = \sqrt{\{S(S+1)\}}$)
E_g	The ground-state energy of the system
E_0	The 'molecular field' ground-state energy of the basic array
$\boldsymbol{\kappa}$	A wave vector
κ_i	Wave-vector components
$\sum^{abc}_{\text{n.n.}}$	Summation over all nearest neighbours with connexions in the directions labelled by a, b, and c
$\sum_{\text{n.n}}$	Summation over all nearest neighbours
$\sum^{abc}_{\text{n.n.n.}}$, $\sum_{\text{n.n.n.}}$	As above, but for next-nearest neighbours
$[p, q]_-$	The commutator pq-qp

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$\langle (S_{jz})_{\text{total}} \rangle$ The time average value of the z component of spin in the complete j sublattice

J Isotropic nearest-neighbour exchange

K Isotropic next-nearest-neighbour exchange

For the face-centred cubic lattice

$J_\alpha, J_\beta, J_\gamma$ Anisotropy parameters defined, such that the interaction between a pair of nearest-neighbour spins S and S' is

$$2(J+J_\alpha)\, S_{x'} S'_{x'} + 2(J+J_\beta)\, S_{y'} S'_{y'} + 2(J+J_\gamma)\, S_z S'_{z'},$$

where x' is the direction of the line connecting the spins, y' is perpendicular to x' in the cube face in which S and S' are situated, and z' is such that $x'y'z'$ form a right-handed orthogonal set of axes

For the body-centred tetragonal lattice and rutile anion positions

ω The ratio (< 1) of the dimensions of the tetragonal unit cell

$J_\alpha, J_\beta, J_\gamma$ Anisotropy parameters defined such that the interaction between a pair of nearest-neighbour spins S and S' is

$$2(J+J_\alpha)\, S_{x'} S'_{x'} + 2(J+J_\beta)\, S_{y'} S'_{y'} + 2(J+J_\gamma)\, S_{z'} S'_{z'},$$

where x' is the tetragonal axis, y' is the axis parallel to the connexion between S (or S') and its neighbour anions and z' such that $x'y'z'$ form a right-handed orthogonal set of axes

D, D', D'' Anisotropy parameters defined such that the anisotropic part of the interaction of a spin S with the crystalline field is

$$2[DS^2_{x'} + D'S^2_{y'} + \mathrm{D}''S^2_{z'}],$$

where x', y', z' are as defined for J_α, J_β, J_γ.

E Crystal-field anisotropy parameter defined by the equation $E = D' - D''$

$K_\alpha, K_\beta, K_\gamma$ Anisotropy parameters defined such that the interaction between a pair of next-nearest neighbour spins S and S' is

$$2(K+K_\alpha)\, S_{x''} S'_{x''} + 2(K+K_\beta)\, S_{y''} S'_{y''} + 2(K+K_\gamma)\, S_{z''} S'_{z''},$$

where x'' is the direction of the line connecting the spins, y'' is a direction normal to the plane containing x'' and the tetragonal axis, and z'' is such that x'', y'', z'' form a right-handed orthogonal set of axes

1. Introduction

In a previous paper (ter Haar & Lines 1962; in the following referred to as A and its equations as, for example, (A 2·6); we shall as far as possible use the same notation as in A) we have applied a molecular-field treatment to the theory of anisotropic antiferromagnetics. In the present paper we shall consider the problem from a spin-wave point of view. We shall again use a Hamiltonian of the type (A 1·15). We do not wish to discuss the adequacy of this Hamiltonian (see, for instance, Slater 1953 for such a discussion), but accept it as a suitable model for antiferromagnetics, and hope that it will explain their behaviour—at least in a semi-quantitative manner.

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Even if the Hamiltonian (A 1·15) were the correct one, there remains the task of solving the quantum-mechanical eigenvalue problem and the statistical problem of evaluating the thermodynamic behaviour of the systems governed by this Hamiltonian. A rigorous treatment has so far not been found and various approximate methods have been evolved. Some of these are particularly suited for temperatures well above the Curie temperature while others are particularly suited for temperatures well below the Curie temperature. Unfortunately there does not seem a satisfactory theory for the perhaps most interesting temperature region in the neighbourhood of the Curie temperature. Of the high-temperature approximations the simplest one is the molecular field theory which we used in A. The main reason for using this rather crude approximation is that one hopes that it will describe the properties of complicated antiferromagnetic substances qualitatively, at least, while its relatively simple mathematics enables one actually to obtain some results. Opechowski's T^{-1}-expansion method (1937, 1939) and Li's adaptation (1951) of the Bethe–Weiss method are two more-accurate high-temperature approximations. We must mention that Li's predictions about the occurrence or non-occurrence of antiferromagnetic structures are different from the predictions obtained from the molecular field approach. Also, the behaviour of the susceptibility above the Curie temperature is different in the two theories—the predictions of Li's theory being in better agreement with actual experimental results. The Bethe–Weiss method breaks down in the low-temperature region (Anderson 1950) as it predicts a second, lower critical temperature below which the order disappears again. Several authors have modified either the $1/T$ approach (Kubo, Obata & Ohno 1951, 1952) or the Bethe–Weiss approach (Oguchi & Obata 1953; Nakamura 1953; Brown & Luttinger 1955), but without very great success in the low-temperature region.

The most successful low-temperature approximation is the spin-wave approach (Hulthén 1936; Anderson 1952; Ziman 1952 *a*, *b*, 1953; van Kranendonk & Van Vleck 1958, and many others). The method consists essentially in expressing the Hamiltonian for the system in terms of the deviation of the spins from a basic, antiparallel-ordered arrangement. Marshall's work (1955) suggests that the antiferromagnetic ground state does not show long-range order, but he has also shown that the ordered state lies very close to the ground state and so far the spin-wave theory has been—perhaps unaccountably—rather successful when applied to antiferromagnetics. We shall therefore apply it to some of the antiferromagnetic arrangements studied in A.

It is well known that the basic, ordered states of an antiferromagnetic such as the ones given by the molecular-field method and discussed in A are not eigenstates of the Hamiltonian. For three-dimensional antiferromagnetics in which the basic antiferromagnetic ordered state may be divided into two interlocking ferromagnetic sublattices which are such that all the nearest neighbours of a spin on one sublattice are on the other sublattice, Anderson (1952) using a spin-wave theory has shown that the ground state is not too far removed from the basic molecular-field state. However, if we are dealing with a face-centred cubic (f.c.c.) lattice, one cannot find two such sublattices, and the work of both Li (1951) and Ziman (1953) seems to indicate that—at least in the case when the only interactions present are isotropic nearest-neighbour exchange interactions—there is no low-lying ordered state. As the f.c.c. case is such an important one empirically, it is of some

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interest to investigate how second-nearest-neighbour interactions and the anisotropy of nearest-neighbour interactions can affect the stability of the basic, ordered molecular field states.

Our programme will be as follows. We take as the basic array on which to base the spin-wave treatment the molecular-field orders found in A. We then express the Hamiltonian in terms of the deviations of the spins from the basic ordered antiparallel arrangement. This Hamiltonian is then treated by the usual spin-wave methods to give us the ground-state energy and also the magnitude of the spin on the sublattices in the spin-wave (that is, the low temperature) approximation. If the deviation of sublattice spins from the basic array is small, the method is consistent and we shall assume that the results are good approximations and that the order is therefore a stable one. Most calculations have to be done numerically and the dependence of the various quantities of interest to us are plotted as functions of the available parameters—mainly the anisotropy parameters.

In § 2 we discuss f.c.c. lattices, considering in § 2 (*a*) type 1 order, in subsection 2 (*b*) type 2 order, and in § 2 (*c*) type 3 A order. In § 3 we discuss body-centred tetragonal (b.c.t.) lattices, considering in subsection 3 (*a*) type 1 order, and in § 3 (*b*) type 2 (the so-called rutile type diagonal) order. Finally, we discuss in § 4 antiferromagnetic resonance.

2. The face-centred cubic lattice

We saw in A that, depending on the relative magnitude of the various exchange parameters, in a f.c.c. magnetic lattice various types of order may occur; we also noted that, in fact, several of these types of order have been observed experimentally. As we shall find the mathematics of the spin-wave treatment to be much more complicated than for the molecular-field theory, we shall only consider nearest-neighbour and second-nearest-neighbour interactions. In that case, type 4 order will not occur, and we are left with types 1, 2, and 3. Experimentally, MnO, CoO, NiO, and αMnS show type 2 order with spins ordered somewhere in the ferromagnetic planes; FeO type 2 order with spins alined at right angles to the ferromagnetic planes; MnS_2 and βMnS type 3 A order; and $MnTe_2$ type 1 order. We shall therefore consider these three types of order in the present section.

2 (*a*) *Type* 1 *order in the f.c.c. lattice*

We saw in A that type 1 order may occur with all spins alined either parallel to the unique cubic axis or at right angles to this axis, depending on whether the anisotropy parameter J_γ (see (A 2·2)) is negative or positive. We shall treat these two cases separately.

2 *a* (i) *Type* 1 *order; all spins parallel to the Z axis*

We first consider the case where the nearest-neighbour exchange energy, which is given by the equation (see (A 2·1))

$$V = 2J_1 S_{1x'} S_{2x'} + 2J_2 S_{1y'} S_{2y'} + 2J_3 S_{1z'} S_{2z'}, \tag{2·1}$$

is such that, provided we choose our x' axis in the direction of the line connecting the spins, our y' axis at right angles to the x' axis in the cube face in which the two spins are situated, and the z' axis so as to form a right-handed set of Cartesian co-ordinates with the x' and y' axes (see figure A 2), and provided we write (see (A 2·2))

$$J_1 = J + J_\alpha, \quad J_2 = J + J_\beta, \quad J_3 = J + J_\gamma, \quad J_\alpha + J_\beta + J_\gamma = 0, \tag{2·2}$$

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J_y is negative. In that case ordering is along the unique cubic axis, which we shall call the Z axis.

More generally we may choose a set of axes x, y, z such that the preferred direction of ordering is z. Although in the present section z and Z are the same, we shall find it convenient, for use in later sections, to treat the more general case at this stage.

Consider now figure 1, and consider the spins labelled 8d and 8a. Let Σ' denote the x, y, z system of co-ordinates and Σ the X, Y, Z system, and let a_{ij} be the components of the

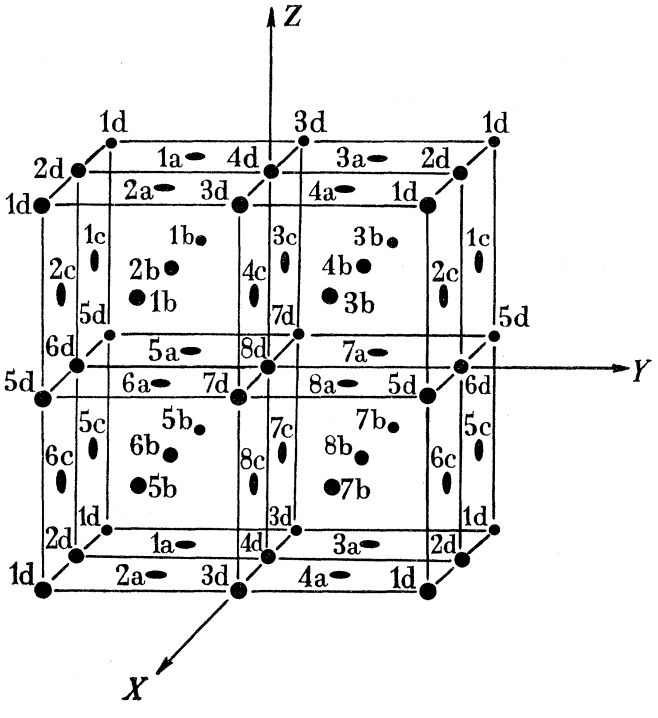

FIGURE 1. The f.c.c. lattice.

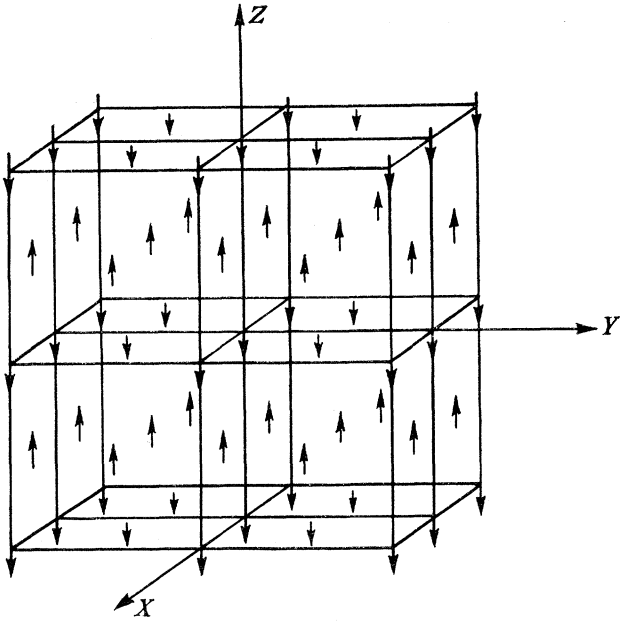

FIGURE 2. Type 1 order in the f.c.c. lattice.

transformation matrix A which transforms Σ into Σ' (see equation (A 2·3)). We then get for the exchange interaction between the 8d and 8a spins the expression (A 2·5).

$$\begin{aligned} V_{8d,\,8a} = {} & J_1[(a_{11}+a_{12})\,S_{1x}+(a_{21}+a_{22})\,S_{1y}+(a_{31}+a_{32})\,S_{1z}] \\ & \times[(a_{11}+a_{12})\,S_{2x}+(a_{21}+a_{22})\,S_{2y}+(a_{31}+a_{32})\,S_{2z}] \\ & +J_2[(a_{11}-a_{12})\,S_{1x}+(a_{21}-a_{22})\,S_{1y}+(a_{31}-a_{32})\,S_{1z}] \\ & \times[(a_{11}-a_{12})\,S_{2x}+(a_{21}-a_{22})\,S_{2y}+(a_{31}-a_{32})\,S_{2z}] \\ & +2J_3[a_{13}S_{1x}+a_{23}S_{1y}+a_{33}S_{1z}]\,[a_{13}S_{2x}+a_{23}S_{2y}+a_{33}S_{2z}], \end{aligned} \tag{2·3}$$

where S_1 and S_2 refer to the 8d and 8a spins. One can write similar expressions for the exchange interactions of the 8d spin with its other nearest-neighbours and for the exchange interactions with the next-nearest neighbours. If we neglect all more remote neighbours, we can write the Hamiltonian of the total lattice in the form

$$H = \sum_{\text{n.n.}} V_{lm} + \sum_{\text{n.n.n.}} V_{pq}, \tag{2·4}$$

where the first sum is over all nearest-neighbour pairs and the second one over all next-nearest-neighbour pairs.

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We now make the basic spin-wave-theory assumption that the actual state of the lattice is not far removed from the type 1 order given in figure 2. We shall denote all 'up' spins by a suffix j or j' and all 'down' spins by k or k'. The transformation matrix A of (A 2·3) can now for use in the present section be taken to be the unit matrix. In writing down the total Hamiltonian we must bear in mind that we are dealing with anisotropic interactions, in general, and the various terms in the sum over the nearest neighbours will be different depending on the direction of the line connecting the two spins. The same would be true for the sum over the next-nearest neighbours, if we introduced the anisotropy also in that case. We shall, however, not explicitly take the next-nearest-neighbour anisotropy into account,* and assume that we have an exchange interaction such as (2·1) with all exchange parameters equal to one another ($= K$). We introduce the notation $\sum^{i}_{\text{n.n.}}$ with the superscript i distinguishing between the six different directions of nearest-neighbour connexions. The superscripts 1, 2, 3, 4, 5, and 6 correspond respectively to the directions (0, 1, 1) (4b, 6b); (0, 1, −1) (2b, 8b); (1, 0, 1) (4c, 7c); (1, 0, −1) (3c, 8c); (1, 1, 0) (8a, 5a); and (1, −1, 0) (6a, 7a), where the second brackets indicate the nearest neighbours (see figure 1). Whenever a summation sign carries more than one superscript, summation over all the directions which are indicated is intended: $\sum^{135}_{\text{n.n.}}$ is thus equivalent to $\sum^{1}_{\text{n.n.}}+\sum^{3}_{\text{n.n.}}+\sum^{5}_{\text{n.n.}}$, and so on. A summation sign without a superscript indicates summation over all nearest (or next-nearest) neighbours.

The total Hamiltonian is now of the form

$$\begin{aligned} H = {} & \sum^{1234}_{\text{n.n.}} 2J(\mathbf{S}_j.\mathbf{S}_k)+\sum^{56}_{\text{n.n.}} J[(\mathbf{S}_j.\mathbf{S}_{j'})+(\mathbf{S}_k.\mathbf{S}_{k'})]+\sum_{\text{n.n.n.}} K[(\mathbf{S}_j.\mathbf{S}_{j'})+(\mathbf{S}_k.\mathbf{S}_{k'})] \\ & +\sum^{1}_{\text{n.n.}}\Phi^{+}_{xyz}(jk)+\sum^{2}_{\text{n.n.}}\Phi^{-}_{xyz}(jk)+\sum^{3}_{\text{n.n.}}\Phi^{+}_{yzx}(jk) \\ & +\sum^{4}_{\text{n.n.}}\Phi^{-}_{yzx}(jk)+\tfrac{1}{2}\sum^{5}_{\text{n.n.}}[\Phi^{+}_{zxy}(jj')+\Phi^{+}_{zxy}(kk')]+\tfrac{1}{2}\sum^{6}_{\text{n.n.}}[\Phi^{-}_{zxy}(jj')+\Phi^{-}_{zxy}(kk')], \end{aligned} \tag{2·5}$$

where
$$\Phi^{\pm}_{xyz}(jk) = J_\alpha(S_{jy}\pm S_{jz})(S_{ky}\pm S_{kz})+J_\beta(S_{jy}\mp S_{jz})(S_{ky}\mp S_{kz})+2J_\gamma S_{jx}S_{kx}. \tag{2·6}$$

We now introduce the semi-classical approximation as well as the basic spin-wave-theory assumption, and write for any spin

$$S^2_x+S^2_y+S^2_z = S^2_{\text{c}}, \tag{2·7}$$

where $S_{\text{c}} = \sqrt{\{S(S+1)\}}$ is the classical total spin of an atom with spin-quantum number S. Moreover, we write

$$\left.\begin{aligned} S_{jz} = \sqrt{(S^2_{\text{c}}-S^2_{jx}-S^2_{jy})} \doteqdot S_{\text{c}}-\frac{S^2_{jx}+S^2_{jy}}{2S_{\text{c}}}, \\ S_{kz} \doteqdot -S_{\text{c}}+\frac{S^2_{kx}+S^2_{ky}}{2S_{\text{c}}}. \end{aligned}\right\} \tag{2·8}$$

In writing down (2·8) we have used the fact that in the basic array all S_{jz} are equal to S_{c} and all S_{kz} equal to $-S_{\text{c}}$ and also the fact that we may assume all S_x and S_y to be small compared to S_{c}.

* Details of some of the consequences of introducing next-nearest-neighbour anisotropy can be found in M. E. Lines's Oxford D.Phil. Thesis.

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Substituting (2·8) into (2·5) we get in the same approximation

$$\begin{aligned} H = {} & \Delta_1 S_c^2 + \Delta_2 (S_{jx}^2 + S_{jy}^2 + S_{kx}^2 + S_{ky}^2) + \lambda_1 (S_{jx} S_{j'x} + S_{kx} S_{k'x}) \\ & + \lambda_2 (S_{jy} S_{j'y} + S_{ky} S_{k'y}) + \mu_1 S_{jx} S_{kx} + \mu_2 S_{jy} S_{ky} \\ & + \nu_1 (S_{jx} S_{j'y} + S_{jy} S_{j'x} + S_{kx} S_{k'y} + S_{ky} S_{k'x}) + \nu_2 (S_{jx} S_{ky} + S_{jy} S_{kx}), \end{aligned} \tag{2·9}$$

where Δ_1, Δ_2, λ_1, λ_2, μ_1, μ_2, ν_1, and ν_2 are operators which are given by the equations

$$\left.\begin{aligned} \Delta_1 &= (-\tfrac{2}{3}J + \tfrac{4}{3}J_\gamma) \sum_{\text{n.n.}} + 2K \sum_{\text{n.n.n.}}, \\ \Delta_2 &= (\tfrac{1}{3}J - \tfrac{2}{3}J_\gamma) \sum_{\text{n.n.}} - K \sum_{\text{n.n.n.}}, \\ \lambda_1 &= \lambda_2 = (J - \tfrac{1}{2}J_\gamma) \sum_{\text{n.n.}}^{56} + K \sum_{\text{n.n.n.}}, \\ \mu_1 &= 2(J + J_\gamma) \sum_{\text{n.n.}}^{12} + (2J - J_\gamma) \sum_{\text{n.n.}}^{34}, \\ \mu_2 &= (2J - J_\gamma) \sum_{\text{n.n.}}^{12} + 2(J + J_\gamma) \sum_{\text{n.n.}}^{34}, \\ \nu_1 &= \tfrac{1}{2} J_{\alpha\beta} [\sum_{\text{n.n.}}^{5} - \sum_{\text{n.n.}}^{6}], \quad J_{\alpha\beta} = J_\alpha - J_\beta, \\ \nu_2 &= 0. \end{aligned}\right\} \tag{2·10}$$

We have in (2·9) included the term with ν_2 to have as general a Hamiltonian as possible. In fact, we shall see later on that a Hamiltonian of the form (2·9) occurs for all types of order in the f.c.c. case.

We now introduce two sets of spin waves, one pair for the j sublattice and one pair for the k sublattice:

$$\left.\begin{aligned} S_{jx} &= \left(\frac{2S}{N}\right)^{\frac{1}{2}} \sum_{\boldsymbol{\kappa}} e^{i(\boldsymbol{\kappa}.\mathbf{j})} Q_{\boldsymbol{\kappa}}, \qquad S_{jy} = \left(\frac{2S}{N}\right)^{\frac{1}{2}} \sum_{\boldsymbol{\kappa}} e^{-i(\boldsymbol{\kappa}.\mathbf{j})} P_{\boldsymbol{\kappa}}, \\ S_{kx} &= \left(\frac{2S}{N}\right)^{\frac{1}{2}} \sum_{\boldsymbol{\kappa}} e^{-i(\boldsymbol{\kappa}.\mathbf{k})} R_{\boldsymbol{\kappa}}, \qquad S_{ky} = -\left(\frac{2S}{N}\right)^{\frac{1}{2}} \sum_{\boldsymbol{\kappa}} e^{i(\boldsymbol{\kappa}.\mathbf{k})} S_{\boldsymbol{\kappa}}, \end{aligned}\right\} \tag{2·11}$$

where N is the total number of spins in the lattice, and where $\boldsymbol{\kappa}$ runs over $\frac{1}{2}N$ values in the first Brillouin zone of the f.c.c. reciprocal lattice.

From (2·11) it follows that

$$\left.\begin{aligned} Q_{\boldsymbol{\kappa}} &= \left(\frac{2}{NS}\right)^{\frac{1}{2}} \sum_{j} e^{-i(\boldsymbol{\kappa}.\mathbf{j})} S_{jx}, \qquad P_{\boldsymbol{\kappa}} = \left(\frac{2}{NS}\right)^{\frac{1}{2}} \sum_{j} e^{i(\boldsymbol{\kappa}.\mathbf{j})} S_{jy}, \\ R_{\boldsymbol{\kappa}} &= \left(\frac{2}{NS}\right)^{\frac{1}{2}} \sum_{k} e^{i(\boldsymbol{\kappa}.\mathbf{k})} S_{kx}, \qquad S_{\boldsymbol{\kappa}} = -\left(\frac{2}{NS}\right)^{\frac{1}{2}} \sum_{k} e^{-i(\boldsymbol{\kappa}.\mathbf{k})} S_{ky}. \end{aligned}\right\} \tag{2·12}$$

The S_x and S_y satisfy the usual commutation rules for spin components and it follows from (2·12) that

$$\left.\begin{aligned} Q_{\boldsymbol{\kappa}} P_{\boldsymbol{\kappa}'} - P_{\boldsymbol{\kappa}'} Q_{\boldsymbol{\kappa}} &= \frac{2i}{NS} \delta_{\boldsymbol{\kappa}\boldsymbol{\kappa}'} \sum_{j} S_{jz} \doteq i\delta_{\boldsymbol{\kappa}\boldsymbol{\kappa}'}, \\ R_{\boldsymbol{\kappa}} S_{\boldsymbol{\kappa}'} - S_{\boldsymbol{\kappa}'} R_{\boldsymbol{\kappa}} &\doteq i\delta_{\boldsymbol{\kappa}\boldsymbol{\kappa}'}, \end{aligned}\right\} \tag{2·13}$$

and other commutators vanishing. We have used in deriving (2·13) the relation

$$\sum_{j} S_{jz} \doteq \tfrac{1}{2}NS.$$

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Substituting (2·11) into (2·9) we get

$$H = \alpha S_c^2 + \sum_{\kappa} \{\tfrac{1}{2}\beta_1(Q_\kappa Q_{-\kappa} + R_\kappa R_{-\kappa}) + \tfrac{1}{2}\beta_2(P_\kappa P_{-\kappa} + S_\kappa S_{-\kappa}) + \gamma_1 Q_\kappa R_\kappa - \gamma_2 P_\kappa S_\kappa + \tfrac{1}{2}\delta_1(Q_\kappa P_\kappa + P_\kappa Q_\kappa - R_\kappa S_\kappa - S_\kappa R_\kappa) + \delta_2(P_\kappa R_{-\kappa} - Q_\kappa S_{-\kappa})\}, \quad (2\cdot14)$$

where the α, β_1, β_2, γ_1, γ_2, δ_1, and δ_2 are given by the equations

$$\left.\begin{aligned} \alpha &= N(-4J + 8J_\gamma + 6K), \\ \beta_1 = \beta_2 = \beta &= S[(2J - J_\gamma)\sum_{\text{n.n.}}^{56} e^{i(\kappa.l)} + 2K \sum_{\text{n.n.n.}} e^{i(\kappa.l)} + 8J - 16J_\gamma - 12K], \\ \gamma_1 &= S[2(J + J_\gamma)\sum_{\text{n.n.}}^{12} e^{i(\kappa.l)} + (2J - J_\gamma)\sum_{\text{n.n.}}^{34} e^{i(\kappa.l)}], \\ \gamma_2 &= S[(2J - J_\gamma)\sum_{\text{n.n.}}^{12} e^{i(\kappa.l)} + (2J + 2J_\gamma)\sum_{\text{n.n.}}^{34} e^{i(\kappa.l)}], \\ \delta_1 &= SJ_{\alpha\beta}[\sum_{\text{n.n.}}^{5} e^{i(\kappa.l)} - \sum_{\text{n.n.}}^{6} e^{i(\kappa.l)}], \\ \delta_2 &= 0. \end{aligned}\right\} \quad (2\cdot15)$$

The term with δ_2 has again been included in order to have as general a Hamiltonian as possible. In (2·15) $\mathbf{l}$ is the vector connecting the nearest (or next-nearest) neighbours over which is summed.

We note that the Hamiltonian of (2·14) is a quadratic expression in the P_κ, Q_κ, R_κ, and S_κ, that is, we are working in the 'small vibrations' approximation. This means that one can diagonalize (2·14) after which it will be a sum of harmonic oscillator terms. If the eigenvalues of the small vibrations are E_i, the eigenvalues of the Hamiltonian will be $\Sigma_i (n_i + \frac{1}{2}) E_i$. There are for each (positive) κ eight degrees of freedom corresponding to P_κ, $P_{-\kappa}$, Q_κ, $Q_{-\kappa}$, R_κ, $R_{-\kappa}$, S_κ, and $S_{-\kappa}$ and we are thus led to an eight by eight determinant for the secular equation. This determinant can be reduced to the square of the following four by four determinant

$$\begin{vmatrix} iE + \delta_1 & -\delta_2 & \beta_1 & \gamma_1 \\ \delta_2 & iE - \delta_1 & \gamma_1 & \beta_1 \\ -\beta_2 & \gamma_2 & iE - \delta_1 & -\delta_2 \\ \gamma_2 & -\beta_2 & \delta_2 & iE + \delta_1 \end{vmatrix}. \quad (2\cdot16)$$

We then get for E^2 the result

$$E^2 = \delta_2^2 - \delta_1^2 + \beta_1\beta_2 - \gamma_1\gamma_2 \pm [(\beta_2\gamma_1 - \beta_1\gamma_2)^2 + 4(\delta_1\gamma_2 - \beta_2\delta_2)(\delta_1\gamma_1 - \beta_1\delta_2)]^{\frac{1}{2}}, \quad (2\cdot17)$$

leading to two different positive E-values, $E_{1\kappa}$ and $E_{2\kappa}$; we have given the E_i a subscript κ to indicate that they depend on κ as β_1, β_2, γ_1, γ_2, and δ_1 are functions of κ (see (2·15)). The eigenvalues of (2·14) are thus given by the equation

$$E_{n_1 n_2} = \alpha S_c^2 + \sum_{\kappa} [(n_{1\kappa} + \tfrac{1}{2}) E_{1\kappa} + (n_{2\kappa} + \tfrac{1}{2}) E_{2\kappa}], \quad (2\cdot18)$$

and the ground-state energy E_g is given by

$$E_g = \alpha S_c^2 + \tfrac{1}{2} \sum_{\kappa} (E_{1\kappa} + E_{2\kappa}). \quad (2\cdot19)$$

In (2·18) the quantum numbers $n_{1\kappa}$ and $n_{2\kappa}$ are called the spin-wave numbers.

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To simplify our calculations we shall for the time being assume J_α to be equal to J_β so that we can put $\delta_1 = \delta_2 = 0$, and (2·17) and (2·19) reduce to

$$E_{1\kappa} = \sqrt{\{(\beta_1+\gamma_1)\,(\beta_2-\gamma_2)\}}, \quad E_{2\kappa} = \sqrt{\{(\beta_1-\gamma_1)\,(\beta_2+\gamma_2)\}}, \tag{2·20}$$

$$E_g = \alpha S_c^2 + \tfrac{1}{2}\sum_{\kappa}[\sqrt{\{(\beta_1+\gamma_1)\,(\beta_2-\gamma_2)\}}+\sqrt{\{(\beta_1-\gamma_1)\,(\beta_2+\gamma_2)\}}]. \tag{2·21}$$

We note that the allowed $\boldsymbol{\kappa}$ values are given by the equation

$$\boldsymbol{\kappa} = \frac{2\pi}{L}[n_1\mathbf{b}_1+n_2\mathbf{b}_2+n_3\mathbf{b}_3], \tag{2·22}$$

where we have assumed the crystal to be a cube of dimensions L measured in lattice spacings along the basis vectors, where the n_i are integers: $-\frac{1}{2}L \leqslant n_i < \frac{1}{2}L$, and where the $\mathbf{b}_i$ are vectors reciprocal to the basis vectors $\mathbf{a}_i$ which are given by $\mathbf{a}_1 = \mathbf{j}+\mathbf{k}$, $\mathbf{a}_2 = \mathbf{k}+\mathbf{i}$, $\mathbf{a}_3 = \mathbf{i}+\mathbf{j}$ with $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ vectors of equal length along the X, Y, Z axes.

If we write

$$\kappa_i = 2\pi n_i/L, \tag{2·23}$$

we have

$$\left.\begin{aligned}
\sum_{\text{n.n.}}^{12} e^{i(\boldsymbol{\kappa}.\mathbf{l})} &= 2\cos\kappa_1 + 2\cos(\kappa_2-\kappa_3),\\
\sum_{\text{n.n.}}^{34} e^{i(\boldsymbol{\kappa}.\mathbf{l})} &= 2\cos\kappa_2 + 2\cos(\kappa_3-\kappa_1),\\
\sum_{\text{n.n.}}^{56} e^{i(\boldsymbol{\kappa}.\mathbf{l})} &= 2\cos\kappa_3 + 2\cos(\kappa_1-\kappa_2),\\
\sum_{\text{n.n.n.}} e^{i(\boldsymbol{\kappa}.\mathbf{l})} &= 2\cos(-\kappa_1+\kappa_2+\kappa_3) + 2\cos(\kappa_1-\kappa_2+\kappa_3) + 2\cos(\kappa_1+\kappa_2-\kappa_3).
\end{aligned}\right\} \tag{2·24}$$

Using (2·24) we can express β_1, β_2, γ_1, and γ_2 in terms of the n_i, and we can write (2·21) in the form

$$E_g = \alpha S_c^2 + \tfrac{1}{4}N\langle[\sqrt{\{(\beta_1+\gamma_1)\,(\beta_2-\gamma_2)\}}+\sqrt{\{(\beta_1-\gamma_1)\,(\beta_2+\gamma_2)\}}]\rangle, \tag{2·25}$$

where the pointed brackets indicate an average over the n_i—each n_i running from $-\frac{1}{2}L$ to $\frac{1}{2}L$.

A case of particular interest is that of nearest-neighbour interactions only, including anisotropy. Ziman (1952 *a*, *b*, 1953) has shown that if $J_\alpha = J_\beta = J_\gamma = 0$, the f.c.c. will not support type 3A order. We shall find that under these conditions the f.c.c. lattice will not support any antiferromagnetic order.

We have computed numerically E_g for the case where $K = 0$ for various values of $|J_\gamma|/J$ between 0 and 0·4, on the Oxford University Mercury computer. The results are shown in figure 3. For comparison we have also plotted E_g for the case $S \to \infty$, which corresponds to the molecular-field ground state.

It is instructive to write E_g in terms of the molecular-field (or classical spin) ground state E_0

$$E_g = E_0(1+\rho/S); \tag{2·26}$$

the energy scale is fixed by putting the energy of the ferromagnetic ground state equal to $12NJS^2$. The coefficient ρ as function of $|J_\gamma|/J$ is shown in figure 4.

To see whether or not these results are likely to be good approximations to the real ground-state energies, it is necessary to examine whether our assumptions about S_x and S_y

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being much smaller than S_c are valid. For the case where $\delta_1 = \delta_2 = 0$, the Hamiltonian (2·14) can by canonical transformations be reduced to the form

$$H = \alpha S_c^2 + \tfrac{1}{2}\sum_\kappa [(\beta_1+\gamma_1)\, q_{1\kappa}^2 + (\beta_2-\gamma_2)\, p_{1\kappa}^2 + (\beta_1-\gamma_1)\, q_{2\kappa}^2 + (\beta_2+\gamma_2)\, p_{2\kappa}^2], \tag{2·27}$$

where $p_{1\kappa}$, $q_{1\kappa}$, $p_{2\kappa}$, and $q_{2\kappa}$ satisfy the commutation relations

$$[q_{l\kappa}, p_{j\kappa'}]_- = \mathrm{i}\delta_{\kappa\kappa'}\delta_{lj}, \quad [q_{l\kappa}, q_{j\kappa'}]_- = [p_{l\kappa}, p_{j\kappa'}]_- = 0. \tag{2·28}$$

As the potential and kinetic energies of a harmonic oscillator have the same average values we can write

$$\left.\begin{aligned} \langle q_{1\kappa}^2\rangle\,(\beta_1+\gamma_1) &= \langle p_{1\kappa}^2\rangle\,(\beta_2-\gamma_2) = c_{1\kappa}, \\ \langle q_{2\kappa}^2\rangle\,(\beta_1-\gamma_1) &= \langle p_{2\kappa}^2\rangle\,(\beta_2+\gamma_2) = c_{2\kappa}, \end{aligned}\right\} \tag{2·29}$$

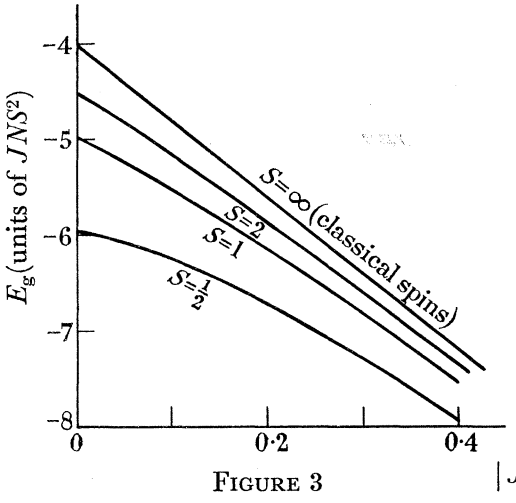

FIGURE 3

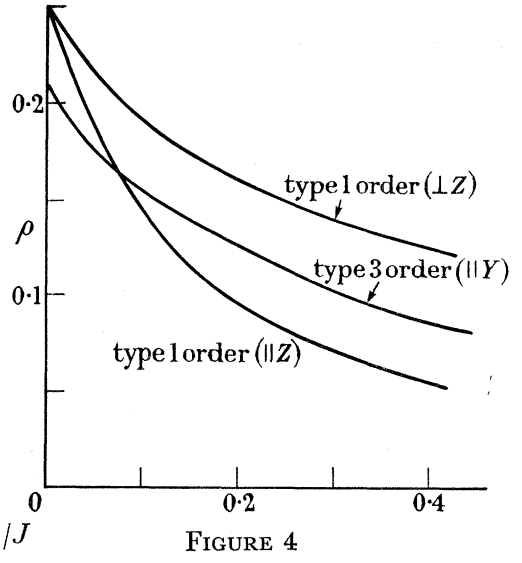

FIGURE 4

FIGURE 3. The ground state energy E_g plotted for the case of f.c.c. type 1 order with all spins along the unique cubic axis as function of the anisotropy parameter for various values of the spin-quantum number S.

FIGURE 4. The quantity ρ from (2·26) as function of the anisotropy parameter for f.c.c. type 1 and type 3A order.

and for the ground state we have (compare (2·19))

$$c_1 = \tfrac{1}{2}E_{1\kappa}, \quad c_2 = \tfrac{1}{2}E_{2\kappa}. \tag{2·30}$$

Combining (2·29), (2·30), and (2·20) we have for the ground state

$$2\langle q_{1\kappa}^2\rangle = \frac{1}{2\langle p_{1\kappa}^2\rangle} = \sqrt{\left(\frac{\beta_2-\gamma_2}{\beta_1+\gamma_1}\right)}; \quad 2\langle q_{2\kappa}^2\rangle = \frac{1}{2\langle p_{2\kappa}^2\rangle} = \sqrt{\left(\frac{\beta_2+\gamma_2}{\beta_1-\gamma_1}\right)}. \tag{2·31}$$

Consider now the j sublattice. We have

$$\begin{aligned} (S_{jz})_{\text{total}} &= \sum_j S_{jz} = \tfrac{1}{2}NS_c - \sum_j \frac{S_{jx}^2+S_{jy}^2}{2S^2} \\ &= \tfrac{1}{2}NS_c - \frac{S}{2S_c}\sum_\kappa (Q_\kappa Q_{-\kappa} + P_\kappa P_{-\kappa}) \\ &= \tfrac{1}{2}NS_c - \frac{S}{4S_c}\sum_\kappa (q_{1\kappa}^2 + q_{2\kappa}^2 + p_{1\kappa}^2 + p_{2\kappa}^2 + q_{1\kappa}q_{2\kappa} + p_{1\kappa}p_{2\kappa}). \end{aligned} \tag{2·32}$$

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As $(S_{jz})_{\text{total}}$ is not a constant of motion, we must take the time average of (2·32). As

$$\langle q_{1\kappa} q_{2\kappa} \rangle = \langle p_{1\kappa} p_{2\kappa} \rangle = 0,$$

we get

$$\langle (S_{jz})_{\text{total}} \rangle = \tfrac{1}{2} N S_c - \frac{SN}{16 S_c} \left\langle \frac{\epsilon_{1\kappa}}{E_{1\kappa}} + \frac{\epsilon_{2\kappa}}{E_{2\kappa}} \right\rangle, \tag{2·33}$$

where we have used (2·31), (2·20), and where

$$\epsilon_{1\kappa} = \beta_1 + \beta_2 + \gamma_1 - \gamma_2, \quad \epsilon_{2\kappa} = \beta_1 + \beta_2 - \gamma_1 + \gamma_2. \tag{2·34}$$

If we consider a state characterized by spin-wave numbers $n_{i\kappa}$ instead of the ground state, we get instead of (2·33)

$$\langle (S_{jz})_{\text{total}} \rangle = \tfrac{1}{2} N S_c - \frac{SN}{8 S_c} \left\langle (n_{1\kappa} + \tfrac{1}{2}) \frac{\epsilon_{1\kappa}}{E_{1\kappa}} + (n_{2\kappa} + \tfrac{1}{2}) \frac{\epsilon_{2\kappa}}{E_{2\kappa}} \right\rangle. \tag{2·35}$$

To get the average value of $(S_{jz})_{\text{total}}$ in a lattice at temperature T, we must take an ensemble average (indicated by $\langle\ \rangle_T$) of (2·35) which means that we must replace the $n_{i\kappa}$ by their statistical average which is given by the equation

$$\begin{aligned} \langle n_{i\kappa} + \tfrac{1}{2} \rangle_T &= \frac{\sum_{n_{i\kappa}} (n_{i\kappa} + \tfrac{1}{2}) \exp\{-\beta (n_{i\kappa} + \tfrac{1}{2}) E_{i\kappa}\}}{\sum_{n_{i\kappa}} \exp\{-\beta (n_{i\kappa} + \tfrac{1}{2}) E_{i\kappa}\}} \\ &= \tfrac{1}{2} \coth (\tfrac{1}{2} \beta E_{i\kappa}), \end{aligned} \tag{2·36}$$

where (k being Boltzmann's constant)

$$\beta = 1/kT. \tag{2·37}$$

We get thus from (2·35)

$$\langle (S_{jz})_{\text{total}} \rangle_T = \tfrac{1}{2} N S_c - \frac{S}{8 S_c} \sum_{\kappa} \left[\frac{\epsilon_{1\kappa}}{E_{1\kappa}} \coth \tfrac{1}{2} \beta E_{1\kappa} + \frac{\epsilon_{2\kappa}}{E_{2\kappa}} \coth \tfrac{1}{2} \beta E_{2\kappa} \right]. \tag{2·38}$$

We can now use (2·38) to investigate how the total sublattice spin depends on the temperature and on the exchange interaction parameters. We must mention that the numerical evaluation of the sums (or averages) occurring in (2·38) are more complicated than of those occurring in (2·25) as the summands are far less smooth in the former case. This means that our results for the sublattice spins are therefore probably less accurate than those for E_g. This is particularly the case in the regions where the ground state differs considerably from the basic molecular-field state, as in those regions the summand becomes very large for certain values. We must also bear in mind that all results of a semi-classical spin-wave treatment should be valid to order S^{-1}—or perhaps even to order $(zS)^{-1}$, where z is the net number of antiparallel spins with large exchange interactions with a particular spin; for instance, $z = 4$ for type 1 order—as the semi-classical approximations are valid to this order (Anderson 1952). The case $S = \frac{1}{2}$ is thus a bad one; (2·33) gives, for instance, the impossible result $\langle (S_{jz})_{\text{total}} \rangle > \frac{1}{2} NS$ for this case.

Once again we consider the case $J_{\alpha\beta} \equiv J_\alpha - J_\beta = 0$, $K = 0$. In the isotropic case when $J_\gamma = 0$, we see that $E_{1\kappa} = E_{2\kappa} = 0$ along several lines in $\boldsymbol{\kappa}$-space, for example, $\kappa_1 = 0$, $\kappa_2 = \kappa_3$ and $\kappa_2 = 0$, $\kappa_3 = \kappa_1$. The expression for $\langle (S_{jz})_{\text{total}} \rangle_T$ does not diverge at zero-temperature, but diverges at any non-zero temperature. This can be seen from (2·38). Near the lines where $E_{1\kappa}$ and $E_{2\kappa}$ vanish the sum over $\boldsymbol{\kappa}$ is approximately equal to

$$\sum_{\kappa} \left[\frac{2\epsilon_{1\kappa}}{\beta E_{1\kappa}^2} + \frac{2\epsilon_{2\kappa}}{\beta E_{2\kappa}^2} \right]. \tag{2·39}$$

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The integral replacing this sum diverges logarithmically, if $J_\gamma = 0$. If $J_\gamma \neq 0$, however, $E_{1\kappa}$ and $E_{2\kappa}$ are zero only at isolated points, and (2·38) converges for non-vanishing temperatures. For the cases where there is no divergence we may replace (2·38) by (2·33) at very low temperatures. We have computed the right-hand side of (2·33) as a function of $|J_\gamma|/J$ in the limit of S large—putting $S_c = S + \frac{1}{2}$—and put the results in the form

$$\langle (S_{jz}) \rangle_{\text{total}} = \tfrac{1}{2}N(S - D), \tag{2·40}$$

where D is a numerical constant. We show in figure 5 the left-hand side of (2·40) as function of $|J_\gamma|/J$. We note that D decreases with increasing $|J_\gamma|/J$, and we conclude that for small, but non-vanishing temperature the f.c.c. antiferromagnetic with isotropic nearest-neighbour interactions only does not have a stable type 1 order, but that this type of order is

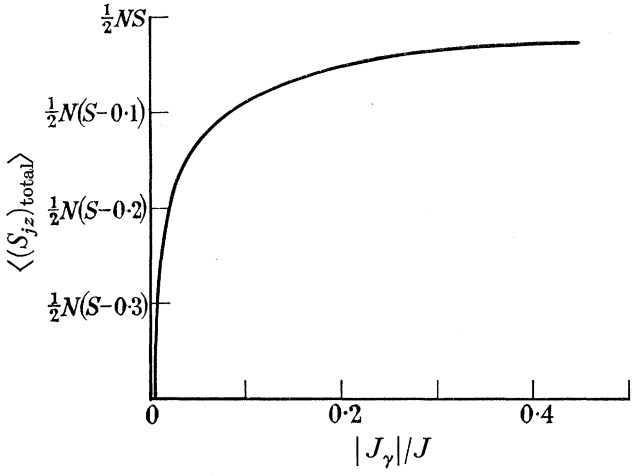

FIGURE 5. The average spin component as function of $|J_\gamma|/J$ for f.c.c. type 1 order with all spins along the unique cubic axis.

stabilized by even a very small amount of (J_γ negative) type dipolar interaction. It is interesting to note that for the simple cubic lattice with isotropic nearest-neighbour interactions only, $D = 0{\cdot}078$ (Anderson 1952). A similar value of D for type 1 order in a f.c.c. lattice would correspond to $|J_\gamma|/J \sim 0{\cdot}125$.

In an actual antiferromagnetic with type 1 order, however, the second-neighbour isotropic exchange parameter K is likely to be of the same order of magnitude as J_γ. A ferromagnetic K will increase the stability, but an antiferromagnetic K will reduce the value of $\langle (S_{jz})_{\text{total}} \rangle$ for the type of order considered in the present subsection. In fact, in the latter case the order vanishes if $K \geqslant \frac{3}{2}J_\gamma$. However, the effect of third-neighbour interactions is largely to counterbalance the effect of K, so that we probably gain little by attempting to include K without also introducing even more remote interactions. As we expect $J \gg K$, the nearest-neighbour-only results are probably quite reasonable approximations.

2 *a* (ii) *Type* 1 *order; all spins in the XY plane*

We now consider the case where $J_\gamma > 0$. In A we found that in this case the spins were alined somewhere in the XY plane, say in the $(a_1, a_2, 0)$ direction, but we were not able to

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obtain any further information about a_1 and a_2. We shall see presently that the spin-wave treatment will provide us with some more information about a_1 and a_2. We can proceed as in § 2 *a* (i) and are led to a Hamiltonian of the form (2·14) where now

$$\left.\begin{aligned}
\alpha &= N(-4J-4J_\gamma+6K),\\
\beta_1 &= S[2(J+J_\gamma)\sum_{\text{n.n.}}^{56}\mathrm{e}^{\mathrm{i}(\boldsymbol{\kappa}.\mathbf{l})}+2K\sum_{\text{n.n.n.}}\mathrm{e}^{\mathrm{i}(\boldsymbol{\kappa}.\mathbf{l})}+8J+8J_\gamma-12K],\\
\beta_2 &= S[(2J-J_\gamma-2a_1a_2J_{\alpha\beta})\sum_{\text{n.n.}}^{5}\mathrm{e}^{\mathrm{i}(\boldsymbol{\kappa}.\mathbf{l})}+(2J-J_\gamma+2a_1a_2J_{\alpha\beta})\sum_{\text{n.n.}}^{6}\mathrm{e}^{\mathrm{i}(\boldsymbol{\kappa}.\mathbf{l})}\\
&\qquad +2K\sum_{\text{n.n.n.}}\mathrm{e}^{\mathrm{i}(\boldsymbol{\kappa}.\mathbf{l})}+8J+8J_\gamma-12K],\\
\gamma_1 &= S[(2J-J_\gamma)\sum_{\text{n.n.}}^{1234}\mathrm{e}^{\mathrm{i}(\boldsymbol{\kappa}.\mathbf{l})}],\\
\gamma_2 &= S[(2J-a_1^2J_\gamma+2a_2^2J_\gamma)\sum_{\text{n.n.}}^{12}\mathrm{e}^{\mathrm{i}(\boldsymbol{\kappa}.\mathbf{l})}+(2J+2a_1^2J_\gamma-a_2^2J_\gamma)\sum_{\text{n.n.}}^{34}\mathrm{e}^{\mathrm{i}(\boldsymbol{\kappa}.\mathbf{l})}],\\
\delta_1 &= 0,\\
\delta_2 &= SJ_{\alpha\beta}[-a_1\sum_{\text{n.n.}}^{1}\mathrm{e}^{\mathrm{i}(\boldsymbol{\kappa}.\mathbf{l})}+a_1\sum_{\text{n.n.}}^{2}\mathrm{e}^{\mathrm{i}(\boldsymbol{\kappa}.\mathbf{l})}+a_2\sum_{\text{n.n.}}^{3}\mathrm{e}^{\mathrm{i}(\boldsymbol{\kappa}.\mathbf{l})}-a_2\sum_{\text{n.n.}}^{4}\mathrm{e}^{\mathrm{i}(\boldsymbol{\kappa}.\mathbf{l})}].
\end{aligned}\right\} \tag{2·41}$$

The co-ordinate system Σ' was chosen such that the transformation matrix A of (A 2·3) was of the form

$$A \equiv \begin{Vmatrix} 0 & 0 & 1\\ a_2 & -a_1 & 0\\ a_1 & a_2 & 0 \end{Vmatrix}. \tag{2·42}$$

Having obtained the Hamiltonian, we can proceed as before. The ground-state energy E_g is now a function of a_1 and a_2 and we can minimize E_g with respect to these parameters. If we put

$$a_1 = \cos\theta, \quad a_2 = \sin\theta, \tag{2·43}$$

and put $J_{\alpha\beta} = 0$, we find that E_g is a minimum for $\theta = 0$ or $\frac{1}{2}\pi$, corresponding to the preferred direction of ordering being along one of the cubic axes in the XY plane. This result is likely to be approximately true even if $J_{\alpha\beta} \neq 0$, at least as long as J_γ is not small compared to $|J_{\alpha\beta}|$. This conclusion is based upon the fact that those regions of $\boldsymbol{\kappa}$ space for which $E_{1\boldsymbol{\kappa}}$ and $E_{2\boldsymbol{\kappa}}$ vanish or are nearly zero in the isotropic case—that is, along or near the lines $\kappa_1 = 0$, $\kappa_2 = \kappa_3$, $\kappa_2 = 0$, $\kappa_1 = \kappa_3$, $\kappa_1 = \pi$, $\kappa_2 - \kappa_3 = \pi$, and $\kappa_2 = \pi$, $\kappa_3 - \kappa_1 = \pi$—will provide the main anisotropy contributions to E_g. In those regions $J_{\alpha\beta}$ contributes little or nothing to E_g so that we expect J_γ to affect E_g to a much greater extent than $J_{\alpha\beta}$.

We shall now put $J_{\alpha\beta} = 0$, $K = 0$, $a_1 = 1$, and $a_2 = 0$—assuming thus that the basic array is ordered along the X axis. We can then evaluate E_g as a function of J_γ/J. The results are given in figures 4 and 6. In figure 4 we have given the quantity ρ defined by (2·26) and in figure 6 E_g itself for various values of S.

As far as $\langle (S_{jz})_{\text{total}} \rangle$ is concerned, however, we find that it diverges, whatever the value of J_γ/J. This is a consequence of the fact that $\beta_2 - \gamma_2$ vanishes along the line $\kappa_2 = 0$, $\kappa_1 = \kappa_3$ while $\beta_2 + \gamma_2$ vanishes along the line $\kappa_2 = \pi$, $\kappa_3 - \kappa_1 = \pi$ when $K = J_{\alpha\beta} = 0$, $a_1 = 1$, $a_2 = 0$. One can show that the divergence does not disappear when $J_\alpha \neq J_\beta$, but that it can be removed by an isotropic ferromagnetic second-neighbour interaction or by antiferromagnetic second- and third-neighbour exchange parameters K and L (see (A 2·12)),

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provided $4L > K$. This type of order has been found experimentally in $MnTe_2$ (Corliss, Elliott & Hastings 1959).

The question arises how much reliance can be placed upon our results about the ground-state energy, as we have just seen that the order, for which the energy was calculated, is not stable. However, a similar situation occurs for the spin-wave theory of the linear chain (Anderson 1952); in that case it has been shown that the ground-state energy derived by the spin-wave method is, nevertheless, a fair approximation to the exact ground-state energy which is known in this case (Bethe 1931). One can only suppose that the basic assumption that the sublattice spin is large and nearly equal to S is fulfilled temporarily over sufficiently large regions of the lattice so that the energy parameter is not badly approximated. It is thus possible that the same is true for our lattices and that the ground-state energies which we have calculated are therefore worth recording.

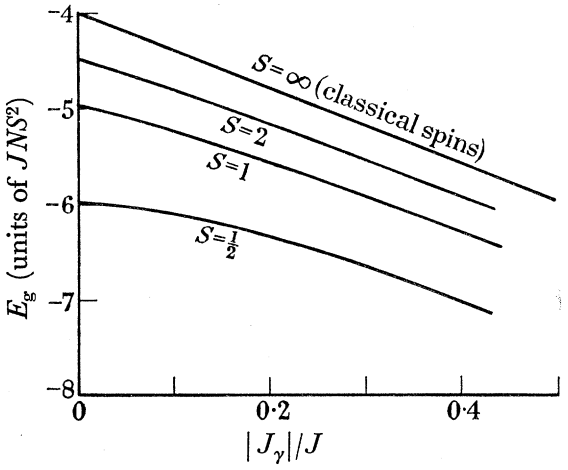

FIGURE 6. The ground-state energy E_g plotted for the case of f.c.c. type 1 order with all spins at right angles to the unique cubic axis as function of the anisotropy parameter for various values of the spin-quantum number S.

It is important to note that the result concerning the preferred direction of ordering which was derived from the ground-state energy-expression still holds when we include the more remote interactions to stabilize the order. This is a consequence of the fact that the order can be stabilized by including isotropic interactions only. This result has, however, only been proved for the case where the anisotropy is entirely due to nearest-neighbour exchange. It must be mentioned that if the anisotropy is mainly due to dipole-dipole interactions, we may get considerable anisotropy from more remote neighbours, as the dipole-dipole interactions only decrease as r^{-3}.

2 (*b*) *Type 2 order in the f.c.c. lattice*

We shall consider as the basic arrangement that of figure 7. This ordered arrangement consists of ferromagnetic $[1, 1, -1]$ planes, with adjacent planes antiferromagnetically alined. Again there are two cases: if $J_{\alpha\beta} > 0$, the preferred direction is the $(1, 1, -1)$ direction; if $J_{\alpha\beta} < 0$, the spins are alined somewhere in the $[1, 1, -1]$ plane, say, in the $(a_1, a_2, a_1 + a_2)$ direction. We shall consider these two cases separately.

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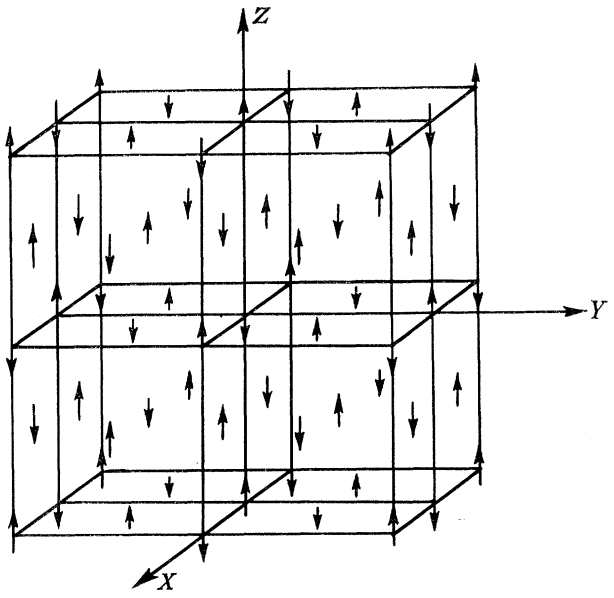

FIGURE 7. Type 2 order in the f.c.c. lattice.

2 (*b*) (i) *Type 2 order; all spins in the* (1, 1, −1) *direction*

The analysis proceeds as before and we get again a Hamiltonian of the form (2·14) where now

$$\left.\begin{aligned}
\alpha &= N(-4J_{\alpha\beta}-6K),\\
\beta_1 &= S[8J_{\alpha\beta}+12K+(2J+\tfrac{4}{3}J_\alpha+\tfrac{1}{6}J_\gamma)\sum_{\text{n.n.}}^{13}e^{i(\kappa.l)}+(2J+\tfrac{2}{3}J_\beta+\tfrac{4}{3}J_\gamma)\sum_{\text{n.n.}}^{6}e^{i(\kappa.l)}],\\
\beta_2 &= S[8J_{\alpha\beta}+12K+(2J+\tfrac{1}{2}J_\gamma)\sum_{\text{n.n.}}^{13}e^{i(\kappa.l)}+2(J+J_\alpha)\sum_{\text{n.n.}}^{6}e^{i(\kappa.l)}],\\
\gamma_1 &= S[(2J+\tfrac{4}{3}J_\beta+\tfrac{1}{6}J_\gamma)\sum_{\text{n.n.}}^{24}e^{i(\kappa.l)}+(2J+\tfrac{2}{3}J_\alpha+\tfrac{4}{3}J_\gamma)\sum_{\text{n.n.}}^{5}e^{i(\kappa.l)}+2K\sum_{\text{n.n.n.}}e^{i(\kappa.l)}],\\
\gamma_2 &= S[(2J+\tfrac{1}{2}J_\gamma)\sum_{\text{n.n.}}^{24}e^{i(\kappa.l)}+2(J+J_\beta)\sum_{\text{n.n.}}^{5}e^{i(\kappa.l)}+2K\sum_{\text{n.n.n.}}e^{i(\kappa.l)}],\\
\delta_1 &= \frac{S}{\sqrt{12}}(J_\beta-3J_\alpha+2J_\gamma)\left[\sum_{\text{n.n.}}^{1}e^{i(\kappa.l)}-\sum_{\text{n.n.}}^{3}e^{i(\kappa.l)}\right],\\
\delta_2 &= \frac{S}{\sqrt{12}}(J_\alpha-3J_\beta+2J_\gamma)\left[\sum_{\text{n.n.}}^{2}e^{i(\kappa.l)}-\sum_{\text{n.n.}}^{4}e^{i(\kappa.l)}\right].
\end{aligned}\right\}\qquad(2\cdot44)$$

The transformation matrix in this case was chosen to be given by the equation

$$A=\frac{1}{\sqrt{6}}\begin{Vmatrix}1 & 1 & 2\\ \sqrt{3} & -\sqrt{3} & 0\\ \sqrt{2} & \sqrt{2} & -\sqrt{2}\end{Vmatrix}.\qquad(2\cdot45)$$

In this case one cannot put $\delta_1=\delta_2=0$ without discarding all anisotropy-parameters, and E_g must be obtained from the more general equations (2·17) and (2·19). For the isotropic case one finds that the order considered is stable, if $2K>J$, but not, if $2K\leqslant J$. If $2K=J$, one can, however, find values of the anisotropy parameters such that the order is stable. If $2K<J$ the spin-wave theory breaks down dramatically for the type of order considered and the energy becomes imaginary. We must note that the spin-wave approximations become poor in the immediate vicinity of $2K=J$ because our basic assumption that the true ground state is near the basic ordered state considered becomes progressively

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less valid when we approach $2K = J$. To see this we have computed the values of the sub-lattice spins for the isotropic case. The results are given in figure 8. As $K/J \to \infty$ the f.c.c. type 2 order becomes equivalent to four independent simple cubic lattices. This provides us with a limit for the average spin component as $K/J \to \infty$, and we have used Anderson's

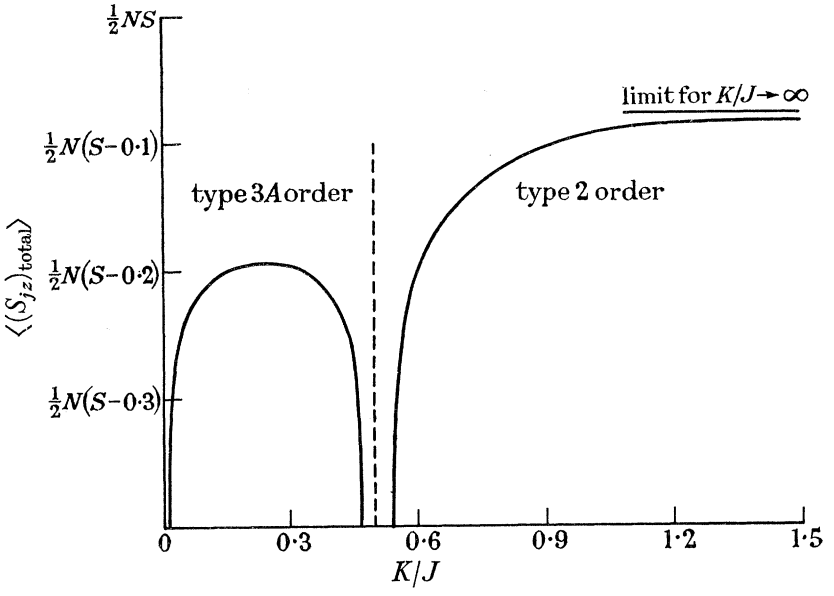

FIGURE 8. The average spin component as function of K/J for the isotropic case for f.c.c. type 2 and type 3A order.

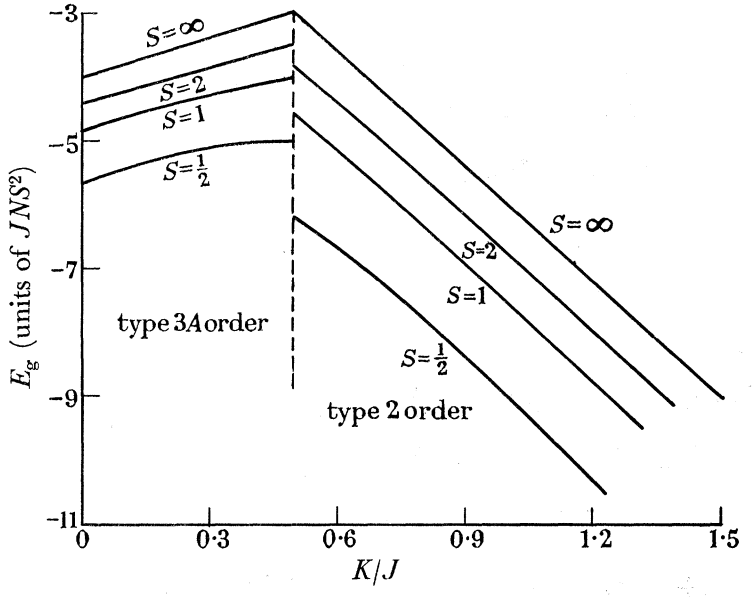

FIGURE 9. The isotropic ground-state energy for f.c.c. type 2 and type 3A order as function of K/J for different values of S.

data (1952) for the simple cubic lattice. The limit for $\langle (S_{jz})_{\text{total}} \rangle$ is $\frac{1}{2}N(S-0{\cdot}078)$. In figures 9 and 10 we give the ground-state energy for the isotropic case and the parameter ρ of (2·26). In figure 10 we have again indicated the limit of ρ as $K/J \to \infty$; this limit is 0·097. We note that in figures 8, 9, and 10 we have also given the behaviour of the various parameters for $2K < J$ when type 3A order is the stable one, as we shall see presently.

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2 (*b*) (ii) *Type 2 order; all spins in the* [1, 1, −1] *plane*

In this case we choose for A the matrix

$$\left.\begin{aligned} A \equiv \begin{Vmatrix} 3^{-\frac{1}{2}} & 3^{-\frac{1}{2}} & -3^{-\frac{1}{2}} \\ a_3 & a_4 & a_3+a_4 \\ a_1 & a_2 & a_1+a_2 \end{Vmatrix}, \\ a_3^2 = \tfrac{2}{3}-a_1^2, \quad a_4^2 = \tfrac{2}{3}-a_2^2, \end{aligned}\right\} \tag{2·46}$$

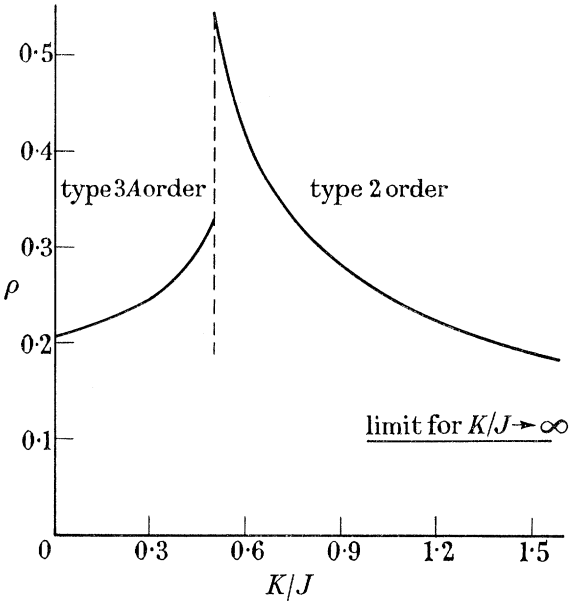

FIGURE 10. The quantity ρ from (2·26) for the isotropic case as function of K/J for f.c.c. type 2 and type 3A order.

and we find for the coefficients of (2·14)

$$\left.\begin{aligned} \alpha &= N(2J_{\alpha\beta}-6K), \\ \beta_1 &= S[-4J_{\alpha\beta}+12K+(2J-\tfrac{2}{3}J_{\alpha\beta})\sum_{\text{n.n.}}^{136} e^{i(\kappa.l)}], \\ \beta_2 &= S[-4J_{\alpha\beta}+12K+(2J+\tfrac{1}{2}J_\gamma-2a_3a_4J_{\alpha\beta}+3a_3a_4J_\gamma)\sum_{\text{n.n.}}^{6} e^{i(\kappa.l)} \\ &\quad +(2J+a_3^2J_\gamma+4a_4^2J_\alpha+4a_3a_4J_\alpha)\sum_{\text{n.n.}}^{1} e^{i(\kappa.l)} \\ &\quad +(2J+a_4^2J_\gamma+4a_3^2J_\alpha+4a_3a_4J_\alpha)\sum_{\text{n.n.}}^{3} e^{i(\kappa.l)}], \\ \gamma_1 &= S[(2J+\tfrac{2}{3}J_{\alpha\beta})\sum_{\text{n.n.}}^{245} e^{i(\kappa.l)}+2K\sum_{\text{n.n.n.}} e^{i(\kappa.l)}], \\ \gamma_2 &= S[(2J+\tfrac{1}{2}J_\gamma+2a_3a_4J_{\alpha\beta}+3a_3a_4J_\gamma)\sum_{\text{n.n.}}^{5} e^{i(\kappa.l)}+(2J+a_3^2J_\gamma+4a_4^2J_\beta+4a_3a_4J_\beta) \\ &\quad \times\sum_{\text{n.n.}}^{2} e^{i(\kappa.l)}+(2J+a_4^2J_\gamma+4a_3^2J_\beta+4a_3a_4J_\beta)\sum_{\text{n.n.}}^{4} e^{i(\kappa.l)}+2K\sum_{\text{n.n.n.}} e^{i(\kappa.l)}], \\ \delta_1 &= \frac{2S}{\sqrt{3}}J_{\gamma\beta}[a_3\sum_{\text{n.n.}}^{1} e^{i(\kappa.l)}+a_4\sum_{\text{n.n.}}^{3} e^{i(\kappa.l)}-(a_3+a_4)\sum_{\text{n.n.}}^{6} e^{i(\kappa.l)}], \\ \delta_2 &= \frac{2S}{\sqrt{3}}J_{\gamma\alpha}[a_3\sum_{\text{n.n.}}^{2} e^{i(\kappa.l)}+a_4\sum_{\text{n.n.}}^{4} e^{i(\kappa.l)}-(a_3+a_4)\sum_{\text{n.n.}}^{5} e^{i(\kappa.l)}], \\ J_{\gamma\alpha} &= J_\gamma-J_\alpha, \quad J_{\gamma\beta}=J_\gamma-J_\beta. \end{aligned}\right\} \tag{2·47}$$

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To find a_3 and a_4 we should now minimize the energy with respect to these variables. This we have not been able to do, since the Hamiltonian is of the general form (2·17) rather than (2·20). The coefficients (2·47) will, however, be used in connexion with the discussion of antiferromagnetic resonance in § 4. In the limit of isotropic exchange only, the equations (2·47) and (2·44) are, of course, identical.

2 (*c*) *Type 3A order in the f.c.c. lattice*

The basic arrangement is that given in figure 11 with the Y axis as the unique cubic axis. Again there are two cases depending on whether J_γ is positive or negative. In the first case the preferred direction of the spins is parallel to the Y axis, and in the second case somewhere in the XZ plane. We consider these two cases separately.

2*c* (i) *Type 3A order; all spins parallel to the Y axis*

In this case we have for A the matrix

$$A \equiv \begin{Vmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{Vmatrix} \tag{2·48}$$

and for the coefficients in the Hamiltonian the expressions

$$\left.\begin{aligned}
\alpha &= N(-4J-4J_\gamma+2K),\\
\beta_1 &= S[(J-\tfrac{1}{2}J_\gamma)\sum_{\text{n.n.}}^{12} e^{i(\kappa.l)}+(J+J_\gamma)\sum_{\text{n.n.}}^{56} e^{i(\kappa.l)}+2K\sum_{\text{n.n.n.}}^{13} e^{i(\kappa.l)}+8J+8J_\gamma-4K],\\
\beta_2 &= S[(J+J_\gamma)\sum_{\text{n.n.}}^{12} e^{i(\kappa.l)}+(J-\tfrac{1}{2}J_\gamma)\sum_{\text{n.n.}}^{56} e^{i(\kappa.l)}+2K\sum_{\text{n.n.n.}}^{13} e^{i(\kappa.l)}+8J+8J_\gamma-4K],\\
\gamma_1 &= S[(J-\tfrac{1}{2}J_\gamma)\sum_{\text{n.n.}}^{12} e^{i(\kappa.l)}+(J+J_\gamma)\sum_{\text{n.n.}}^{56} e^{i(\kappa.l)}+(2J-J_\gamma)\sum_{\text{n.n.}}^{34} e^{i(\kappa.l)}+2K\sum_{\text{n.n.n.}}^{2} e^{i(\kappa.l)}],\\
\gamma_2 &= S[(J+J_\gamma)\sum_{\text{n.n.}}^{12} e^{i(\kappa.l)}+(2J-J_\gamma)\sum_{\text{n.n.}}^{34} e^{i(\kappa.l)}+(J-\tfrac{1}{2}J_\gamma)\sum_{\text{n.n.}}^{56} e^{i(\kappa.l)}+2K\sum_{\text{n.n.n.}}^{2} e^{i(\kappa.l)}],\\
\delta_1 &= 0,\\
\delta_2 &= SJ_{\alpha\beta}[\sum_{\text{n.n.}}^{3} e^{i(\kappa.l)}-\sum_{\text{n.n.}}^{4} e^{i(\kappa.l)}],
\end{aligned}\right\} \tag{2·49}$$

where $\sum_{\text{n.n.n.}}^{1}$, $\sum_{\text{n.n.n.}}^{2}$, and $\sum_{\text{n.n.n.}}^{3}$ refer to sums over only those next-nearest neighbours with connecting vectors in the $(1,0,0)$, the $(0,1,0)$, and the $(0,0,1)$ directions, respectively.

One can show that the situation is now similar to the one in subsection 2*a* (ii): (i) for the isotropic case the ground state shows order, but an infinitesimal amount of thermal energy is sufficient to make the order unstable; (ii) the inclusion of nearest-neighbour anisotropy does not stabilize this order (the sum (2·39) diverges along $\kappa_3 = \pi$, $\kappa_1 - \kappa_2 = \pi$); (iii) a small amount of next-nearest-neighbour (antiferromagnetic) isotropic exchange does, however, stabilize the order. Using the same arguments as in subsection 2*a* (ii) we feel that the ground-state energy computed for nearest-neighbour interactions only may well give a fair approximation to the actual ground-state energy for this case. We have computed E_g as a function of J_γ/J for various values of S, assuming $J_{\alpha\beta} = 0$. The results are given in figures 12 and 4.

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2*c* (ii) *Type* 3*A order; all spins in the XZ plane*

The molecular-field theory was not able to predict whether or not this type of order was a 'proper' one, that is, whether the spins in adjacent *XZ* planes (between which there was in the molecular-field theory no interaction) were alined in the same direction. However,

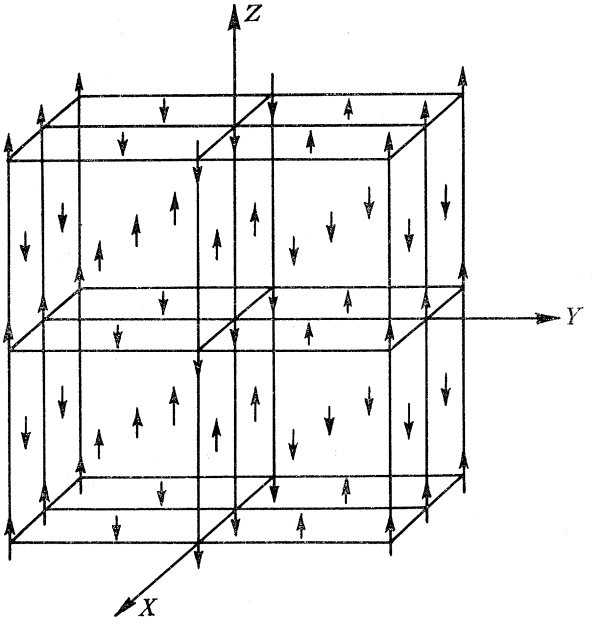

FIGURE 11. Type 3A order in the f.c.c. lattice.

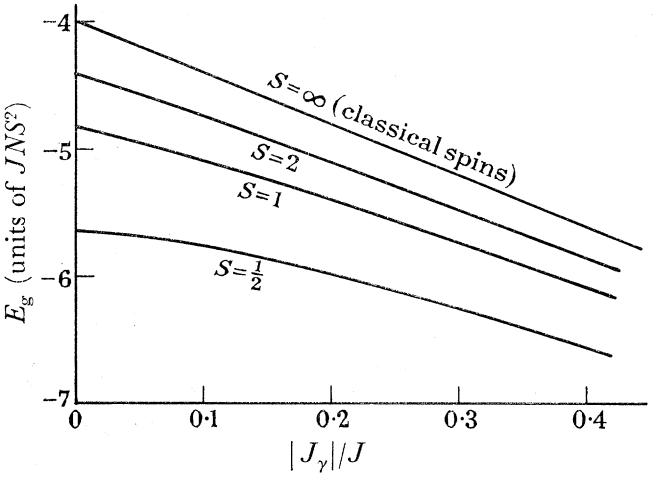

FIGURE 12. The ground-state energy E_g plotted for the f.c.c. type 3A order with all spins alined parallel to the unique cubic axis as function of the anisotropy parameter for various values of S.

if one uses spin-wave theory one can prove that the ground-state energy of this type of order is a minimum if the angle between the preferred directions in adjacent *XZ* planes vanishes (M. E. Lines, unpublished Oxford D.Phil. Thesis). The actual direction of the ordering can also be found by minimizing the ground-state energy. The result of the minimization is that if $J_{\alpha\beta} = 0$, the preferred direction is along either the *X* axis or the *Z* axis. We can

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thus choose the transformation matrix A to be the unit matrix and we get for the coefficients in the Hamiltonian the expression (we have put $J_{\alpha\beta} = 0$)

$$\left.\begin{aligned}
\alpha &= N[-4J+2J_\gamma+2K],\\
\beta_1 &= S[(J+J_\gamma)\sum_{\text{n.n.}}^{12} e^{i(\kappa.l)}+(J-\tfrac{1}{2}J_\gamma)\sum_{\text{n.n.}}^{56} e^{i(\kappa.l)}+2K\sum_{\text{n.n.n.}}^{13} e^{i(\kappa.l)}+8J-4J_\gamma-4K],\\
\beta_2 &= S[(J-\tfrac{1}{2}J_\gamma)\sum_{\text{n.n.}}^{1256} e^{i(\kappa.l)}+2K\sum_{\text{n.n.n.}}^{13} e^{i(\kappa.l)}+8J-4J_\gamma-4K],\\
\gamma_1 &= S[(J+J_\gamma)\sum_{\text{n.n.}}^{12} e^{i(\kappa.l)}+(2J-J_\gamma)\sum_{\text{n.n.}}^{34} e^{i(\kappa.l)}+(J-\tfrac{1}{2}J_\gamma)\sum_{\text{n.n.}}^{56} e^{i(\kappa.l)}+2K\sum_{\text{n.n.n.}}^{2} e^{i(\kappa.l)}],\\
\gamma_2 &= S[(J-\tfrac{1}{2}J_\gamma)\sum_{\text{n.n.}}^{1256} e^{i(\kappa.l)}+2(J+J_\gamma)\sum_{\text{n.n.}}^{34} e^{i(\kappa.l)}+2K\sum_{\text{n.n.n.}}^{2} e^{i(\kappa.l)}],\\
\delta_1 &= \delta_2 = 0.
\end{aligned}\right\} \quad (2{\cdot}50)$$

We are not able to evaluate the ground-state energy for the case of nearest-neighbour interactions only, since it is imaginary except in the limit $J_\gamma = 0$. The energy is real, however, and the order stabilized, if we include suitable isotropic second- and third-neighbour interactions. For the isotropic case the order is stable with just antiferromagnetic nearest- and next-nearest-neighbour interactions provided $2K < J$. For larger K/J ratios type 2 order takes over.

We have calculated the values of $\langle (S_{jz})_{\text{total}} \rangle$, E_g, and ρ for the isotropic case and for various values of K/J; the results of these calculations are plotted in figures 8, 9, and 10. We may mention here that at $2K = J$ the molecular-field theory gives the same value of E_g for type 2 and type 3A order, while spin-wave theory gives a lower E_g value for type 2 order.

From the molecular-field theory of A we saw that the net interaction between neighbouring XZ planes for the type 3A order with nearest-neighbour exchange only is zero. The order then consists of isolated plane quadratic layers of spins. When we examine the type 1 order with nearest-neighbour exchange only, we find that there exists an interaction proportional to $12J_\gamma(a_{13}^2 - a_{12}^2)\,S^2$ between adjacent YZ planes and another, proportional to $12J_\gamma(a_{13}^2 - a_{11}^2)\,S^2$, between adjacent XZ planes in the basic array. For the case of a negative J_γ, $a_{13}^2 = 1$, $a_{11} = a_{12} = 0$, and both these interactions are equal to $12J_\gamma S^2$. For the case of positive J_γ, $a_{13} = 0$, and we can separate the structure into isolated plane quadratic layers, if either a_{11} or a_{12} is zero. The latter condition is just the one which is obtained by minimizing the spin-wave ground-state energy. The spin-wave analysis shows that for the case of nearest-neighbour exchange only, the types 3A order are not stable, the type 1 order (J_γ negative) is stable, and the type 1 order (J_γ positive) is unstable.

From this evidence it would seem likely that a necessary (though perhaps not sufficient) condition for an order to be stable is that there should not be any plane within the basic array which has vanishing net interactions with the rest of the lattice.

A further instructive example of the importance of the 'out of plane' interactions for stabilizing the order is the case of the isotropic type 3A order with nearest-neighbour and next-nearest-neighbour interactions. In the limit $K = 0$, the XZ planes are isolated. Any spin in the lattice has four parallel next-nearest neighbours, and only two antiparallel ones. In spite of the larger number of parallel next-nearest neighbours, the spin-wave theory shows that we require an antiferromagnetic interaction to stabilize the order. We note

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that the two antiparallel next-nearest neighbours are just the ones which are not contained in the same XZ plane as the central spin. The four parallel next-nearest neighbours are in this XZ plane and do not appear therefore to be effective in stabilizing the order.

3. The body-centred tetragonal lattice

Of the types of order found in A for a b.c.t. magnetic lattice, the most commonly found experimentally is the type 1 order (see figure 13). Type 1 order with the Z axis (which we take along the tetragonal axis) as the preferred direction is found for MnF_2, FeF_2, and CoF_2.

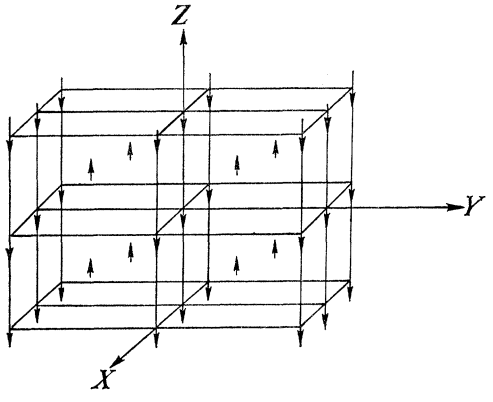

Figure 13. Type 1 order in the b.c.t. lattice.

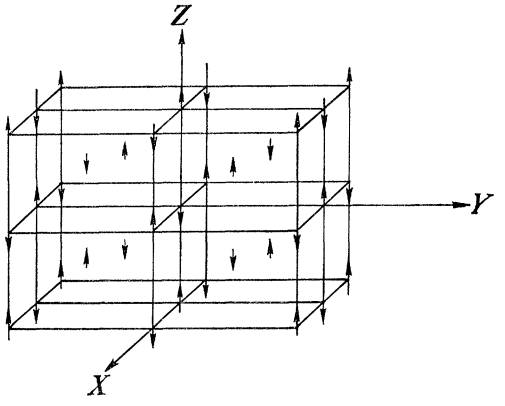

Figure 14. Type 2 order in the b.c.t. lattice.

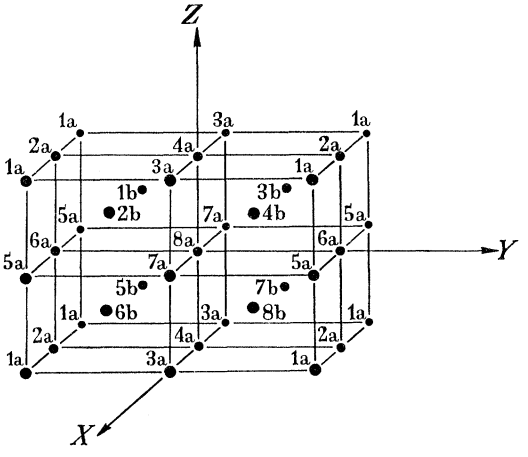

Figure 15. The b.c.t. lattice.

This is a type of order which can be separated into two interlocking simple tetragonal ferromagnetic sublattices and can easily be treated by spin-wave methods. Type 2 order (see figure 14) with the a and b sublattices being both antiferromagnetically ordered with a preferred direction perpendicular to the Z axis, but with mutually perpendicular preferred directions has been suggested for MnO_2 (but see Yoshimori 1959) and is of particular interest since it does not have a unique preferred direction. This type of ordering we called in A the rutile type diagonal ordering. This can also be treated by spin-wave methods, but instead of two sets of spin-waves, we must introduce four sets. In figure 15 we have given the sublattices of the b.c.t. lattice.

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3 (*a*) *Type* 1 *order in the b.c.t. lattice*

We shall include in our considerations the nearest- and next-nearest-neighbour exchange interactions, and assume to begin with that they are anisotropic. We shall also include the anisotropy due to the crystalline field (see equation (A 7·12)). We shall use the expressions for the exchange energies obtained in A, dropping, however, the terms with L_α, L_β, and L_γ in (A 7·4). The derivation of the Hamiltonian is straightforward but tedious and we shall not give all details. The next-nearest neighbour pairs are here split into four groups corresponding to the following four directions for the connexions between the neighbours: 1: $(1, 1, -w)$; 2: $(1, 1, w)$; 3: $(1, -1, -w)$; 4: $(1, -1, w)$, where $w = c_0/a_0$ is the ratio of the dimensions of the unit cell in the Z and X directions. If we designate again all 'up' spins by the suffix j and all 'down' spins by the suffix k, we get again for the Hamiltonian an equation of the form (2·9) where the various operators are now given by the expression

$$\left.\begin{aligned}
\Delta_1 &= 2D\sum_{\text{n.}} + 2(J+J_\alpha)\sum_{\text{n.n.}} - (2K+2w^2K_\alpha P^2+8K_\gamma Q^2w^{-2})\sum_{\text{n.n.n.}},\\
\Delta_2 &= -\tfrac{3}{2}D\sum_{\text{n.}} - (J+J_\alpha)\sum_{\text{n.n.}} + (K+w^2K_\alpha P^2+4K_\gamma Q^2w^{-2})\sum_{\text{n.n.n.}},\\
\lambda_1 &= \lambda_2 = (J-\tfrac{1}{2}J_\alpha)\sum_{\text{n.n.}},\\
\mu_1 &= \mu_2 = (2K+2K_\alpha P^2+K_\beta+2K_\gamma Q^2)\sum_{\text{n.n.n.}},\\
\nu_1 &= 0,\\
\nu_2 &= (2K_\alpha P^2-K_\beta+2K_\gamma Q^2)\,[\sum_{\text{n.n.n.}}^{12} - \sum_{\text{n.n.n.}}^{34}],
\end{aligned}\right\} \tag{3·1}$$

where $\sum_{\text{n.}}$ indicates a sum over all spins in the lattice, where P and Q are given by the equations (see A (6·3))

$$P = \frac{1}{\sqrt{(2+w^2)}}, \quad Q = \frac{w}{\sqrt{(4+2w^2)}}, \tag{3·2}$$

and where J_α, J_β, J_γ, K_α, K_β, and K_γ are the anisotropy of the nearest- and next-nearest-neighbour exchange interactions (see A, § 7).

We now introduce the spin-waves as in § 2; the only difference is that $\boldsymbol{\kappa}$ now runs over $\frac{1}{2}N$ values in the first Brillouin zone of the b.c.t. reciprocal lattice. The analysis proceeds as before, and we are led to a Hamiltonian of the form (2·14) with the coefficients given by the expressions

$$\left.\begin{aligned}
\alpha &= N(2J+2J_\alpha+2D-8K-8w^2K_\alpha P^2-32K_\gamma Q^2w^{-2}),\\
\beta_1 = \beta_2 = \beta &= S[(2J-J_\alpha)\sum_{\text{n.n.}} e^{i(\boldsymbol{\kappa}.\mathbf{l})} - 4J-4J_\alpha-6D+16K+16w^2K_\alpha P^2+64K_\gamma Q^2w^{-2}],\\
\gamma_1 = \gamma_2 = \gamma &= S(2K+2K_\alpha P^2+K_\beta+2K_\gamma Q^2)\sum_{\text{n.n.n.}} e^{i(\boldsymbol{\kappa}.\mathbf{l})},\\
\delta_1 = 0, \quad \delta_2 &= S(2K_\alpha P^2-K_\beta+2K_\gamma Q^2)\,[\sum_{\text{n.n.n.}}^{12} e^{i(\boldsymbol{\kappa}.\mathbf{l})} - \sum_{\text{n.n.n.}}^{34} e^{i(\boldsymbol{\kappa}.\mathbf{l})}].
\end{aligned}\right\} \tag{3·3}$$

For the $E_{i\boldsymbol{\kappa}}$ we find

$$E_{1\boldsymbol{\kappa}} = \sqrt{\{(\beta+\delta_2)^2-\gamma^2\}}, \quad E_{2\boldsymbol{\kappa}} = \sqrt{\{(\beta-\delta_2)^2-\gamma^2\}}. \tag{3·4}$$

and for the ground-state energy E_g

$$E_g = \alpha S_c^2 + \tfrac{1}{4}N\langle[\sqrt{\{(\beta+\delta_2)^2-\gamma^2\}}+\sqrt{\{(\beta-\delta^2)^2-\gamma^2\}}]\rangle. \tag{3·5}$$

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As this type of order requires a considerable next-nearest-neighbour exchange, it would not be a good approximation to put $\delta_2 = 0$ in this case. However, if we do not do this the evaluation of the total sublattice spin becomes too cumbersome, and we have therefore assumed isotropic interaction for our actual calculations so that we can again use equations (2·33) and (2·38).

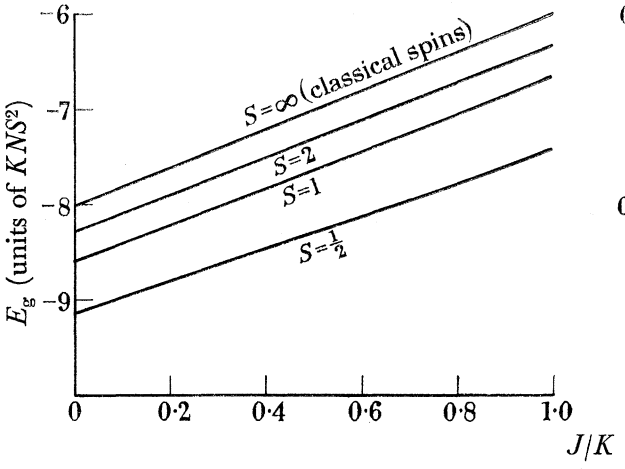

FIGURE 16. The ground-state energy E_g plotted for the isotropic b.c.t. type 1 order as function of J/K for various values of S.

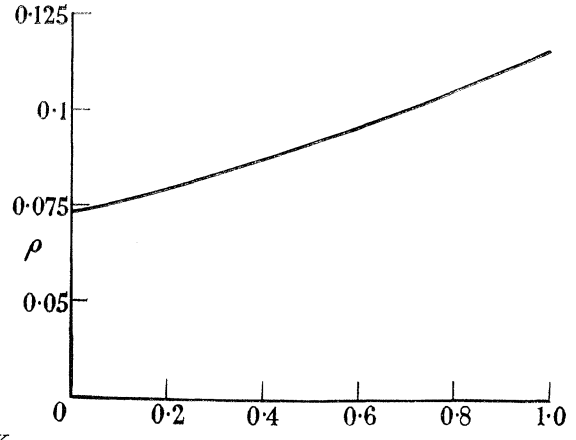

FIGURE 17. The quantity ρ from (2·26) as function of J/K for the isotropic b.c.t. type 1 order.

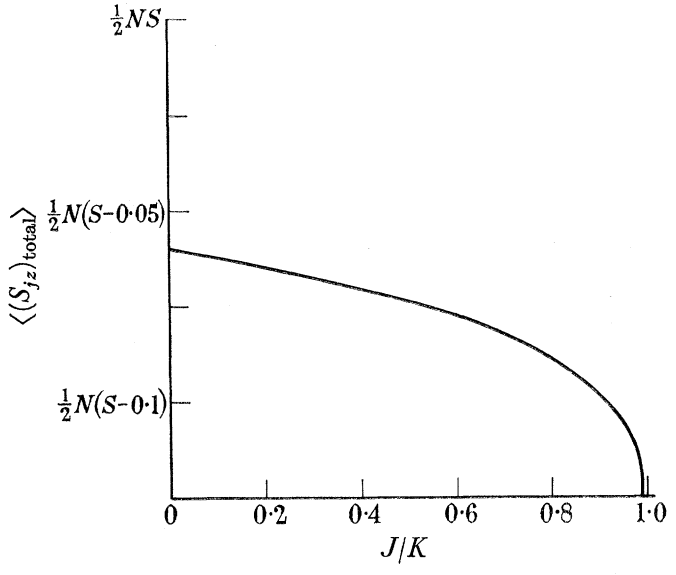

FIGURE 18. The average spin component as function of J/K for the isotropic b.c.t. type 1 order.

As long as $J < K$, we find that the ground state is ordered at non-vanishing temperatures even for the case of isotropic exchange interactions only. If $J > 2K$, type 2 order is stable, but none of the types of order found in A is stable if $K < J < 2K$. Yoshimori (1959) has, however, found a screw-type order where each XY plane has its spins ferromagnetically alined perpendicularly to the Z axis and where the spin directions form a spiral along the Z axis,

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the pitch of which depends upon the ratio J/K. Yoshimori investigated this type of order by both molecular-field and spin-wave methods. It is stable just in the range $K < J < 2K$. The reason why we did not find it in A is that it has a periodicity which is greater than two unit cell lengths in the Z direction, and those types of order were explicitly excluded from our considerations.

Assuming isotropic exchange interactions we have evaluated E_g, ρ, and $\langle (S_{jz})_{\text{total}} \rangle$ for various values of the ratio J/K between 0 and 1. The results are shown in figures 16, 17, and 18.

3 (*b*) *Type 2 order in the b.c.t. lattice*

We saw in A that the basic arrangement of figure 14 shows a rutile diagonal spin pattern provided $D > J_\alpha$, or $D < J_\alpha$, but $3\,|D - J_\alpha| < |J_\beta - J_\gamma - E|$. We shall assume that $J_\beta - J_\gamma > E$; in that case, the spins will be pointing towards their neighbouring anions in the XY plane, as we saw in A. The spins on the a sublattice will thus point in the $(1, 1, 0)$ or the $(-1, -1, 0)$ direction, while the spins on the b sublattice will point in the $(1, -1, 0)$ or the $(-1, 1, 0)$ direction. We shall label those four different types of spins by suffices j, k, r and s, respectively. The transformation matrix A is here chosen to be given by the equation

$$A = \frac{1}{\sqrt{2}} \begin{Vmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & \sqrt{2} \end{Vmatrix}, \tag{3·6}$$

which means that in the basic array the j, k spins are alined along the y axis, and the r, s spins along the x axis.

We have the following approximate equations for our spins

$$\left.\begin{aligned} S_{jy} &= S_c - \frac{S_{jx}^2 + S_{jz}^2}{2S_c}, \\ S_{ky} &= -S_c + \frac{S_{kx}^2 + S_{kz}^2}{2S_c}, \\ S_{rx} &= S_c - \frac{S_{ry}^2 + S_{rz}^2}{2S_c}, \\ S_{sx} &= -S_c + \frac{S_{sy}^2 + S_{sz}^2}{2S_c}. \end{aligned}\right\} \tag{3·7}$$

We now introduce four sets of spin waves

$$\left.\begin{aligned} S_{jz} &= \sqrt{\left(\frac{4S}{N}\right)} \sum_{\kappa} e^{i(\kappa.j)} Q_\kappa, & S_{jx} &= \sqrt{\left(\frac{4S}{N}\right)} \sum_{\kappa} e^{-i(\kappa.j)} P_\kappa; \\ S_{kz} &= \sqrt{\left(\frac{4S}{N}\right)} \sum_{\kappa} e^{-i(\kappa.k)} R_\kappa, & S_{kx} &= -\sqrt{\left(\frac{4S}{N}\right)} \sum_{\kappa} e^{i(\kappa.k)} S_\kappa; \\ S_{ry} &= \sqrt{\left(\frac{4S}{N}\right)} \sum_{\kappa} e^{i(\kappa.r)} Q'_\kappa, & S_{rz} &= \sqrt{\left(\frac{4S}{N}\right)} \sum_{\kappa} e^{-i(\kappa.r)} P'_\kappa; \\ S_{sy} &= \sqrt{\left(\frac{4S}{N}\right)} \sum_{\kappa} e^{-i(\kappa.s)} R'_\kappa, & S_{sz} &= -\sqrt{\left(\frac{4S}{N}\right)} \sum_{\kappa} e^{i(\kappa.s)} S'_\kappa; \end{aligned}\right\} \tag{3·8}$$

where the sums over κ are over its allowed $\frac{1}{4}N$ values.

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The Hamiltonian is now of the form

$$H = \alpha S_c^2 + \sum [\tfrac{1}{2}\beta_1(Q_\kappa Q_{-\kappa} + R_\kappa R_{-\kappa} + P'_\kappa P'_{-\kappa} + S'_\kappa S'_{-\kappa}) + \tfrac{1}{2}\beta_2(P_\kappa P_{-\kappa} + S_\kappa S_{-\kappa} + Q'_\kappa Q'_{-\kappa} + R'_\kappa R'_{-\kappa}) + \gamma_1(Q_\kappa R_\kappa - P'_\kappa S'_\kappa) + \gamma_2(Q'_\kappa R'_\kappa - P_\kappa S_\kappa) + \epsilon(Q_\kappa P'_\kappa + R_\kappa P'_{-\kappa} - Q_\kappa S'_{-\kappa} - R_\kappa S'_\kappa) + \rho_1(Q_\kappa Q'_{-\kappa} + Q_\kappa R'_\kappa + R_\kappa Q'_\kappa + R_\kappa R'_{-\kappa}) + \rho_2(P_\kappa P'_{-\kappa} - P_\kappa S'_\kappa - S_\kappa P'_\kappa + S_\kappa S'_{-\kappa})], \quad (3{\cdot}9)$$

where

$$\left.\begin{aligned}
\alpha &= N(-2J - 2J_\beta + 2D'),\\
\beta_1 &= S(4D + 4J + 4J_\beta - 4D'),\\
\beta_2 &= S(4D'' + 4J + 4J_\beta - 4D'),\\
\gamma_1 &= S(2J + 2J_\alpha) \sum_{\text{n.n.}} e^{i(\kappa.l)},\\
\gamma_2 &= S(2J + 2J_\gamma) \sum_{\text{n.n.}} e^{i(\kappa.l)},\\
\epsilon &= S(K + w^2 K_\alpha P^2 + 4K_\gamma Q^2 w^{-2}) \sum_{\text{n.n.n.}} e^{i(\kappa.l)},\\
\rho_1 &= S\sqrt{2}\,(2K_\gamma Q^2 w^{-1} - wK_\alpha P^2)\,[\sum_{\text{n.n.n.}}{}^{1} e^{i(\kappa.l)} - \sum_{\text{n.n.n.}}{}^{2} e^{i(\kappa.l)}],\\
\rho_2 &= S\sqrt{2}\,(2K_\gamma Q^2 w^{-1} - wK_\alpha P^2)\,[\sum_{\text{n.n.n.}}{}^{3} e^{i(\kappa.l)} - \sum_{\text{n.n.n.}}{}^{4} e^{i(\kappa.l)}].
\end{aligned}\right\} \quad (3{\cdot}10)$$

As we expect the important anisotropy affects to result from the nearest-neighbour interactions and the crystalline field, we shall put $K_\alpha = K_\beta = K_\gamma = 0$ so that $\rho_1 = \rho_2 = 0$. This simplifies our Hamiltonian, and we can now diagonalize it by the following canonical transformation:

$$\left.\begin{aligned}
Q_\kappa &= \tfrac{1}{2}\sigma[Q_{1,\kappa} + P'_{2,\kappa} + Q_{2,\kappa}\sqrt{2} + iQ_{1,-\kappa} + iP'_{2,-\kappa} + iQ_{2,-\kappa}\sqrt{2}],\\
R_\kappa &= \tfrac{1}{2}\sigma[Q_{1,-\kappa} + P'_{2,-\kappa} - Q_{2,-\kappa}\sqrt{2} + iQ_{1,\kappa} + iP'_{2,\kappa} - iQ_{2,\kappa}\sqrt{2}],\\
P_\kappa &= \tfrac{1}{2}\sigma[P_{1,-\kappa} - Q'_{2,-\kappa} + P_{2,-\kappa}\sqrt{2} + iP_{1,\kappa} - iQ'_{2,\kappa} + iP_{2,\kappa}\sqrt{2}],\\
S_\kappa &= \tfrac{1}{2}\sigma[P_{1,\kappa} - Q'_{2,\kappa} - P_{2,\kappa}\sqrt{2} + iP_{1,-\kappa} - iQ'_{2,-\kappa} - iP_{2,-\kappa}\sqrt{2}],\\
Q'_\kappa &= \tfrac{1}{2}\sigma[-P_{1,\kappa} - Q'_{2,\kappa} + Q'_{1,\kappa}\sqrt{2} - iP_{1,-\kappa} - iQ'_{2,-\kappa} + iQ'_{1,-\kappa}\sqrt{2}],\\
R'_\kappa &= \tfrac{1}{2}\sigma[P_{1,-\kappa} + Q'_{2,-\kappa} + P'_{1,-\kappa}\sqrt{2} + iP_{1,\kappa} + iQ'_{2,\kappa} + iQ'_{1,\kappa}\sqrt{2}],\\
P'_\kappa &= \tfrac{1}{2}\sigma[Q_{1,-\kappa} - P'_{2,-\kappa} + P'_{1,-\kappa}\sqrt{2} + iQ_{1,\kappa} - iP'_{2,\kappa} + iP'_{1,\kappa}\sqrt{2}],\\
S'_\kappa &= \tfrac{1}{2}\sigma[-Q_{1,\kappa} + P'_{2,\kappa} + P'_{1,\kappa}\sqrt{2} - iQ_{1,-\kappa} + iP'_{2,-\kappa} + iP'_{1,-\kappa}\sqrt{2}],
\end{aligned}\right\} \quad (3{\cdot}11)$$

where

$$\sigma = e^{\frac{3}{4}\pi i}/\sqrt{2}. \quad (3{\cdot}12)$$

Substituting (3·11) into (3·9) we get the Hamiltonian in the form of a sum of harmonic oscillator terms

$$H = \alpha S_c^2 + \sum_\kappa [Q_{1\kappa}^2(\tfrac{1}{2}\beta_1 + \tfrac{1}{2}\gamma_1 + \epsilon) + P_{1\kappa}^2(\tfrac{1}{2}\beta_2 - \tfrac{1}{2}\gamma_2) + \tfrac{1}{2}Q_{1\kappa}'^2(\beta_2 + \gamma_2) + \tfrac{1}{2}P_{1\kappa}'^2(\beta_1 - \gamma_1) + \tfrac{1}{2}Q_{2\kappa}^2(\beta_1 - \gamma_1) + \tfrac{1}{2}P_{2\kappa}^2(\beta_2 + \gamma_2) + \tfrac{1}{2}Q_{2\kappa}'^2(\beta_2 - \gamma_2) + \tfrac{1}{2}P_{2\kappa}'^2(\beta_1 + \gamma_1 - 2\epsilon)]. \quad (3{\cdot}13)$$

From (3·13) we get for the energy levels of our system

$$E = \alpha S_c^2 + \sum_\kappa [(n_{1\kappa} + \tfrac{1}{2})\sqrt{\{(\beta_1 + \gamma_1 + 2\epsilon)(\beta_2 - \gamma_2)\}} + (n'_{1\kappa} + \tfrac{1}{2})\sqrt{\{(\beta_2 + \gamma_2)(\beta_1 - \gamma_1)\}} + (n_{2\kappa} + \tfrac{1}{2})\sqrt{\{(\beta_1 - \gamma_1)(\beta_2 + \gamma_2)\}} + (n'_{2\kappa} + \tfrac{1}{2})\sqrt{\{(\beta_2 - \gamma_2)(\beta_1 + \gamma_1 - 2\epsilon)\}}], \quad (3{\cdot}14)$$

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and for the ground-state energy

$$E_g = \alpha S_c^2 + \tfrac{1}{8}N\langle\sqrt{\{(\beta_1+\gamma_1+2\epsilon)\,(\beta_2-\gamma_2)\}}+2\sqrt{\{(\beta_2+\gamma_2)\,(\beta_1-\gamma_1)\}} + \sqrt{\{(\beta_1+\gamma_1-2\epsilon)\,(\beta_2-\gamma_2)\}}\rangle. \quad (3{\cdot}15)$$

To see whether the order is a stable one, we must calculate the value of the total sublattice spin upon one of the four sublattices, for which we shall choose the j sublattice. Once again we must take the average value of this quantity and we find (compare the derivation of (2·33))

$$\langle(S_{jy})_{\text{total}}\rangle = \tfrac{1}{4}NS_c - \frac{S}{8S_c}\sum_{\kappa}[\langle P_{1\kappa}^2\rangle+\langle Q_{1\kappa}^2\rangle+2\langle P_{2\kappa}^2\rangle+2\langle Q_{2\kappa}^2\rangle+\langle P_{2\kappa}'^2\rangle+\langle Q_{2\kappa}'^2\rangle], \quad (3{\cdot}16)$$

or, using the Hamiltonian (3·13),

$$\langle(S_{jy})_{\text{total}}\rangle = \tfrac{1}{4}NS_c - \frac{S}{16S_c}\sum_{\kappa}\left[\sqrt{\left(\frac{\beta_1+\gamma_1+2\epsilon}{\beta_2-\gamma_2}\right)}+\sqrt{\left(\frac{\beta_2-\gamma_2}{\beta_1+\gamma_1+2\epsilon}\right)} + \sqrt{\left(\frac{\beta_1+\gamma_1-2\epsilon}{\beta_2-\gamma_2}\right)}+\sqrt{\left(\frac{\beta_2-\gamma_2}{\beta_1+\gamma_1-2\epsilon}\right)}+2\sqrt{\left(\frac{\beta_2+\gamma_2}{\beta_1-\gamma_1}\right)}+2\sqrt{\left(\frac{\beta_1-\gamma_1}{\beta_2+\gamma_2}\right)}\right]. \quad (3{\cdot}17)$$

The rutile-type diagonal order will be stable—at least for low temperatures—as long as the denominators occurring inside the radicals in (3·17) do not vanish along any line in $\boldsymbol{\kappa}$ space. As long as $3(D-J_\alpha)+(J_{\beta\gamma}-E)>0$, $J_\beta-J_\gamma-E>0$ and $J>2K$ this condition is satisfied. These are just the conditions that the basic array chosen should be the one preferred by the molecular-field theory. This means that as long as the basic arrangement is stable according to the molecular-field theory, this order will be stable in the spin-wave approximation as well.

4. Antiferromagnetic resonance

The values of the energies $E_{i\boldsymbol{\kappa}}$ for $\boldsymbol{\kappa}=0$ give us the low temperature resonance frequencies in zero external magnetic field. We are therefore now able to find the antiferromagnetic resonance frequencies as functions of the isotropic and anisotropic exchange parameters. We note that as $\boldsymbol{\kappa}\to 0$ in all cases which we have considered in the previous sections $\delta_1\to 0$ and $\delta_2\to 0$ and the resonance frequencies ω_1 and ω_2 are thus for very low temperatures given by the simple equations (compare (2·20))

$$\hbar\omega_1 = \sqrt{\{(\beta_1-\gamma_1)\,(\beta_2+\gamma_2)\}}, \quad \hbar\omega_2 = \sqrt{\{(\beta_1+\gamma_1)\,(\beta_2-\gamma_2)\}}. \quad (4{\cdot}1)$$

We shall calculate ω_1 and ω_2 for the few cases where we have available data about the exchange parameters.

We first consider MnO which shows f.c.c. type 2 order with the preferred direction of alinement in a [1, 1, 1] plane. Keffer, Sievers & Tinkham (1961) have recently observed at low temperatures a resonance at a wavelength of about 364 μ. From (2·47) and (4·1) we find for ω_1

$$\hbar\omega_1 = S\sqrt{\{-12J_{\alpha\beta}(24J+24K-4J_{\alpha\beta})\}} \quad \hbar\omega_2 = 0. \quad (4{\cdot}2)$$

(These results are unchanged, if we include next-nearest-neighbour anisotropy.)

Coles, Orton & Owen (1960) have performed paramagnetic resonance experiments on Mn pairs in MgO and obtained reliable values for the anisotropy of the nearest- and next-nearest-neighbour interactions in the mixed salt. They conclude that the anisotropy is

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mainly due to dipole-dipole interactions although there is another contribution which makes $J_\beta \neq J_\gamma$. They also find that J and K are about equal and their value in temperature units is about 14 °K. As there is a small difference in lattice parameters between MgO and MnO we adjusted the anisotropy parameters to allow for this, assuming an inverse-cube dependence upon spacing. We left the value of J as a parameter to be obtained from (4·2), putting $J = K$, taking $J_{\alpha\beta}$ from the data of Coles *et al.* and ω_1 from the resonance data. This leads us to a value of about 4·3 °K. This value agrees rather better with the value of 5·6 °K obtained from susceptibility measurements which differs by more than a factor 2 from the mixed-salt data. We must emphasize that our calculation only gives an order of magnitude as we have neglected anisotropy contributions from more remote dipole-dipole interactions as well as isotropic exchange interactions from more remote neighbours. If we include more-remote-neighbour dipole-dipole terms we find a value of J and K of about 5·5 °K.

The result $\omega_2 = 0$ should be taken to mean that there will be another resonance arising from anisotropy which cannot be expressed in the general form (2·1). If our assumption that the main anisotropy can be expressed in the general form (2·1) is approximately correct, this second zero-field resonance will take place at a frequency which is much smaller than ω_1. Keffer & O'Sullivan (1957) predicted a resonance at a frequency of about $0{\cdot}1\omega_1$.

We next consider MnF_2 which shows b.c.t. type 1 order. Johnson & Nethercot (1959) found a resonance at 1·15 mm. The anisotropy in MnF_2 is largely dipole with a smaller crystal field contribution (Keffer 1952). We shall use Tinkham's crystal field parameters (1956). From (3·3) and (4·1) we get

$$\hbar\omega_1 = \hbar\omega_2 = S\sqrt{\left\{\left[-6(D+J_\alpha)+\frac{24}{2+w^2}(2K_\gamma+w^2K_\alpha)\right]\right.}$$
$$\left.\times\left[32K-6D-6J_\alpha+\frac{8}{2+w^2}(2K_\gamma+w^2K_\alpha)\right]\right\}. \quad (4{\cdot}3)$$

As the main anisotropy is due to dipole-dipole interactions, one should include the effect of more distant neighbours. We can easily include third-nearest neighbours by replacing J_α in (4·3) by $J_\alpha - L_\alpha$ where we have taken the third-nearest neighbour anisotropy interaction to be of the form $2L_\alpha S_x S'_x - L_\alpha S_y S'_y - L_\alpha S_z S'_z$, if the connexion between the spins $\mathbf{S}$ and $\mathbf{S}'$ is in the x direction. From (4·3) we then get a resonance wavelength of about 0·95 mm, using a value for K of about 2 °K which follows from susceptibility data. This is quite satisfactory agreement with the experimental resonance wavelength. If in equations (4·2) and (4·3) we consider the inter-spin anisotropy to be entirely dipole-dipole, then our expressions reduce to those previously considered by Keffer (1952) and Keffer & O'Sullivan (1957) except that they include dipole terms out to infinity, whereas our expressions include only a few of the nearer-neighbour terms.

We shall finally consider K_2IrCl_6 and $(NH_4)_2IrCl_6$. These are of interest as they possess a very large nearest-neighbour anisotropy which must be mainly due to superexchange pseudo-dipole effects (Griffiths, Owen, Park & Partridge 1959). Paramagnetic resonance experiments indicate that the interactions between nearest neighbours are much larger than those which exist between more distant neighbours. It appears thus that we should be able to treat these salts theoretically to a fair approximation by considering nearest neighbours only.

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At the moment the types of order which these salts exhibit are not yet known. If nearest-neighbour exchange is dominant, however, we should expect (see A) that the order in both cases must be either f.c.c. type 1 or type 3A. Coles (unpublished Oxford D.Phil. Thesis; compare Owen 1959) has found that J_γ is positive in both cases so that the type 1 order will have the preferred direction at right angles to the unique cubic axis and the preferred direction for the type 3A order will be along the unique cubic axis.

For the type 1 order we find from (2·41) and (4·1)

$$\hbar\omega_1^{(1)} = S\sqrt{\{24J_\gamma(32J+8J_\gamma)\}}, \quad \hbar\omega_2^{(1)} = 0, \tag{4·4}$$

while for the type 3A order we and from (2·49) and (4·1)

$$\hbar\omega_1^{(3\,A)} = \hbar\omega_2^{(3\,A)} = S\sqrt{\{12J_\gamma(32J+8K+8J_\gamma)\}}. \tag{4·5}$$

We see that for the type 1 order there will again be a resonance which is due solely to that part of the anisotropy which is not caused by an interaction of the form (2·1). As that part of the anisotropy is expected to be small, this would mean a low resonance frequency, probably at centimetre or near-centimetre wavelengths.

If our assumption, that we can get a very good approximation to both the total isotropic and anisotropic exchange interactions by considering nearest neighbours only, is valid we may estimate the other possible resonance frequencies for the two salts, using the exchange parameters given by Griffiths *et al.* (1959). We find for $(NH_4)_2IrCl_6$

$$\omega_1^{(1)} = 15{\cdot}0\,\mathrm{cm}^{-1}, \quad \omega^{(3\,A)} = 10{\cdot}6\,\mathrm{cm}^{-1}, \tag{4·6}$$

and for K_2IrCl_6

$$\omega_1^{(1)} = 19{\cdot}1\,\mathrm{cm}^{-1}, \quad \omega^{(3\,A)} = 13{\cdot}5\,\mathrm{cm}^{-1}. \tag{4·7}$$

We should like to express our gratitude to Dr J. H. E. Griffiths, Dr J. Owen, and Dr J. H. M. Thornley for very helpful discussions and to the Director of the Oxford University Computing Laboratory for providing us with computing facilities on the Mercury computer.

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