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A MOLECULAR-FIELD THEORY OF ANISOTROPIC FERROMAGNETICA

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CONTENTS

After a brief introduction discussing the basis of molecular-field theories, we introduce a generalization of Anderson's treatment of antiferromagnetism which enables us to take higher-order exchange interactions into account as well as anisotropy terms. We restrict ourselves to terms quadratic in the spins. This theory is developed in detail for face-centred cubic, body-centred cubic, simple cubic, and body-centred tetragonal magnetic lattices as well as for rutile structure antiferromagnetics. The general theory is developed in such a way that we can predict the possible preferred directions along which the spins in the antiferromagnetics will be alined. Until more information is available about the values of the various exchange parameters, it is not possible to predict theoretically which of the possible spin arrangements will, in fact, be the most stable one. On comparing experimental evidence on the spin arrangements in face-centred cubic and rutile structure antiferromagnetics we find, however, that almost all arrangements found experimentally are included in those predicted by the theory.

1. Introduction

It is well known that the Weiss molecular-field treatment is a very suitable theory for ferromagnetism (for instance, Seitz 1940, p. 608). In this theory one assumes, on the one hand, that the local effective field $\mathbf{H}^{\text{eff.}}$ is given by the relation

$$\mathbf{H}^{\text{eff.}} = \mathbf{H}_{\text{ext.}} + \alpha\mathbf{M}, \tag{1·1}$$

where $\mathbf{H}_{\text{ext.}}$ is the externally applied field, $\mathbf{M}$ the magnetization, and α a constant which we shall see presently to be related to the strength of the exchange interactions in the crystal. On the other hand, one assumes that the magnetization is determined by the local field in the well-known way

$$M = \xi B(\nu H^{\text{eff.}}), \tag{1·2}$$

where B is a Brillouin function (Seitz 1940, p. 581), and ξ and ν are two constants. Substituting (1·1) into (1·2) then gives us an equation for M which in the absence of an external field has only the solution $M = 0$ at high temperatures, but at low temperatures, that is at temperatures T below the so-called Curie temperature T_C there is also a solution $M \neq 0$, even when $H_{\text{ext.}} = 0$, and that solution is the stable one. If one solves (1·2) for M at temperatures T above T_C and uses the high-temperature expansion for the Brillouin function one finds for the susceptibility χ the Curie–Weiss law

$$\chi = \frac{T_C}{\alpha(T-T_C)} \quad (T > T_C). \tag{1·3}$$

The αM term in (1·1) can be derived from an averaging process applied to the exchange interaction term. Let V_{ij} be the exchange-interaction energy due to the two spins i and j. For the moment, let us assume that this interaction is isotropic so that we can write

$$V_{ij} = -2J(\mathbf{S}_i . \mathbf{S}_j), \tag{1·4}$$

where $\mathbf{S}_i$ and $\mathbf{S}_j$ are the spins of the ith and the jth atom, and where J is an exchange integral. In the ferromagnetic case, the average value $\langle \mathbf{S}_j \rangle$ of $\mathbf{S}_j$, say, will be independent of j and will be proportional to $\mathbf{M}$. If we replace (1·4) by the averaged expression

$$V_{ij} = -2J(\mathbf{S}_i . \langle \mathbf{S}_j \rangle), \tag{1·5}$$

we see that, as far as the ith atom is concerned, the contribution to its energy due to the jth atom is given by the expression

$$-g\mu_B(\mathbf{S}_i . \mathbf{H}'), \tag{1·6}$$

with

$$\mathbf{H}' = \frac{J\langle \mathbf{S}_j \rangle}{g\mu_B} = \frac{J\mathbf{M}}{Ng^2\mu_B^2}, \tag{1·7}$$

where μ_B is the Bohr magneton, g the Landé g-factor, and N the total number of atoms in the lattice and where the factor $\frac{1}{2}$ arises from the fact that only one-half of V_{ij} should be assigned to the ith atom. We see then that, indeed, the averaging which replaced (1·4) by (1·5) leads to the molecular-field theory, as each of the V_{ij} will give rise to a term in $\mathbf{H}^{\text{eff.}}$ proportional to $\mathbf{M}$.

The situation becomes more complicated, if we are dealing with an antiferromagnetic substance, that is, a substance which has a vanishing magnetization below the Curie point, even though the spins are ordered. In the simple case where the lattice can be subdivided into two equivalent sublattices, the spins on the one sublattice will be all parallel in the completely ordered state and the spins on the other sublattice will also be all parallel, but they will be antiparallel to the spins on the first sublattice. In this case, the exchange constant will be negative, $-J$, thus favouring the antiparallel alinement, and one has to be more careful in performing the averaging (1·5). The simple case of two equivalent sublattices was discussed by Van Vleck (1941). One again uses (1·2) which in the region around and above the Curie temperature can be written in the form

$$\langle \mathbf{S}_i \rangle = \tfrac{1}{3}\beta S(S+1)\, g\mu_B \mathbf{H}_i^{\text{eff.}}, \tag{1·8}$$

where S is the spin-quantum number of an individual atom, and where $\mathbf{H}_i^{\text{eff.}}$ is the effective field acting upon the ith atom. As there is a tendency for antiparallel alinement, $\mathbf{H}_i^{\text{eff.}}$ will be different for different sublattices. Finally, in (1·8)

$$\beta = 1/kT, \tag{1·9}$$

where k is Boltzmann's constant.

If we assume that we may neglect for the moment all interactions bar those between neighbouring spins, the effective field $\mathbf{H}_i^{\text{eff.}}$ will be given by the equation

$$\mathbf{H}_i^{\text{eff.}} = \mathbf{H}_{\text{ext.}} - \lambda \mathbf{M}_j \quad (i = 1, 2, j = 1, 2, i \neq j), \tag{1·10}$$

and λ will be proportional to the (positive) exchange constant J (compare (1·1) and (1·7); the change in sign corresponds to the fact that the exchange constant is now $-J$ rather than J), where $\mathbf{M}_i$ is the magnetization of the ith sublattice which will be proportional to $\langle \mathbf{S}_i \rangle$. From (1·8) and (1·10) we get thus

$$\mathbf{M}_i = \beta\tau(\mathbf{H}_{\text{ext.}} - \lambda \mathbf{M}_j), \tag{1·11}$$

where τ is a constant, $\tau = (\frac{1}{3}S(S+1)\, g\mu_B)\,(\frac{1}{2}Ng\mu_B)$. For the total magnetization $\mathbf{M}$ we find

$$\mathbf{M} = \sum_{i=1}^{2} \mathbf{M}_i = \beta\tau[2\mathbf{H}_{\text{ext.}} - \lambda \mathbf{M}], \tag{1·12}$$

and for the susceptibility
$$\chi = \frac{|\mathbf{M}|}{|\mathbf{H}_{\text{ext.}}|} = \frac{2\tau}{k(T+\Theta)} \quad (k\Theta = \lambda\tau). \tag{1·13}$$

The Curie temperature is obtained by putting $\mathbf{H}_{\text{ext.}} = 0$ in (1·11) and finding the condition that the homogeneous linear equations in $\mathbf{M}_1$ and $\mathbf{M}_2$ have a solution. One finds easily that this occurs if

$$T = T_C = \Theta. \tag{1·14}$$

It has been pointed out by Anderson (1950) that T_C is always proportional to the maximum exchange energy one can obtain by assuming constant magnetization on each of the sublattices, a theorem which we shall use many times in later sections.

Van Vleck's theory was generalized by Anderson (1950) in two directions. First of all, Anderson pointed out that for many known antiferromagnetics, Van Vleck's theory was inapplicable, since their lattice structure would not allow a splitting up into two equivalent sublattices. The most common case is that of a face-centred cubic (f.c.c.) lattice where one needs at least four sublattices. The theory proceeds along the same lines as before, that is, one writes down (1·10) but instead of one term λM_j one now has a sum $\lambda \Sigma M_j$ where the summation is over all sublattices but the one on which the ith spin is situated. One finds again a susceptibility of the form (1·13) and by putting $H_{\text{ext.}} = 0$ and solving a secular equation, one finds T_C, but now we have no longer (1·14). In fact, Anderson found $\Theta/T_C = 3$ which agreed satisfactorily with the experimental ratios for FeO, MnS, and MnSe. Anderson found, however, that he could not account on this theory for the value $\Theta/T_C = 5$ which was found for MnO, and he investigated the influence of next-nearest-neighbour interactions and found that—at a pinch—he could obtain the value 5 for Θ/T_C by including next-nearest-neighbour interactions. In this case he used eight sublattices.

In the present paper we shall further generalize the molecular-field theory of antiferromagnetics. First of all, we shall consider third- and fourth-nearest-neighbour interactions, and secondly, we shall replace the isotropic interaction (1·4) by an anisotropic expression. There were two reasons for including anisotropy terms: first, we know from experiments by Griffiths, Owen, Park & Partridge (1959) that in the antiferromagnetic K_2IrCl_6 and $(NH_4)_2IrCl_6$ salts the nearest-neighbour exchange interactions show a considerable anisotropy. Secondly, we expect that the inclusion of anisotropy terms may enable us to make more definite predictions about the directions along which the spins in the ordered state will be alined than was possible in the isotropic models considered by Anderson (1950) and Smart (1952).

We shall write the exchange energy for nearest neighbours in the form

$$V_{ij} = 2J_x S_{ix} S_{jx} + 2J_y S_{iy} S_{jy} + 2J_z S_{iz} S_{jz}, \tag{1·15}$$

where J_x, J_y, and J_z are exchange integrals, and where x, y, and z are mutually perpendicular directions. We shall follow Baker & Bleaney (1955) and Judd (1958) and assume that an expression such as (1·15) is general enough to give a good approximation to the actual anisotropy existing in the antiferromagnetic structures with which we shall be concerned.

The anisotropy in an antiferromagnetic arises, in general, from three different effects: the dipole-dipole interaction between magnetic moments, the anisotropic exchange (or pseudo-dipolar) interaction, and the anisotropy energy due to the crystalline electric field. Expression (1·15) is general enough to include all dipole-dipole and pseudo-dipolar terms in the Hamiltonian—at least as long as g is isotropic (see Nagamija, Yosida & Kubo 1955)—but we must consider the effect of the crystalline field in somewhat more detail.

For a cubic crystal structure the largest term appearing in the expression for the crystalline-field anisotropy involves the fourth powers of the spin components. This term is likely to be small compared with the one arising from the dipole-dipole or the pseudo-dipolar anisotropy, and we shall neglect it in the present paper. For the body-centred tetragonal lattice, however, the crystalline-field term arises from a lower-order perturbation than for the case of cubic symmetry (Pryce 1950), and this term is thus relatively more important in this case. As it can be written in terms of the squares of the spin components it can, however, be assumed to be already included in the general term (1·15) for the case where $i = j$.

We shall follow Anderson and assume that the molecular-field theory is at least adequate in a semi-quantitative way, without delving too deeply in the extremely vexed question of the antiferromagnetic ground state.

In the next section we shall consider the case of an f.c.c. magnetic lattice. In our theoretical discussion in that section we shall assume that we may neglect the possible presence of anions. We introduce thirty-two sublattices, anisotropic interactions between nearest and next-nearest neighbours, and isotropic interactions between third- and fourth-nearest neighbours. This allows us to consider patterns of order with a periodicity in any one direction of not more than two unit cell lengths, including types of order which Anderson with his eight sublattices could not consider and which appear to occur in MnS_2, βMnS, and CrN. We shall use a formalism in which the orientation of the x, y, z axes is left unspecified; this enables us more easily to find the ordering patterns. For the f.c.c. case—as for all the other cubic cases—we find that the Weiss constant Θ is independent of the anisotropy, but can be as large as $15T_C$ when not unreasonable values for the second-, third-, and fourth-nearest-neighbour interactions are used.

In §3 we compare the results of §2 with experimental data, including those referring to f.c.c magnetic lattices with anions present which destroy the f.c.c. symmetry.

In §§4 and 5 we repeat the considerations of §2, but for the body-centred cubic (b.c.c.) and simple cubic (s.c.) magnetic lattices. We introduce respectively sixteen and eight sublattices, and assume anisotropic first-, second-, and third-nearest-neighbour interactions.

In §§ 6 and 7 we consider the body-centred tetragonal (b.c.t.) magnetic lattices, again with first-, second-, and third-nearest-neighbour anisotropic interactions and with sixteen sublattices. In § 6 we consider a pure b.c.t. lattice and in § 7 a rutile structure, where the magnetic lattice has a b.c.t. structure. In § 8, finally, we compare the theoretical results of § 7 with experimental data.

2. The face-centred cubic magnetic lattice

In this section we shall consider an f.c.c. magnetic lattice and, for the moment, we shall assume for the sake of simplicity that there no anions. We shall introduce first-, second-, third-, and fourth-nearest-neighbour interactions and we assume that the first two are anisotropic and the last two isotropic. We neglect all remoter interactions. We shall use a model with thirty-two sublattices and are thus able to include in our treatment any possible type of order which has a periodicity of not more than two-unit cell lengths in any direction.

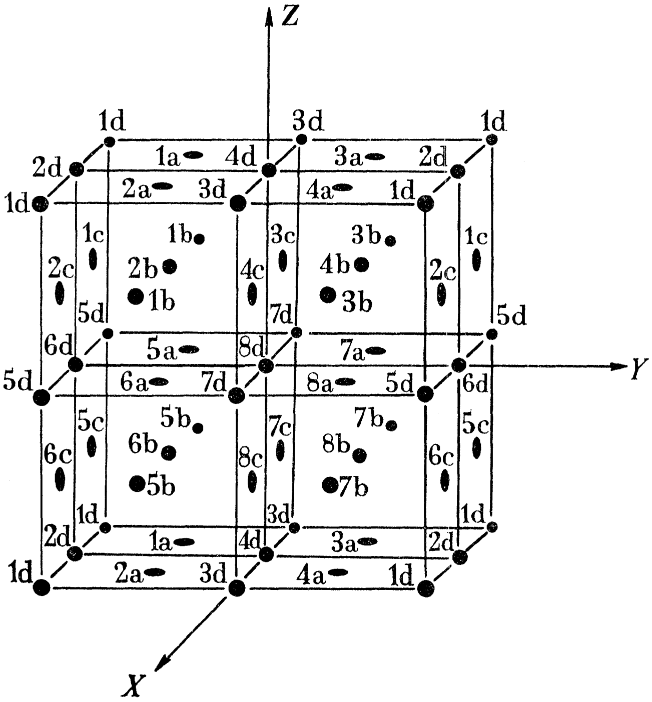

Figure 1. The thirty-two sublattices of the f.c.c. magnetic lattice.

In figure 1 we show an array of eight unit cells—each cube edge having the length of two unit cell lengths. In this figure we have labelled each lattice site according to the sublattice to which it belongs. The thirty-two sublattices are denoted by 1a, 2a, ..., 8a, 1b, 2b, ..., 8b, 1c, ..., 8c; 1d, ..., 8d. We note that neither the first-, nor the second-, or third-, or fourth-nearest-neighbours of an atom belong to the same sublattice as the atom itself; this is, of course, essential for the model. If we take an atom on an 8d site as the central atom, its 12 nearest (or first) neighbours are on 5a, 6a, 7a, 8a, 3c, 4c, 7c, 8c, 2b, 4b, 6b and 8b sites; its 6 next-nearest (or second) neighbours are on 4d, 6d, and 7d sites (2 on each sublattice); its 24 third-nearest (or third) neighbours are on 1a, 2a, 3a, 4a, 1b, 3b, 5b, 7b, 1c, 2c, 5c, and 6c sites (2 on each sublattice); and its 12 fourth-nearest (or fourth) neighbours are on 2d, 3d, and 5d sites (4 on each sublattice). The XYZ axes in figure 1 are along the cubic axes of symmetry of the f.c.c. lattice.

Consider now the energy of the interaction between the central 8d atom and its 8a first neighbour (figure 2). To be able to take into account the crystal structure we choose x', y', and z' axes along the (1, 1, 0), (−1, 1, 0), and (0, 0, 1) directions and write (compare (1·15))

$$V_{8\mathrm{d},\,8\mathrm{a}} = 2J_1 S^{8\mathrm{d}}_{x'} S^{8\mathrm{a}}_{x'} + 2J_2 S^{8\mathrm{d}}_{y'} S^{8\mathrm{a}}_{y'} + 2J_3 S^{8\mathrm{d}}_{z'} S^{8\mathrm{a}}_{z'}, \tag{2·1}$$

where the superscripts on the S denote the atoms to which the spins belong, and the subscripts their components. For later discussions it is convenient to write the J_i as the sum of an isotropic and an anisotropic contribution

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

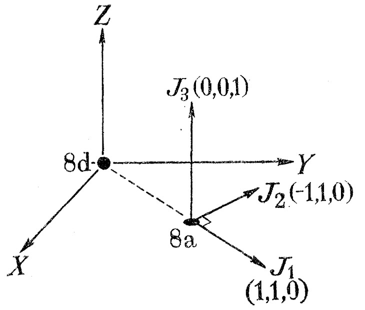

FIGURE 2. Nearest-neighbour interactions in the f.c.c. case.

In many cases we shall find that the stable antiferromagnetic order corresponds to all spins alined parallel or antiparallel to a given direction, **n**. In that case it is convenient to introduce a system of co-ordinates Σ'—the x, y, z system—such that this preferred direction **n** is along the x axis, say. In that case we may in the molecular field approximation put all y and z components of spins equal to zero. The system Σ' may be obtained from the co-ordinate system Σ, which is the X, Y, Z system by a real orthogonal transformation

$$\Sigma' = A\Sigma, \tag{2·3}$$

where A is a unitary operator which can be represented by a 3×3 matrix with elements a_{ij} which satisfy the unitarity conditions

$$\sum_i a_{ij} a_{ik} = \sum_i a_{ji} a_{ki} = \delta_{jk}, \tag{2·4}$$

where δ_{jk} is the Kronecker δ symbol.

In the co-ordinate system Σ' we get for $V_{8\mathrm{d},\,8\mathrm{a}}$ the complicated expression

$$\begin{aligned} V_{8\mathrm{d},\,8\mathrm{a}} = J_1[&(a_{11}+a_{12})\, S^{8\mathrm{d}}_x + (a_{21}+a_{22})\, S^{8\mathrm{d}}_y + (a_{31}+a_{32})\, S^{8\mathrm{d}}_z]\,[(a_{11}+a_{12})\, S^{8\mathrm{a}}_x + (a_{21}+a_{22}) \\ &\times S^{8\mathrm{a}}_y + (a_{31}+a_{33})\, S^{8\mathrm{a}}_z] + J_2[(a_{12}-a_{11})\, S^{8\mathrm{d}}_x + (a_{22}-a_{21})\, S^{8\mathrm{d}}_y + (a_{32}-a_{31})\, S^{8\mathrm{d}}_z] \\ &\times [(a_{12}-a_{11})\, S^{8\mathrm{a}}_x + (a_{22}-a_{21})\, S^{8\mathrm{a}}_y + (a_{32}-a_{31})\, S^{8\mathrm{a}}_z] \\ &+ 2J_3[a_{13} S^{8\mathrm{d}}_x + a_{23} S^{8\mathrm{d}}_y + a_{33} S^{8\mathrm{d}}_z]\,[a_{13} S^{8\mathrm{a}}_x + a_{23} S^{8\mathrm{a}}_y - a_{33} S^{8\mathrm{a}}_z]. \end{aligned} \tag{2·5}$$

If we consider the interaction between the central 8d spin and its 3c first neighbour, we get

$$V_{8\mathrm{d},\,3\mathrm{c}} = 2J_1 S^{8\mathrm{d}}_{x''} S^{3\mathrm{c}}_{x''} + 2J_2 S^{8\mathrm{d}}_{y''} S^{3\mathrm{c}}_{y''} + 2J_3 S^{8\mathrm{d}}_{z''} S^{3\mathrm{c}}_{z''}, \tag{2·6}$$

where now the x'', y'', z'' are along the $(-1,0,1)$, $(1,0,1)$, and $(0,1,0)$ directions in Σ. We can again transform from Σ to Σ' and get an equation similar to (2·5). After that we consider in turn the other first neighbours and transform in each case the corresponding energy expression—in each of which the components of the spins which multiply J_1, J_2, and J_3, respectively, are those along appropriately chosen axes which are different in each case—from Σ to Σ'.

To find the total interaction energy due to first neighbours, $V^{8\mathrm{d}}$, we have to sum the resultant twelve expressions. The resultant expression is highly complicated. Assuming, however, that the Σ' system is, indeed, one in which the x axis is along the direction of the spin alinement in the ordered state, we can invoke the molecular field approximation, take the averages of all spin components, and put all y and z components equal to zero. In that case $V_1^{8\mathrm{d}}$ reduces to the expression

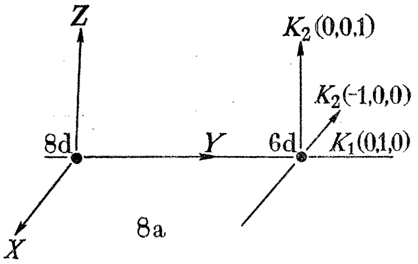

FIGURE 3. Second-neighbour interactions in the f.c.c. case.

$$\begin{aligned}V_1^{8\mathrm{d}} = S_x^{8\mathrm{d}}\{&J_1[(a_{11}+a_{12})^2\,(S_x^{5\mathrm{a}}+S_x^{8\mathrm{a}})+(a_{11}-a_{12})^2\,(S_x^{6\mathrm{a}}+S_x^{7\mathrm{a}})+(a_{12}+a_{13})^2\,(S_x^{4\mathrm{b}}+S_x^{6\mathrm{b}})\\&+(a_{12}-a_{13})^2\,(S_x^{2\mathrm{b}}+S_x^{8\mathrm{b}})+(a_{11}+a_{13})^2\,(S_x^{4\mathrm{c}}+S_x^{7\mathrm{c}})+(a_{11}-a_{13})^2\,(S_x^{3\mathrm{c}}+S_x^{8\mathrm{c}})]\\&+J_2[(a_{11}-a_{12})^2\,(S_x^{5\mathrm{a}}+S_x^{8\mathrm{a}})+(a_{11}+a_{12})^2\,(S_x^{6\mathrm{a}}+S_x^{7\mathrm{a}})+(a_{12}-a_{13})^2\,(S_x^{4\mathrm{b}}+S_x^{6\mathrm{b}})\\&+(a_{12}+a_{13})^2\,(S_x^{2\mathrm{b}}+S_x^{8\mathrm{b}})+(a_{11}-a_{13})^2\,(S_x^{4\mathrm{c}}+S_x^{7\mathrm{c}})+(a_{11}+a_{13})^2\,(S_x^{3\mathrm{c}}+S_x^{8\mathrm{c}})]\\&+2J_3[a_{13}^2(S_x^{5\mathrm{a}}+S_x^{8\mathrm{a}}+S_x^{6\mathrm{a}}+S_x^{7\mathrm{a}})+a_{11}^2(S_x^{4\mathrm{b}}+S_x^{6\mathrm{b}}+S_x^{2\mathrm{b}}+S_x^{8\mathrm{b}})+a_{12}^2(S_x^{4\mathrm{c}}+S_x^{7\mathrm{c}}+S_x^{3\mathrm{c}}+S_x^{8\mathrm{c}})]\}.\end{aligned} \tag{2·7}$$

In the following we shall whenever we have used the molecular-field approximation in expressions such as (2·7) drop the subscripts x to simplify our notation.

We now consider the second-neighbour interactions (see figure 3). If we consider, for instance, the 8d–6d interaction, we see that the Y axis is a fourfold axis of symmetry so that we should expect only two different parameters at most. Choosing the x', y', z' axes along the $(0,1,0)$, $(-1,0,0)$ and $(0,0,1)$ directions, we can write

$$V_{8\mathrm{d},\,6\mathrm{d}} = 2K_1 S_{x'}^{8\mathrm{d}} S_{x'}^{6\mathrm{d}} + 2K_2 S_{y'}^{8\mathrm{d}} S_{y'}^{6\mathrm{d}} + 2K_2 S_{z'}^{8\mathrm{d}} S_{z'}^{6\mathrm{d}}, \tag{2·8}$$

where we shall later write

$$K_1 = K+K_0, \quad K_2 = K+K_i, \quad K_0+2K_i = 0. \tag{2·9}$$

Transforming to the Σ' system and using the molecular-field approximation we get

$$V_{8\mathrm{d},\,6\mathrm{d}} = S_x^{8\mathrm{d}}[2K_1 a_{12}^2 S_x^{6\mathrm{d}} + 2K_2 a_{11}^2 S_x^{6\mathrm{d}} + 2K_2 a_{13}^2 S_x^{6\mathrm{d}}], \tag{2·10}$$

and for the total interaction due to second neighbours, $V_2^{8\mathrm{d}}$, we get

$$\begin{aligned}V_2^{8\mathrm{d}} = S^{8\mathrm{d}}\{&4K_1[a_{11}^2 S^{7\mathrm{d}} + a_{12}^2 S^{6\mathrm{d}} + a_{13}^2 S^{4\mathrm{d}}]\\&+4K_2[(a_{12}^2+a_{13}^2)\,S^{7\mathrm{d}} + (a_{11}^2+a_{13}^2)\,S^{6\mathrm{d}} + (a_{11}^2+a_{12}^2)S^{4\mathrm{d}}]\}.\end{aligned} \tag{2·11}$$

As we assumed the third- and fourth-neighbour interactions to be isotropic, we can immediately write down the corresponding interaction energies $V_3^{8\mathrm{d}}$ and $V_4^{8\mathrm{d}}$, and we have

$$V_3^{8\mathrm{d}} = 4LS^{8\mathrm{d}}[S^{1\mathrm{a}}+S^{2\mathrm{a}}+S^{3\mathrm{a}}+S^{4\mathrm{a}}+S^{1\mathrm{b}}+S^{3\mathrm{b}}+S^{5\mathrm{b}}+S^{7\mathrm{b}}+S^{1\mathrm{c}}+S^{2\mathrm{c}}+S^{5\mathrm{c}}+S^{6\mathrm{c}}], \quad (2{\cdot}12)$$

$$V_4^{8\mathrm{d}} = 8MS^{8\mathrm{d}}[S^{2\mathrm{d}}+S^{3\mathrm{d}}+S^{5\mathrm{d}}], \quad (2{\cdot}13)$$

where L and M are the isotropic interaction constants.

The total interaction energy $V^{8\mathrm{d}}$ is now given by the expression

$$V^{8\mathrm{d}} = V_1^{8\mathrm{d}}+V_2^{8\mathrm{d}}+V_3^{8\mathrm{d}}+V_4^{8\mathrm{d}}, \quad (2{\cdot}14)$$

and the molecular field $H_{8\mathrm{d}}^{\mathrm{mol.}}$ in which the central field is situated is given by the expression

$$H_{8\mathrm{d}}^{\mathrm{mol.}} = -\frac{V^{8\mathrm{d}}}{g\mu_B S^{8\mathrm{d}}}, \quad (2{\cdot}15)$$

so that the total effective field acting upon the 8d atom, $H_{8\mathrm{d}}^{\mathrm{eff.}}$, is given by the expression

$$H_{8\mathrm{d}}^{\mathrm{eff.}} = H_{\mathrm{ext.}}+H_{8\mathrm{d}}^{\mathrm{mol.}} = H_{\mathrm{ext.}}-\frac{V^{8\mathrm{d}}}{g\mu_B S^{8\mathrm{d}}}. \quad (2{\cdot}16)$$

From (1·8) we now get for the average value of $S^{8\mathrm{d}}$ (note that all S^i except $S^{8\mathrm{d}}$ were already averages)

$$S^{8\mathrm{d}} = \tfrac{1}{3}\beta S(S+1)\, g\mu_B H_{8\mathrm{d}}^{\mathrm{eff.}}, \quad (2{\cdot}17)$$

where we have retained the notation $S^{8\mathrm{d}}$ for its average, so that now all S^i are averages in (2·17). We also note that we have assumed $H_{\mathrm{ext.}}$ to be in the x direction.

If we use (2·7) and (2·11) to (2·17) we get

$$\begin{aligned} S^{8\mathrm{d}} = \phi^{-1}\{g\mu_B H_{\mathrm{ext.}} - [&\lambda(S^{1\mathrm{a}}+S^{2\mathrm{a}}+S^{3\mathrm{a}}+S^{4\mathrm{a}})+\rho_1(S^{5\mathrm{a}}+S^{8\mathrm{a}})+\rho_1'(S^{6\mathrm{a}}+S^{7\mathrm{a}}) \\ &+\lambda(S^{1\mathrm{b}}+S^{3\mathrm{b}}+S^{5\mathrm{b}}+S^{7\mathrm{b}})+\rho_2(S^{4\mathrm{b}}+S^{6\mathrm{b}})+\rho_2'(S^{2\mathrm{b}}+S^{8\mathrm{b}})+\lambda(S^{1\mathrm{c}}+S^{2\mathrm{c}}+S^{5\mathrm{c}}+S^{6\mathrm{c}}) \\ &+\rho_3(S^{4\mathrm{c}}+S^{7\mathrm{c}})+\rho_3'(S^{3\mathrm{c}}+S^{8\mathrm{c}})+\mu(S^{2\mathrm{d}}+S^{3\mathrm{d}}+S^{5\mathrm{d}})+\delta_1 S^{7\mathrm{d}}+\delta_2 S^{6\mathrm{d}}+\delta_3 S^{4\mathrm{d}}]\}, \quad (2{\cdot}18) \end{aligned}$$

where

$$\phi^{-1} = \tfrac{1}{3}\beta S(S+1), \quad (2{\cdot}19)$$

$$\rho_i = (a_{1i}+a_{1i+1})^2 J_1+(a_{1i}-a_{1i+1})^2 J_2+2a_{1i+2}^2 J_3, \quad (2{\cdot}20)$$

$$\rho_i' = (a_{1i}-a_{1i+1})^2 J_1+(a_{1i}+a_{1i+1})^2 J_2+2a_{1i+2}^2 J_3, \quad (2{\cdot}21)$$

$$\delta_i = 4[a_{1i}^2 K_1+(a_{1i+1}^2+a_{1i+2}^2)\, K_2], \quad (2{\cdot}22)$$

$$\lambda = 4L, \quad \mu = 8M, \quad (2{\cdot}23)$$

and where here and henceforth

$$a_{14} \equiv a_{11} \quad \text{and} \quad a_{15} \equiv a_{12}. \quad (2{\cdot}24)$$

We can repeat the procedure with an atom of a different sublattice as the central atom. If we do this for all thirty-two sublattices, and then sum the resultant 32 equations we get

$$\sum_i S^i = \phi^{-1}[32g\mu_B H_{\mathrm{ext.}}-(24J+12K+48L+24M)\sum_i S^i], \quad (2{\cdot}25)$$

where the summations are over 32 spins, one on each of the different sublattices. From (2·25) we get for the total magnetization M which is now given by the equation

$$M = \frac{Ng\mu_B}{32}\sum_i S^i \quad (2{\cdot}26)$$

the expression

$$M = \frac{N(g\mu_B)^2 S(S+1)\, H_{\mathrm{ext.}}}{3k(T+\Theta)}, \quad (2{\cdot}27)$$

where the Weiss constant Θ is given by the expression

$$\Theta = 3(2J+K+4L+2M)\,\psi, \quad (2{\cdot}28)$$

where

$$\psi = \frac{4T}{\phi} = \frac{4S(S+1)}{3k}. \tag{2·29}$$

We note that for the f.c.c. magnetic lattice the Weiss constant does not contain any of the anisotropy constants. This means that the susceptibility χ above the transition temperature should be isotropic.

To find the transition temperature, we put $H_{\text{ext.}} = 0$ in the 32 equations for the 32 S^i, and this leads to a secular equation of the form

$$D_{\text{f.c.c.}} = 0, \tag{2·30}$$

where the 32×32 determinant $D_{\text{f.c.c.}}$ is the one given in figure 4. This determinant can be factorized. The different factors are

$$\left.\begin{array}{rl}
(1) & \phi-\delta_1+\delta_2+\delta_3-\mu+4\lambda-2\rho_2^+, \\
(2) & \phi-\delta_1+\delta_2+\delta_3-\mu-4\lambda+2\rho_2^+, \\
(3) & \phi+\delta_1-\delta_2+\delta_3-\mu+4\lambda-2\rho_3^+, \\
(4) & \phi+\delta_1-\delta_2+\delta_3-\mu-4\lambda+2\rho_3^+, \\
(5) & \phi+\delta_1+\delta_2-\delta_3-\mu+4\lambda-2\rho_1^+, \\
(6) & \phi+\delta_1+\delta_2-\delta_3-\mu-4\lambda+2\rho_1^+, \\
(7) & \phi+\delta_1-\delta_2-\delta_3-\mu+2\rho_2^-, \\
(8) & \phi+\delta_1-\delta_2-\delta_3-\mu-2\rho_2^-, \\
(9) & \phi-\delta_1+\delta_2-\delta_3-\mu+2\rho_3^-, \\
(10) & \phi-\delta_1+\delta_2-\delta_3-\mu-2\rho_3^-, \\
(11) & \phi-\delta_1-\delta_2+\delta_3-\mu+2\rho_1^-, \\
(12) & \phi-\delta_1-\delta_2+\delta_3-\mu-2\rho_1^-, \\
(13) & \phi-\delta_1-\delta_2-\delta_3+3\mu-2\rho_1^--2\rho_2^--2\rho_3^-, \\
(14) & \phi-\delta_1-\delta_2-\delta_3+3\mu-2\rho_1^-+2\rho_2^-+2\rho_3^-, \\
(15) & \phi-\delta_1-\delta_2-\delta_3+3\mu+2\rho_1^--2\rho_2^-+2\rho_3^-, \\
(16) & \phi-\delta_1-\delta_2-\delta_3+3\mu+2\rho_1^-+2\rho_2^--2\rho_3^-, \\
(17) & \phi+\delta_1+\delta_2+\delta_3+3\mu+12\lambda+2\rho_1^++2\rho_2^++2\rho_3^+, \\
(18) & \phi+\delta_1+\delta_2+\delta_3+3\mu-4\lambda+2\rho_1^+-2\rho_2^+-2\rho_3^+, \\
(19) & \phi+\delta_1+\delta_2+\delta_3+3\mu-4\lambda-2\rho_1^++2\rho_2^+-2\rho_3^+, \\
(20) & \phi+\delta_1+\delta_2+\delta_3+3\mu-4\lambda-2\rho_1^+-2\rho_2^++2\rho_3^+,
\end{array}\right\} \tag{2·31}$$

where

$$\rho_i^{\pm} = \rho_i \pm \rho_i' \quad (i = 1, 2, 3). \tag{2·32}$$

Of the 20 factors of (2·31), the first 12 occur twice in $D_{\text{f.c.c.}}$. Each of these factors may separately be put equal to zero, and thus lead to a possible transition temperature. The Curie temperature, T_C, is that temperature at which ordering first sets in, that is, it will be the largest of the possible T_i ($i = 1, \ldots, 20$; i corresponding to the 20 possibilities of (2·31)). Each of the T_i will be a function of the a_{ij}, that is, each of them will depend on the actual orientation of the spins in the ordered antiferromagnetic state, and T_C will be the largest possible T_i, allowing for all possibilities of orientation. We shall thus be able to predict which ordered pattern will occur, as it will be the one for which T_C is a maximum. Once

T_C has been found, the 32 simultaneous homogeneous linear equations for the S^i can be solved, and from these equations we can then find whether the spins on a given sublattice are parallel or antiparallel to the preferred direction of orientation. In practice, we shall not actually solve these equations but use Anderson's theorem (1950) quoted in the previous section that T_C is proportional to the maximum exchange energy which one can obtain by assuming constant magnetization on each of the sublattices.

$$\left|\begin{array}{cccccccc|cccccccc|cccccccc|cccccccc}
\phi & \delta_1 & \delta_2 & \mu & \delta_3 & \mu & \mu & 0 & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_1 & \rho_1' & \rho_1' & \rho_1 & \lambda & \lambda & \lambda & \lambda \\
\delta_1 & \phi & \mu & \delta_2 & \mu & \delta_3 & 0 & \mu & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \rho_1' & \rho_1 & \rho_1 & \rho_1' & \lambda & \lambda & \lambda & \lambda \\
\delta_2 & \mu & \phi & \delta_1 & \mu & 0 & \delta_3 & \mu & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_1' & \rho_1 & \rho_1 & \rho_1' & \lambda & \lambda & \lambda & \lambda \\
\mu & \delta_2 & \delta_1 & \phi & 0 & \mu & \mu & \delta_3 & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \rho_1 & \rho_1' & \rho_1' & \rho_1 & \lambda & \lambda & \lambda & \lambda \\
\delta_3 & \mu & \mu & 0 & \phi & \delta_1 & \delta_2 & \mu & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \lambda & \lambda & \lambda & \lambda & \rho_1 & \rho_1' & \rho_1' & \rho_1 \\
\mu & \delta_3 & 0 & \mu & \delta_1 & \phi & \mu & \delta_2 & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \lambda & \lambda & \lambda & \rho_1' & \rho_1 & \rho_1 & \rho_1' \\
\mu & 0 & \delta_3 & \mu & \delta_2 & \mu & \phi & \delta_1 & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \lambda & \lambda & \lambda & \lambda & \rho_1' & \rho_1 & \rho_1 & \rho_1' \\
0 & \mu & \mu & \delta_3 & \mu & \delta_2 & \delta_1 & \phi & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \lambda & \lambda & \lambda & \rho_1 & \rho_1' & \rho_1' & \rho_1 \\
\hline
\rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho & \lambda & \lambda & \phi & \delta_1 & \delta_2 & \mu & \delta_3 & \mu & \mu & 0 & \rho_1' & \rho_1 & \rho_1 & \rho_1' & \lambda & \lambda & \lambda & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \lambda \\
\rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \delta_1 & \phi & \mu & \delta_2 & \mu & \delta_3 & 0 & \mu & \rho_1 & \rho_1' & \rho_1' & \rho_1 & \lambda & \lambda & \lambda & \lambda & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' \\
\lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 & \delta_2 & \mu & \phi & \delta_1 & \mu & 0 & \delta_3 & \mu & \rho_1 & \rho_1' & \rho_1' & \rho_1 & \lambda & \lambda & \lambda & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \lambda \\
\lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & \mu & \delta_2 & \delta_1 & \phi & 0 & \mu & \mu & \delta_3 & \rho_1' & \rho_1 & \rho_1 & \rho_1' & \lambda & \lambda & \lambda & \lambda & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 \\
\rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \delta_3 & \mu & \mu & 0 & \phi & \delta_1 & \delta_2 & \mu & \lambda & \lambda & \lambda & \lambda & \rho_1' & \rho_1 & \rho_1 & \rho_1' & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \lambda \\
\rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \mu & \delta_3 & 0 & \mu & \delta_1 & \phi & \mu & \delta_2 & \lambda & \lambda & \lambda & \lambda & \rho_1 & \rho_1' & \rho_1' & \rho_1 & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 \\
\lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & \mu & 0 & \delta_3 & \mu & \delta_2 & \mu & \phi & \delta_1 & \lambda & \lambda & \lambda & \lambda & \rho_1 & \rho_1' & \rho_1' & \rho_1 & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \lambda \\
\lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 & 0 & \mu & \mu & \delta_3 & \mu & \delta_2 & \delta_1 & \phi & \lambda & \lambda & \lambda & \lambda & \rho_1' & \rho_1 & \rho_1 & \rho_1' & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' \\
\hline
\rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_1' & \rho_1 & \rho_1 & \rho_1' & \lambda & \lambda & \lambda & \lambda & \phi & \delta_1 & \delta_2 & \mu & \delta_3 & \mu & \mu & 0 & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda \\
\lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \rho_1 & \rho_1' & \rho_1' & \rho_1 & \lambda & \lambda & \lambda & \lambda & \delta_1 & \phi & \mu & \delta_2 & \mu & \delta_3 & 0 & \mu & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda \\
\rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_1 & \rho_1' & \rho_1' & \rho_1 & \lambda & \lambda & \lambda & \lambda & \delta_2 & \mu & \phi & \delta_1 & \mu & 0 & \delta_3 & \mu & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' \\
\lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \rho_1' & \rho_1 & \rho_1 & \rho_1' & \lambda & \lambda & \lambda & \lambda & \mu & \delta_2 & \delta_1 & \phi & 0 & \mu & \mu & \delta_3 & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 \\
\rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \lambda & \lambda & \lambda & \lambda & \rho_1' & \rho_1 & \rho_1 & \rho_1' & \delta_3 & \mu & \mu & 0 & \phi & \delta_1 & \delta_2 & \mu & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda \\
\lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \lambda & \lambda & \lambda & \rho_1 & \rho_1' & \rho_1' & \rho_1 & \mu & \delta_3 & 0 & \mu & \delta_1 & \phi & \mu & \delta_2 & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda \\
\rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \lambda & \lambda & \lambda & \lambda & \rho_1 & \rho_1' & \rho_1' & \rho_1 & \mu & 0 & \delta_3 & \mu & \delta_2 & \mu & \phi & \delta_1 & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 \\
\lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \lambda & \lambda & \lambda & \rho_1' & \rho_1 & \rho_1 & \rho_1' & 0 & \mu & \mu & \delta_3 & \mu & \delta_2 & \delta_1 & \phi & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' \\
\hline
\rho_1 & \rho_1' & \rho_1' & \rho_1 & \lambda & \lambda & \lambda & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \phi & \delta_1 & \delta_2 & \mu & \delta_3 & \mu & \mu & 0 \\
\rho_1' & \rho_1 & \rho_1 & \rho_1' & \lambda & \lambda & \lambda & \lambda & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \delta_1 & \phi & \mu & \delta_2 & \mu & \delta_3 & 0 & \mu \\
\rho_1' & \rho_1 & \rho_1 & \rho_1' & \lambda & \lambda & \lambda & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & \delta_2 & \mu & \phi & \delta_1 & \mu & 0 & \delta_3 & \mu \\
\rho_1 & \rho_1' & \rho_1' & \rho_1 & \lambda & \lambda & \lambda & \lambda & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 & \mu & \delta_2 & \delta_1 & \phi & 0 & \mu & \mu & \delta_3 \\
\lambda & \lambda & \lambda & \lambda & \rho_1 & \rho_1' & \rho_1' & \rho_1 & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \delta_3 & \mu & \mu & 0 & \phi & \delta_1 & \delta_2 & \mu \\
\lambda & \lambda & \lambda & \lambda & \rho_1' & \rho_1 & \rho_1 & \rho_1' & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \rho_2' & \lambda & \rho_2 & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \mu & \delta_3 & 0 & \mu & \delta_1 & \phi & \mu & \delta_2 \\
\lambda & \lambda & \lambda & \lambda & \rho_1' & \rho_1 & \rho_1 & \rho_1' & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \lambda & \lambda & \rho_3 & \rho_3' & \lambda & \lambda & \rho_3' & \rho_3 & \mu & 0 & \delta_3 & \mu & \delta_2 & \mu & \phi & \delta_1 \\
\lambda & \lambda & \lambda & \lambda & \rho_1 & \rho_1' & \rho_1' & \rho_1 & \lambda & \rho_2' & \lambda & \rho_2 & \lambda & \rho_2 & \lambda & \rho_2' & \lambda & \lambda & \rho_3' & \rho_3 & \lambda & \lambda & \rho_3 & \rho_3' & 0 & \mu & \mu & \delta_3 & \mu & \delta_2 & \delta_1 & \phi
\end{array}\right|$$

FIGURE 4. The determinant of the secular equation for the f.c.c. case.

The solutions for the T_i are

$$\left.\begin{aligned}
T_{2j-1} &= [2J-K-4L+2M-(K_0+J_\gamma)\,(1-3a_{1j}^2)]\,\psi,\\
T_{2j} &= [-2J-K+4L+2M-(K_0-J_\gamma)\,(1-3a_{1j}^2)]\,\psi,\\
T_{2j+5} &= [K+2M+2a_{1j}a_{1j+1}(J_\alpha-J_\beta)+K_0(1-3a_{1j+2}^2)]\,\psi,\\
T_{2j+6} &= [K+2M-2a_{1j}a_{1j+1}(J_\alpha-J_\beta)+K_0(1-3a_{1j+2}^2)]\,\psi,\\
T_{13} &= [3K-6M+2(J_\alpha-J_\beta)\,(a_{11}a_{12}+a_{12}a_{13}+a_{13}a_{11})]\,\psi,\\
T_{j+13} &= [3K-6M+2(J_\alpha-J_\beta)\,(a_{1j}a_{1j+1}-a_{1j+1}a_{1j+2}-a_{1j+2}a_{1j})]\,\psi,\\
T_{17} &= -[6J+3K+12L+6M]\,\psi,\\
T_{j+17} &= [2J-3K+4L-6M+2J_\gamma(1-3a_{1j+2}^2)]\,\psi,
\end{aligned}\right\}\qquad(2{\cdot}33)$$

where we have used (2·2), (2·4), (2·9), (2·24), and where each time $j = 1$, 2, or 3.

To see how one can find the types of order we shall discuss the case of T_{18}. This temperature is proportional to a quantity κ_{18} where

$$\kappa_{18} = \delta_1+\delta_2+\delta_3+3\mu-4\lambda+2\rho_1+2\rho_1'-2\rho_2-2\rho_2'-2\rho_3-2\rho_3', \qquad (2\cdot34)$$

and κ_{18} must therefore by Anderson's theorem also be proportional to the exchange energy of the central atom with its surroundings. [If we assume that the J_i, K_i, L, and M are all positive, we see from (2·20) to (2·23) that the δ_i, ρ_i, ρ_i', λ, and μ are also all positive.] From (2·14) and the fact that $V^{8\mathrm{d}}$ should be proportional to κ_{18} we see that the spins on the 1d, 2d, 3d, 4d, 5d, 6d, 7d, 8d, 5a, 6a, 7a, and 8a sublattices must all be parallel to one another and they must be antiparallel to the spins on the 2b, 4b, 6b, 8b, 3c, 4c, 7c, and 8c sublattices which in turn must all be parallel to one another. About the spins on the 1a, 2a, 3a, 4a, 1b, 3b, 5b, 7b, 1c, 2c, 5c, and 6c sublattices we can only say that four of these sublattices must be parallel to the spins on the 8d sublattices and 8 of them antiparallel. By considering either other central atoms, or the original homogeneous equations one can, however, verify that the intuitive choice of 1a, 2a, 3a, and 4a for the first group and 1b, 3b, 5b, 7b, 1c, 2c, 5c, and 6c for the second group is, indeed, the correct one. This type of ordering is called type 1 ordering and the particular ordering pattern corresponding to T_{18} is given in figure 5.

If we perform the same analysis to the other T_i we find that T_{18}, T_{19}, and T_{20} correspond to type 1 order; T_{13}, T_{14}, T_{15}, and T_{16} to type 2 order (see figure 6, which corresponds to T_{14}), T_1, T_2, T_3, T_4, T_5, and T_6 to type 3 order (of which there are two modifications 3A and 3B to be discussed presently, which are drawn in figures 7 and 8; figure 7 corresponds to T_3 and figure 8 to T_4), T_7, T_8, T_9, T_{10}, T_{11}, and T_{12} to type 4 order (see figure 9 which corresponds to T_{11}; here there are also two modifications: if T_{11} corresponds to type 4A, T_{12} will correspond to type 4B), and finally T_{17} corresponds to a ferromagnetic order, where all spins are pointing in the same direction.

We have followed here and everywhere in this paper the usual convention that the number of the type of order increases with increasing dimensions of the repeated magnetic ordered structure.

Having found for each T_i the type of order to which it corresponds, we must now examine the total energy of the lattice. First of all, we find for each T_i the most stable 'proper' antiferromagnetic order; we define a 'proper' order as one for which all spins are parallel or antiparallel to a single direction, $\mathbf{n}$. This direction is found from the expressions for the T_i by maximizing these with respect to the a_{ij}. We finally examine the proper types of order found in this way to see whether they are, in fact, stable; this is done by seeing whether the total interaction energy is an extremum when the S^i are varied. If we do this, we find that all type 1 and type 2 ordering patterns corresponding to a proper antiferromagnetic order are stable.

The situation is different, however, for type 3 and type 4 order. Consider the 3A and 3B ordering patterns of figures 7 and 8, and recall that the total interaction energy will be proportional to T_3 (or T_4). As long as the a and b sublattices together, and also the c and d lattices together, are properly antiferromagnetically ordered, there will be no net interaction energy between the a and b sublattices, on the one hand, and the c and d sublattices, on the other hand. The actual type of ordering which will occur is thus found by setting each

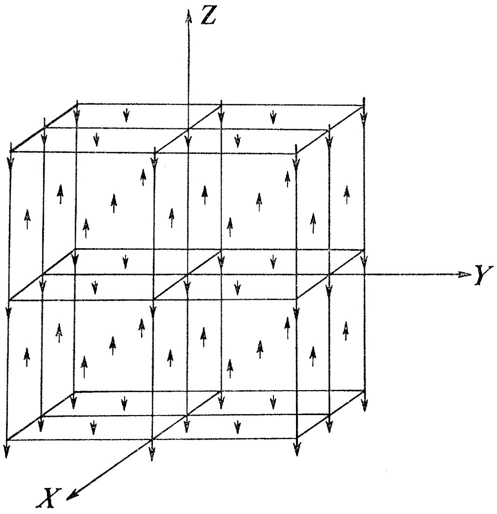

FIGURE 5. Type 1 order for the f.c.c. case.

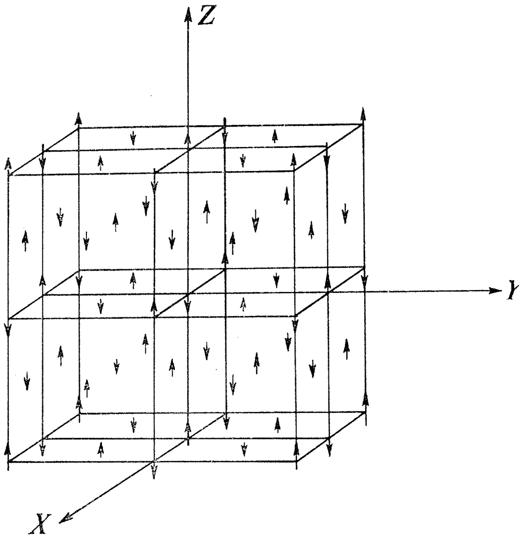

FIGURE 6. Type 2 order for the f.c.c. case.

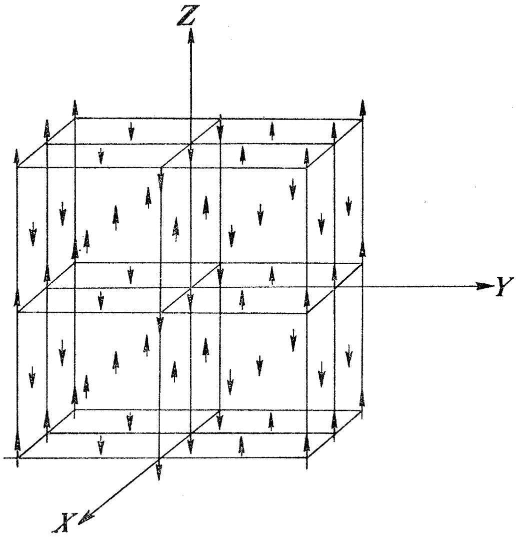

FIGURE 7. Type 3A order for the f.c.c. case.

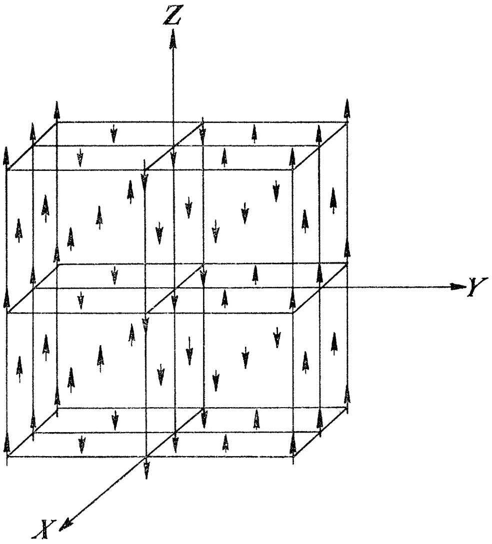

FIGURE 8. Type 3B order for the f.c.c. case.

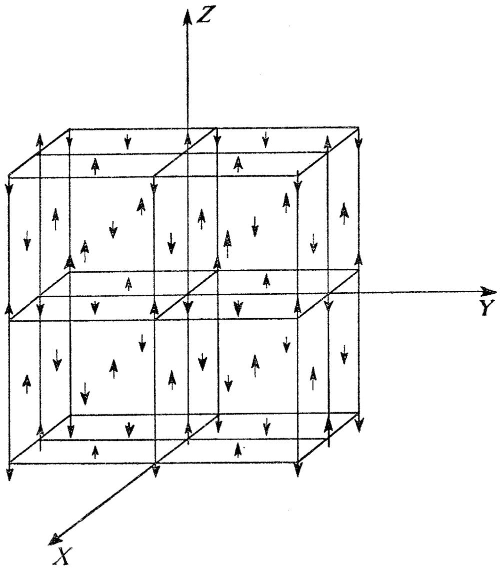

FIGURE 9. Type 4 order for the f.c.c. case.

of these two independent lattices separately into its energetically stable position. This may or may not result in a 'proper' order.

The molecular-field theory gives the type of order which will be most stable at T_C. Whether this order remains the stable one below T_C has been discussed by Smart (1952). In theory there is no reason why there could not be transitions to other types of order below T_C, but there is little empirical evidence for them; we shall therefore assume that they do not take place, so that the type of ordering which will produce the largest value for T_C can be identified with the ordering determined experimentally.

We shall now discuss the various types of order in somewhat more detail.

Ferromagnetic order. There is only one T_i corresponding to ferromagnetic order, and that is T_{17} which is the only T_i which is independent of the anisotropy parameters and of the a_{ij}. Our theory does, therefore, not give any information about the preferred direction of ordering. This means that the kind of anisotropy interaction which fixed the axis of ferromagnetism in a f.c.c. lattice cannot be expressed in the form we have used.

Type 1 *order.* We see from the expressions for T_{18}, T_{19}, and T_{20} that their maximum values are governed by the sign of J_γ. If J_γ is negative, T_{18} is maximum when $a_{13}^2 = 1$, that is

$$a_{13} = \pm 1, \quad a_{11} = a_{12} = 0, \tag{2·35}$$

so that the preferred direction **n** is along the positive or negative Z axis.

If J_γ is negative, T_{19} (T_{20}) corresponds to **n** along the positive or negative X axis (Y axis).

If, on the other hand, J_γ is positive, T_{18} is a maximum when

$$a_{13} = 0, \quad a_{11}^2 + a_{12} = 1, \tag{2·36}$$

so that **n** may be anywhere in the XY plane. Similarly **n** will be anywhere in the YZ plane (XZ plane) for the maximum value of T_{19} (T_{20}).

Type 2 *order.* We see from the expressions for T_{13}, T_{14}, T_{15}, and T_{16} that there will be a different type of order pattern for $J_\alpha > J_\beta$ and $J_\alpha < J_\beta$. To fix our ideas, we shall consider T_{14}. If $J_\alpha > J_\beta$, T_{14} is maximum when

$$a_{11} = a_{12} = -a_{13} = 1/\surd 3. \tag{2·37}$$

The order itself consists of ferromagnetic [1, 1, −1] planes adjacent planes being antiferromagnetically alined (see figure 6). From (2·37) it follows that the spins will point at right angles to these planes, so that **n** is along the (1, 1, −1) direction.

If, on the other hand, $J_\alpha < J_\beta$, T_{14} is maximum when

$$a_{11} + a_{12} - a_{13} = 0, \tag{2·38}$$

corresponding to **n** being somewhere in the [1, 1, −1] plane.

The situation is similar for T_{13}, T_{15}, or T_{16}, where the [1, 1, −1] plane is now replaced by the [1, 1, 1], the [−1, 1, 1], or the [1, −1, 1] plane, respectively. If $J_\alpha > J_\beta$, **n** will be perpendicular to those planes, and if $J_\alpha < J_\beta$, **n** will be somewhere in those planes.

As mentioned before, for types 1 or 2 orders, all alinements are 'proper' so that all spins are either parallel or antiparallel to the preferred direction **n**. This means that in the present theory we shall not encounter models with type 1 or 2 order and spins on different sublattices making angles other than 0 or π with one another; such models have been suggested by other authors (for instance, Li 1955; Roth 1957).

We wish to conclude the discussion of type 2 order by saying a few words about the type 2B order proposed by Li (1955). We do not obtain this type of order, but the reason for this can easily be seen. The theory as we have developed it assumes that the interaction energy of any atom with its surroundings is the same, no matter upon which sublattice the chosen atom may be. Our theory will thus predict only those types of order which are 'homogeneous' in this sense. Although Li's type 2B order is homogeneous when the exchange interaction is assumed to be isotropic, this is no longer the case when anisotropy is introduced. The interaction energy E_d of a d sublattice centre with its surroundings differs from the energies E_a, E_b, and E_c of an a-, b-, or c-sublattice centre with their surroundings, the differences vanishing with J_α, J_β, J_γ, K_0 and K_i. Moreover, we find that the T_i corresponding to the type 2B order would be given by the expression

$$T_{2B} = (3K-6M)\,\psi, \tag{2·39}$$

and we can always make T_{13}, T_{14}, T_{15}, or T_{16} larger than T_{2B} whatever the sign or magnitude of $J_\alpha - J_\beta$. The type 2B order will thus not be stable as long as $J_\alpha \neq J_\beta$.

Type 3A *order*. We see from the expressions for T_1, T_3, and T_5 that the ordering pattern will depend on the sign of $J_\gamma + K_0$. If this quantity is positive **n** will be along the (1, 0, 0), the (0, 1, 0), or the (0, 0, 1) direction depending on whether we are considering T_1, T_3, or T_5. If, however, $J_\gamma + K_0$ is negative **n** will be along an arbitrary direction in the YZ, the XZ or the XY plane, and the ordering is not necessarily a 'proper' one.

Type 3B *order*. We see from the expressions for T_2, T_4, and T_6 that this type of order is only likely to occur, if some interactions are ferromagnetic and some antiferromagnetic; this is in contrast to the other types of order which may well occur with entirely antiferromagnetic interactions. The preferred orientation **n** is now again along the (1, 0, 0), the (0, 1, 0), or the (0, 0, 1) direction if $J_\gamma < K_0$, depending on whether we are considering T_2, T_4, or T_6, while if $J_\gamma > K_0$, **n** will be somewhere in the [1, 0, 0], the [0, 1, 0], or the [0, 0, 1] plane and the ordering need not be proper.

Type 4 *order*. We have really two slightly different type 4 orders. Figure 9 shows the type 4A, and the type 4B is obtained from it by reversing all the spins on the c-sublattice sites. In type 4A order the c and d sublattices together arrange their spins in ferromagnetic planes (in figure 9 the [1, 0, −1] planes), and the a and b sublattices in ferromagnetic planes at right angles to the former planes (in figure 9 the [1, 0, 1] planes). In type 4B order all arrangements are in parallel ferromagnetic planes (if we reverse the spins in figure 9 all spins are in ferromagnetic [1, 0, 1] planes).

The directions of the spins depend on the relations between K_0, J_α, and J_β. We shall give the directions for the type 4A order corresponding to T_{11} and for the type 4B order corresponding to T_{12}. The directions corresponding to T_7, T_8, T_9, and T_{10} can be obtained by cyclic permutations. There are three possibilities: (i) $J_\alpha > J_\beta$, $K_0 > 0$, or $J_\alpha > J_\beta$, $K_0 < 0$, $J_\alpha - J_\beta + 3K_0 > 0$; (ii) $J_\alpha < J_\beta$, $K_0 > 0$, or $J_\alpha < J_\beta$, $K_0 < 0$, $J_\beta - J_\alpha + 3K_0 > 0$; and (iii) $K_0 < 0$, $3\,|K_0| > |J_\alpha - J_\beta|$. In case (iii) **n** will be along the (0, 1, 0) direction for both type 4A and type 4B order; the order is proper. In cases (i) and (ii) the type 4A order is not a proper one: the spins on the a and b sublattices will be at right angles to the spins on the c and d sublattices; the type 4B order will, however, still be a proper one. In both cases (i) and (ii) the spins will be orientated along face-diagonals in the (0, 1, 0) planes; in case (i) they will be oriented at right angles to the ferromagnetic plane in which they are contained, while in case (ii) they will be oriented in those planes.

We note in conclusion that no matter what are the values of the exchange parameters, there is in the present theory no preference for either type 4A or type 4B order.

3. Comparison with experimental data on face-centred cubic magnetic lattices

So far we have considered only an isolated f.c.c. lattice of magnetic atoms, and we have neglected the presence of the non-magnetic atoms. We know that such anions are extremely important as far as the isotropic exchange is concerned, as they are essential for superexchange. We must therefore investigate carefully for each crystal structure whether the position of the anions should force us to modify the form of the anisotropy which we introduced for our magnetic lattice.

Most of the f.c.c. antiferromagnetics for which we have experimental data have the rocksalt crystal structure; the anions are situated midway between each pair of second neighbours. The rhombic symmetry for first neighbours and the axial symmetry for second neighbours are both preserved when the anions are included, and the theory of the preceding section should be applicable.

Recently, Corliss, Elliott & Hastings (1956, 1959) have studied f.c.c. antiferromagnets with zinc blende and with pyrite crystal structures. In neither of these cases are the symmetries of the isolated magnetic lattice preserved. In both cases, however, the positions of the anions lead us to expect that the first-neighbour-exchange energy will be considerably larger than the interaction energies involving more distant neighbours. As we have already rhombic symmetry for the first-neighbour-exchange interaction, we shall suppose that again the theory of the preceding section is applicable—or that it will at least give a fair approximation for these cases.

The best test of the theory is obtained by examining neutron diffraction results for the observed directions of spin alinement in rocksalt-structure f.c.c. antiferromagnets. Examples of such antiferromagnets are MnO, CoO, FeO, NiO, αMnS (Roth 1958), and CrN (Corliss, Elliott & Hastings 1960). All these, except CrN, show type 2 order. FeO has its spins alined at right angles to the ferromagnetic [1, 1, 1] type planes. MnO, NiO, and αMnS have their spins ordered somewhere in the ferromagnetic planes, but experimental data have so far not yet revealed the direction of alinement more precisely. These results are all in accord with the present theory.

The case of CoO is probably slightly anomalous, as is shown by its Θ/T_C value; it is thus not surprising that the spins seem to be alined in a direction slightly out of the ferromagnetic plane.

CrN shows type 4B order, but the preferred direction of spin alinement has not yet been determined. As type 4 order will not occur, unless more-remote-neighbour interactions are taken into account, this case shows the danger of neglecting these interactions.

MnS_2, $MnTe_2$, and $MnSe_2$ (Corliss *et al.* 1959) are pyrite structure f.c.c. antiferromagnetics. MnS_2 shows type 3A order and has its preferred direction of ordering along the unique cubic axis, corresponding thus to a J_γ value which is probably positive (if we make the plausible assumption that $|K_0| < |J_\gamma|$). $MnTe_2$ shows type 1 order with its preferred spin direction at right angles to the unique cubic axis, again pointing to a positive

J_γ value. $MnSe_2$ is of great interest in that it shows a type of order which is not homogeneous. It is easy, however, to adapt the molecular-field theory for this case to find an expression for T_C. We found that this particular type of order can be stable only if anisotropy is included in the exchange energies. Moreover, we found that the observed direction of spin alinement is the direction predicted if J_γ is positive. As the three salts are isomorphic, the prediction of a positive J_γ in each case is, perhaps, not merely coincidental. Finally, βMnS is a zinc blende f.c.c. antiferromagnetic (Corliss *et al.* 1956) which shows type 3A order with spins alined at right angles to the unique axis, indicating a negative J_γ.

A final point of interest is that the extension of the molecular-field theory to include third- and fourth-neighbour interactions has removed the direct conflict between, on the one hand, the large Θ/T_C ratios of about 10 which have been obtained experimentally for some f.c.c. salts (for instance, K_2IrCl_6 and $(NH_4)_2IrCl_6$; see Griffiths *et al.* 1959) and, on the other hand, molecular-field theory. We find, for instance, that if $J = 2K = 4L = 8M$, and $J_\alpha = J_\beta = J_\gamma = K_0 = K_i = 0$, $\Theta/T_i = 15$ for all T except T_{17}. Such values for L and M may be on the large side, but the existence of type 4 order shows—as we mentioned a moment ago—that neighbours beyond the second nearest neighbours may well have to be taken into account. This result is in line with what Anderson (1950) found when he included for the first time second-neighbour interactions. It must be mentioned, that the Θ/T_C ratio decreases when anisotropy is taken into account.

It is generally accepted (cf. Marshall 1955) that the ground state of a f.c.c. antiferromagnetic with isotropic nearest neighbour interactions only will not be an ordered one. This would mean $T_C = 0$, or an infinite Θ/T_C-ratio. The molecular-field method obviously breaks down here as it predicts a Curie temperature equal to $2J\psi$ for that case. We feel that, in fact, the high Θ/T_C ratio found for the chloro-iridates is connected with this breakdown of the molecular-field method and not with the influence of higher order neighbours.

4. The body-centred cubic magnetic lattice

We now treat the body-centred cubic (b.c.c.) lattice by the same methods. We shall again consider a magnetic lattice without anions, and again we shall use enough sublattices to allow for any possible order with a periodicity in any direction of up to two unit cell lengths. We require sixteen sublattices and shall include first-, second-, and third-neighbour exchange interactions which we shall take to be all anisotropic.

The b.c.c. sublattices are shown in figure 10; they are labelled 1a, 2a, ..., 8a, 1b, 2b, ..., and 8b. For the first neighbours we can only define two exchange parameters which are different, because the line connecting two first neighbours is a fourfold axis of symmetry (see figure 11). If we take our x', y', z' axes along the $(1, 1, 1)$, the $(-1, 1, 0)$, and the $(-1, -1, 2)$ directions we can write for the interaction between the (central) 8a atom and its first neighbour on the 4b site

$$V_{8a,4b} = 2J_1 S^{8a}_{x'} S^{4b}_{x'} + 2J_2 S^{8a}_{y'} S^{4b}_{y'} + 2J_2 S^{8a}_{z'} S^{4b}_{z'}. \qquad (4\cdot1)$$

Again transforming to a Σ' system, using the molecular field approximation to put in $\Sigma' : \langle S_y \rangle = \langle S_z \rangle = 0$ for all sublattices, and dropping the subscripts x we get

$$V_{8a,4b} = S^{8a} S^{4b} [\tfrac{2}{3} J_1 (a_{11} + a_{12} + a_{13})^2 + J_2 (a_{11} - a_{12})^2 + \tfrac{1}{3} J_2 (a_{11} + a_{12} - 2a_{13})^2]. \qquad (4\cdot2)$$

We get similar expressions for the interactions of 8a with the first neighbours on the 1b, 2b, 3b, 5b, 6b, 7b, and 8b sites.

There are six second neighbours: two each on the 4a, 6a, and 7a lattice sites. The line connecting the central atom with a second neighbour is again a fourfold axis, and we can introduce the exchange constants K_1 and K_2 in exactly the same way as for the f.c.c. case. There are 12 third neighbours: four each on the 2a, 3a, and 5a sublattices. The corresponding exchange parameters M_1, M_2, and M_3 will be introduced in the same way as J_1, J_2, and J_3 were introduced in the f.c.c. case.

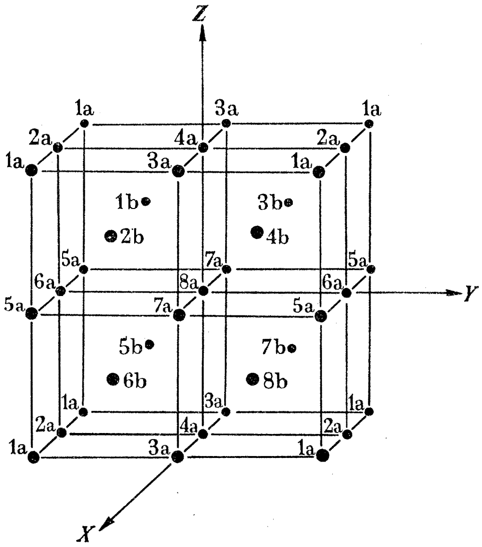

FIGURE 10. The sixteen sublattices of the b.c.c. magnetic lattice.

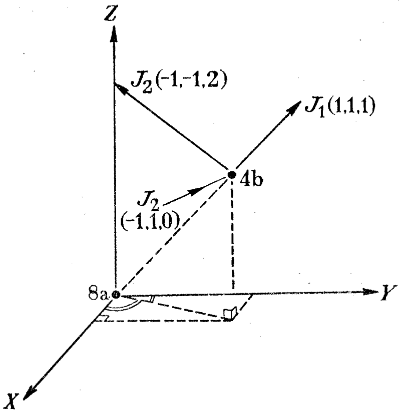

FIGURE 11. First-neighbour interactions in the b.c.c. case.

The total exchange interaction energy corresponding to the 8a atom is finally given by the equation

$$V^{8\mathrm{a}} = S^{8\mathrm{a}}[\rho_1(S^{1\mathrm{b}}+S^{8\mathrm{b}})+\rho_2(S^{4\mathrm{b}}+S^{5\mathrm{b}})+\rho_3(S^{3\mathrm{b}}+S^{6\mathrm{b}}) \\ +\rho_4(S^{2\mathrm{b}}+S^{7\mathrm{b}})+\delta_1 S^{7\mathrm{a}}+\delta_2 S^{6\mathrm{a}}+\delta_3 S^{4\mathrm{a}}+\alpha_1 S^{4\mathrm{a}}+\alpha_2 S^{3\mathrm{a}}+\alpha_3 S^{5\mathrm{a}}], \qquad (4\cdot3)$$

where

$$\rho_1 = \tfrac{2}{3}J_1(a_{11}+a_{12}-a_{13})^2+J_2(a_{11}-a_{12})^2+\tfrac{1}{3}J_2(a_{11}+a_{12}+2a_{13})^2, \qquad (4\cdot4)$$

$$\rho_2 = \tfrac{2}{3}J_1(a_{11}+a_{12}+a_{13})^2+J_2(a_{11}-a_{12})^2+\tfrac{1}{3}J_2(a_{11}+a_{12}-2a_{13})^2, \qquad (4\cdot5)$$

$$\rho_3 = \tfrac{2}{3}J_1(a_{11}-a_{12}-a_{13})^2+J_2(a_{11}+a_{12})^2+\tfrac{1}{3}J_2(a_{11}-a_{12}+2a_{13})^2, \qquad (4\cdot6)$$

$$\rho_4 = \tfrac{2}{3}J_1(a_{11}-a_{12}+a_{13})^2+J_2(a_{11}+a_{12})^2+\tfrac{1}{3}J_2(a_{11}-a_{12}-2a_{13})^2, \qquad (4\cdot7)$$

$$\delta_i = 4K_1 a_{1i}^2+4K_2(a_{1i+1}^2+a_{1i+2}^2), \qquad (4\cdot8)$$

$$\alpha_i = 4(M_1+M_2)\,(a_{1i+1}^2+a_{1i+2}^2)+8M_3 a_{1i}^2. \qquad (4\cdot9)$$

Proceeding as before, we find (cf. (2·25))

$$\sum_i S^i = \phi^{-1}[16g\mu_B H_{\mathrm{ext.}}-(16J+12K+24M)\sum_i S^i], \qquad (4\cdot10)$$

where we have put
$$J_1 = J + J_0, \quad J_2 = J + J_i, \quad J_0 + 2J_i = 0; \tag{4·11}$$
$$K_1 = K + K_0, \quad K_2 = K + K_i, \quad K_0 + 2K_i = 0; \tag{4·12}$$
$$M_1 = M + M_\alpha, \quad M_2 = M + M_\beta, \quad M_3 = M + M_\gamma, \quad M_\alpha + M_\beta + M_\gamma = 0, \tag{4·13}$$
where the summation is over the sixteen sublattices, where ϕ is given by (2·19), and where the external field is supposed to be along the x axis.

From (4·10) we get an isotropic Weiss constant
$$\Theta = (4J + 3K + 6M)\,\psi, \tag{4·14}$$
where ψ is given by (2·29).

$$\begin{vmatrix}
\phi & \delta_1 & \delta_2 & \alpha_3 & \delta_3 & \alpha_2 & \alpha_1 & 0 & \rho_1 & \rho_4 & \rho_3 & \rho_2 & \rho_2 & \rho_3 & \rho_4 & \rho_1 \\
\delta_1 & \phi & \alpha_3 & \delta_2 & \alpha_2 & \delta_3 & 0 & \alpha_1 & \rho_4 & \rho_1 & \rho_2 & \rho_3 & \rho_3 & \rho_2 & \rho_1 & \rho_4 \\
\delta_2 & \alpha_3 & \phi & \delta_1 & \alpha_1 & 0 & \delta_3 & \alpha_2 & \rho_3 & \rho_2 & \rho_1 & \rho_4 & \rho_4 & \rho_1 & \rho_2 & \rho_3 \\
\alpha_3 & \delta_2 & \delta_1 & \phi & 0 & \alpha_1 & \alpha_2 & \delta_3 & \rho_2 & \rho_3 & \rho_4 & \rho_1 & \rho_1 & \rho_4 & \rho_3 & \rho_2 \\
\delta_3 & \alpha_2 & \alpha_1 & 0 & \phi & \delta_1 & \delta_2 & \alpha_3 & \rho_2 & \rho_3 & \rho_4 & \rho_1 & \rho_1 & \rho_4 & \rho_3 & \rho_2 \\
\alpha_2 & \delta_3 & 0 & \alpha_1 & \delta_1 & \phi & \alpha_3 & \delta_2 & \rho_3 & \rho_2 & \rho_1 & \rho_4 & \rho_4 & \rho_1 & \rho_2 & \rho_3 \\
\alpha_1 & 0 & \delta_3 & \alpha_2 & \delta_2 & \alpha_3 & \phi & \delta_1 & \rho_4 & \rho_1 & \rho_2 & \rho_3 & \rho_3 & \rho_2 & \rho_1 & \rho_4 \\
0 & \alpha_1 & \alpha_2 & \delta_3 & \alpha_3 & \delta_2 & \delta_1 & \phi & \rho_1 & \rho_4 & \rho_3 & \rho_2 & \rho_2 & \rho_3 & \rho_4 & \rho_1 \\
\rho_1 & \rho_4 & \rho_3 & \rho_2 & \rho_2 & \rho_3 & \rho_4 & \rho_1 & \phi & \delta_1 & \delta_2 & \alpha_3 & \delta_3 & \alpha_2 & \alpha_1 & 0 \\
\rho_4 & \rho_1 & \rho_2 & \rho_3 & \rho_3 & \rho_2 & \rho_1 & \rho_4 & \delta_1 & \phi & \alpha_3 & \delta_2 & \alpha_2 & \delta_3 & 0 & \alpha_1 \\
\rho_3 & \rho_2 & \rho_1 & \rho_4 & \rho_4 & \rho_1 & \rho_2 & \rho_3 & \delta_2 & \alpha_3 & \phi & \delta_1 & \alpha_1 & 0 & \delta_3 & \alpha_2 \\
\rho_2 & \rho_3 & \rho_4 & \rho_1 & \rho_1 & \rho_4 & \rho_3 & \rho_2 & \alpha_3 & \delta_2 & \delta_1 & \phi & 0 & \alpha_1 & \alpha_2 & \delta_3 \\
\rho_2 & \rho_3 & \rho_4 & \rho_1 & \rho_1 & \rho_4 & \rho_3 & \rho_2 & \delta_3 & \alpha_2 & \alpha_1 & 0 & \phi & \delta_1 & \delta_2 & \alpha_3 \\
\rho_3 & \rho_2 & \rho_1 & \rho_4 & \rho_4 & \rho_1 & \rho_2 & \rho_3 & \alpha_2 & \delta_3 & 0 & \alpha_1 & \delta_1 & \phi & \alpha_3 & \delta_2 \\
\rho_4 & \rho_1 & \rho_2 & \rho_3 & \rho_3 & \rho_2 & \rho_1 & \rho_4 & \alpha_1 & 0 & \delta_3 & \alpha_2 & \delta_2 & \alpha_3 & \phi & \delta_1 \\
\rho_1 & \rho_4 & \rho_3 & \rho_2 & \rho_2 & \rho_3 & \rho_4 & \rho_1 & 0 & \alpha_1 & \alpha_2 & \delta_3 & \alpha_3 & \delta_2 & \delta_1 & \phi
\end{vmatrix}$$

FIGURE 12. The determinant of the secular equation for the b.c.c. case.

To find the transition temperature, we put $H_{\text{ext.}} = 0$ in the 16 equations for the 16 S^i, and this leads to a secular equation of the form
$$D_{\text{b.c.c.}} = 0, \tag{4·15}$$
where the 16×16 determinant $D_{\text{b.c.c.}}$ is the one given in figure 12. This determinant can be factorized. The different factors are
$$\left.\begin{aligned}
&(1) \quad \phi - \delta_1 + \delta_2 + \delta_3 + \alpha_1 - \alpha_2 - \alpha_3, \\
&(2) \quad \phi + \delta_1 - \delta_2 + \delta_3 - \alpha_1 + \alpha_2 - \alpha_3, \\
&(3) \quad \phi + \delta_1 + \delta_2 - \delta_3 - \alpha_1 - \alpha_2 + \alpha_3, \\
&(4) \quad \phi - \delta_1 - \delta_2 - \delta_3 + \alpha_1 + \alpha_2 + \alpha_3, \\
&(5) \quad \phi + \delta_1 - \delta_2 - \delta_3 + \alpha_1 - \alpha_2 - \alpha_3 + 2(-\rho_1 + \rho_2 + \rho_3 - \rho_4), \\
&(6) \quad \phi - \delta_1 + \delta_2 - \delta_3 - \alpha_1 + \alpha_2 - \alpha_3 + 2(\rho_1 - \rho_2 + \rho_3 - \rho_4), \\
&(7) \quad \phi - \delta_1 - \delta_2 + \delta_3 - \alpha_1 - \alpha_2 + \alpha_3 + 2(\rho_1 + \rho_2 - \rho_3 - \rho_4), \\
&(8) \quad \phi + \delta_1 - \delta_2 - \delta_3 + \alpha_1 - \alpha_2 - \alpha_3 - 2(-\rho_1 + \rho_2 + \rho_3 - \rho_4), \\
&(9) \quad \phi - \delta_1 + \delta_2 - \delta_3 - \alpha_1 + \alpha_2 - \alpha_3 - 2(\rho_1 - \rho_2 + \rho_3 - \rho_4), \\
&(10) \quad \phi - \delta_1 - \delta_2 + \delta_3 - \alpha_1 - \alpha_2 + \alpha_3 - 2(\rho_1 + \rho_2 - \rho_3 - \rho_4), \\
&(11) \quad \phi + \delta_1 + \delta_2 + \delta_3 + \alpha_1 + \alpha_2 + \alpha_3 + 2(\rho_1 + \rho_2 + \rho_3 + \rho_4), \\
&(12) \quad \phi + \delta_1 + \delta_2 + \delta_3 + \alpha_1 + \alpha_2 + \alpha_3 - 2(\rho_1 + \rho_2 + \rho_3 + \rho_4).
\end{aligned}\right\} \tag{4·16}$$

Of the 12 factors (4·16) the first 4 occur twice in $D_{\text{b.c.c.}}$. Solving for T_C, we first of all find the values T_i which make the different factors of $D_{\text{b.c.c.}}$ equal to zero. We find

$$\left.\begin{aligned} T_j &= [-K+2M-(K_0-2M_\gamma)(1-3a_{1j}^2)]\,\psi, \\ T_4 &= (3K-6M)\,\psi, \\ T_{4+j} &= [K+2M+(K_0+2M_\gamma)(1-3a_{1j}^2)-\tfrac{8}{3}(J_0-J_i)\,a_{1j+1}a_{1j+2}]\,\psi, \\ T_{7+j} &= [K+2M+(K_0+2M_\gamma)(1-3a_{1j}^2)+\tfrac{8}{3}(J_0-J_i)\,a_{1j+1}a_{1j+2}]\,\psi, \\ T_{11} &= (-4J-3K-6M)\,\psi, \\ T_{12} &= (4J-3K-6M)\,\psi. \end{aligned}\right\} \qquad (4{\cdot}17)$$

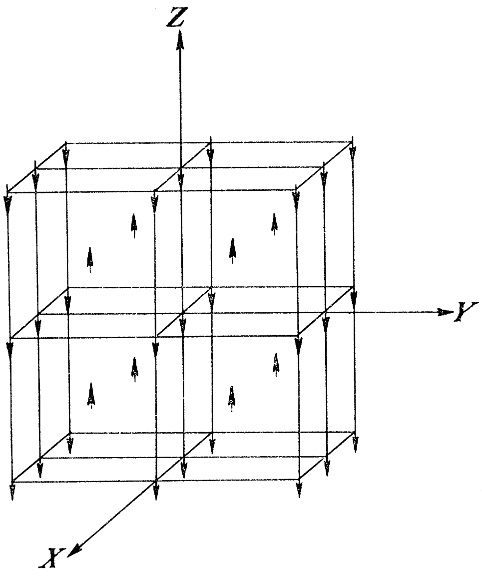

FIGURE 13. Type 1 order for the b.c.c. case.

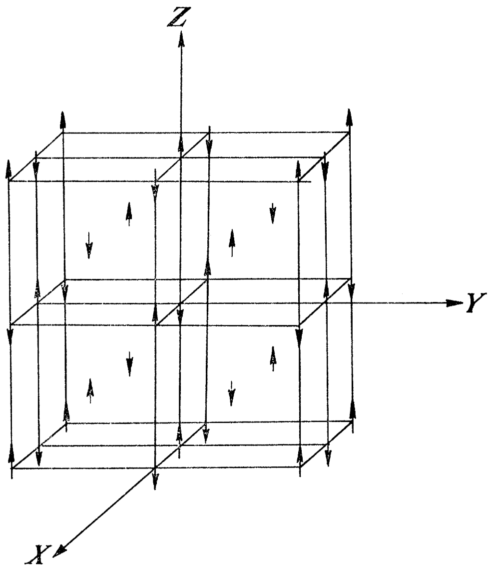

FIGURE 14. Type 2 order for the b.c.c. case.

To find the kind of order corresponding to the different T_i, we perform an analysis similar to the one in § 2. We find that T_{12} corresponds to type 1 order (see figure 13); T_4 to type 2 order (see figure 14); T_5, T_6, T_7, T_8, T_9, and T_{10} to type 3 order (see figure 15, which corresponds to T_6); T_1, T_2, and T_3 to type 4 order (see figure 16, which corresponds to T_1); and T_{11} to ferromagnetic order.

We shall now discuss the various types of order in somewhat more detail.

Ferromagnetic order. As T_{11} is independent of the anisotropy parameters, we cannot make any statement about the preferred direction of ordering.

Type 1 *order.* Again T_{12} is independent of the anisotropy parameters.

Type 2 *order.* Here also, T_4 is independent of the anisotropy parameters. One can show that the a sublattices together must be alined antiferromagnetically, as must the b sublattices. There is the possibility that the preferred directions of the spins may be different for the a and the b sublattices.

Type 3 *order.* To fix our ideas, we shall consider T_6. If K_0+2M_γ is positive, or if

$$K_0+2M_\gamma < 0 \quad \text{and} \quad 9\,|K_0+2M_\gamma| < 4\,|J_1-J_2|,$$

ordering takes place in the XZ plane. If $J_1 > J_2$, the preferred direction will be along the $(1, 0, -1)$ direction, and for $J_1 < J_2$ along the $(1, 0, 1)$ direction. Finally, if

$$K_0+2M_\gamma < 0 \quad \text{and} \quad 9\,|K_0+2M_\gamma| > 4\,|J_1-J_2|,$$

the preferred direction is along the Y axis. The situation is similar for T_5, T_7, T_8, T_9, and T_{10}.

Type 4 *order*. If $K_0 - 2M_\gamma > 0$, the preferred direction for T_1 will be along the X axis, and if $K_0 - 2M_\gamma < 0$, the preferred direction will be somewhere in the YZ plane, while the a and the b sublattices may be ordered with different preferred directions.

If we put $K = \frac{2}{3}J$. $M = \frac{1}{6}J$, and neglect interactions more remote than third-neighbour interactions we can get Θ/T_C as high as 7.

We must emphasize that the b.c.c. magnetic lattice appears but rarely in actual antiferromagnetics so that the discussion in the present section is mainly academic. Many antiferromagnetics exist, however, with a b.c.t. magnetic lattice which resembles the b.c.c. lattice in many ways, so that often the results for the b.c.c. case have been applied, with some success, to tetragonal antiferromagnetics. In § 6 we shall treat the b.c.t. magnetic lattice properly, and we shall then be able to see in how far the b.c.c. case is a good approximation to the tetragonal case.

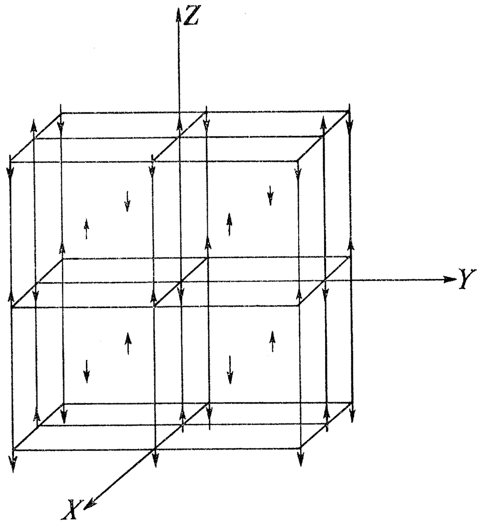

FIGURE 15. Type 3 order for the b.c.c. case.

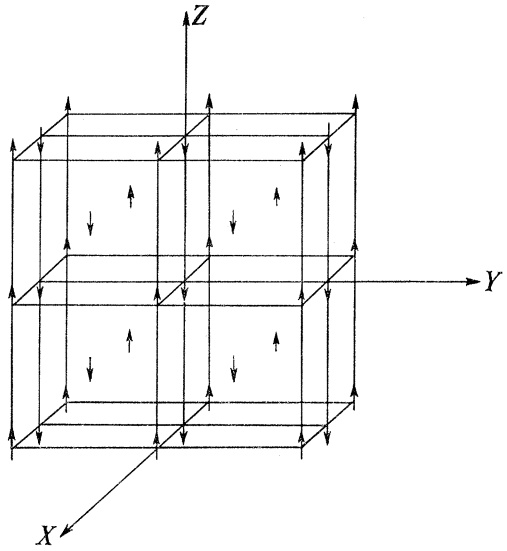

FIGURE 16. Type 4 order for the b.c.c. case.

5. THE SIMPLE CUBIC MAGNETIC LATTICE

The case of the simple cubic (s.c.) lattice is also mainly of academic interest, but we have included it for the sake of completeness. Again we have introduced enough sublattices, eight in this case, to cover all types of ordering with a period of up to two unit cube lengths. The sublattices are shown in figure 17. The central atom is taken on the eighth sublattice. Its 6 first neighbours, two each on the four, six, and seven sublattices, are in the same relative position to the central atom as the second neighbours in the b.c.c. case, and we shall use the same expression for the energy as was done in the previous section so that the first-neighbour-interaction parameters will be denoted by K_1 and K_2. The 12 second neighbours, 4 each on the two, three, and five sublattices, are in the same relative positions as the third neighbours in the b.c.c. case. We shall use the same notation for the corresponding energy expression which will thus involve the exchange parameters M_1, M_2, and M_3. For K_1, K_2, M_1, M_2, and M_3 we shall again use (4·12) and (4·13). The 8 third neighbours on the 1 sublattice are in the same relative position as the first neighbours in the b.c.c. case. The energy expression will thus be of the same form as we have in the previous section. To emphasize that we are dealing with more remote neighbours we shall denote the exchange parameters by letters which are later in the alphabet: P_1 and P_2 for which we shall write

$$P_1 = P+P_0, \quad P_2 = P+P_i, \quad P_0+2P_i = 0. \tag{5·1}$$

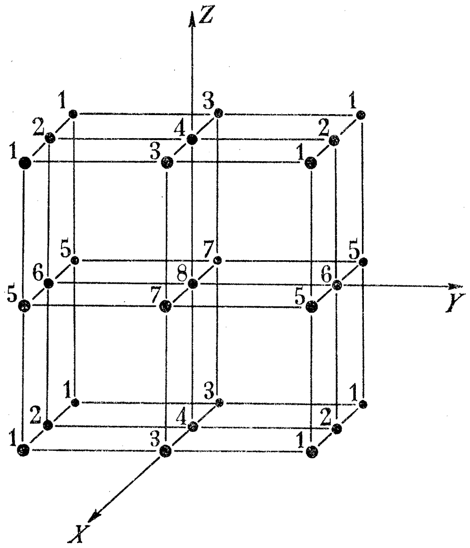

FIGURE 17. The eight sublattices of the s.c. magnetic lattice.

$$\begin{vmatrix}
\phi & \rho_1 & \rho_2 & \delta_3 & \rho_3 & \delta_2 & \delta_1 & \nu \\
\rho_1 & \phi & \delta_3 & \rho_2 & \delta_2 & \rho_3 & \nu & \delta_1 \\
\rho_2 & \delta_3 & \phi & \rho_1 & \delta_1 & \nu & \rho_3 & \delta_2 \\
\delta_3 & \rho_2 & \rho_1 & \phi & \nu & \delta_1 & \delta_2 & \rho_3 \\
\rho_3 & \delta_2 & \delta_1 & \nu & \phi & \rho_1 & \rho_2 & \delta_3 \\
\delta_2 & \rho_3 & \nu & \delta_1 & \rho_1 & \phi & \delta_3 & \rho_2 \\
\delta_1 & \nu & \rho_3 & \delta_2 & \rho_2 & \delta_3 & \phi & \rho_1 \\
\nu & \delta_1 & \delta_2 & \rho_3 & \delta_3 & \rho_2 & \rho_1 & \phi
\end{vmatrix}$$

FIGURE 18. The determinant of the secular equation for the s.c. case.

For the total interaction energy of the central atom we find in the same way as before

$$V^8 = S^8[\rho_1 S^7+\rho_2 S^6+\rho_3 S^4+\delta_1 S^2+\delta_2 S^3+\delta_3 S^5+\nu S^1], \tag{5·2}$$

where we have invoked the molecular-field approximation to put all y and z components equal to their vanishing average value, where we have dropped the indices x, and where

$$\rho_i = 4a_{1i}^2 K_1+4(a_{1i+1}^2+a_{1i+2}^2)\,K_2, \tag{5·3}$$

$$\delta_i = 8a_{1i}^2 M_3+4(a_{1i+1}^2+a_{1i+2}^2)\,(M_1+M_2), \tag{5·4}$$

$$\nu = 16P. \tag{5·5}$$

We get again an isotropic Weiss constant which is now given by

$$\Theta = (3K+6M+4P)\,\psi. \tag{5·6}$$

To find the transition temperature, we must solve a secular equation

$$D_{\text{s.c.}} = 0, \tag{5·7}$$

where the 8×8 determinant $D_{\text{s.c.}}$ is the one given in figure 18. This determinant can be factorized and its eight different factors are

$$\left.\begin{array}{ll}
(1) & \phi+\rho_1-\rho_2-\rho_3+\delta_1-\delta_2-\delta_3+\nu,\\
(2) & \phi-\rho_1+\rho_2-\rho_3-\delta_1+\delta_2-\delta_3+\nu,\\
(3) & \phi-\rho_1-\rho_2+\rho_3-\delta_1-\delta_2+\delta_3+\nu,\\
(4) & \phi-\rho_1+\rho_2+\rho_3+\delta_1-\delta_2-\delta_3-\nu,\\
(5) & \phi+\rho_1-\rho_2+\rho_3-\delta_1+\delta_2-\delta_3-\nu,\\
(6) & \phi+\rho_1+\rho_2-\rho_3-\delta_1-\delta_2+\delta_3-\nu,\\
(7) & \phi-\rho_1-\rho_2-\rho_3+\delta_1+\delta_2+\delta_3-\nu,\\
(8) & \phi+\rho_1+\rho_2+\rho_3+\delta_1+\delta_2+\delta_3+\nu.
\end{array}\right\} \qquad (5{\cdot}8)$$

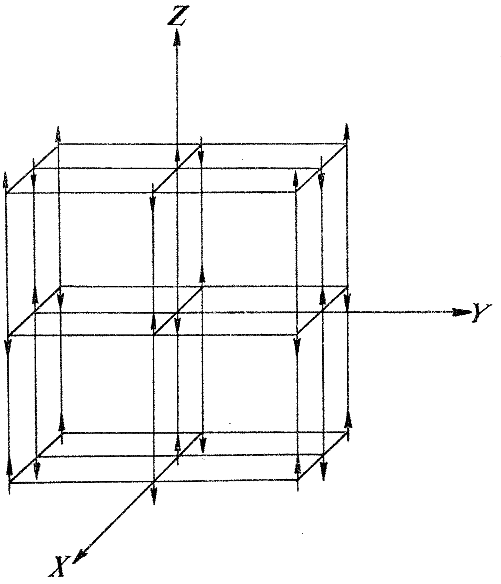

FIGURE 19. Type 1 order for the s.c. case.

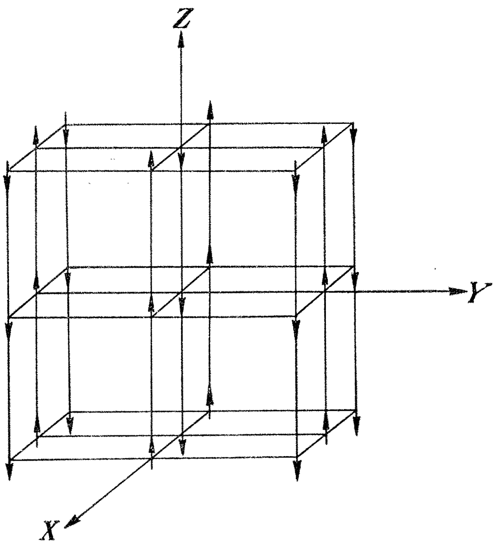

FIGURE 20. Type 2 order for the s.c. case.

The corresponding T_i are

$$\left.\begin{aligned}
T_j &= [K+2M-4P+(K_0+2M_\gamma)\,(1-3a_{1j}^2)]\,\psi,\\
T_{j+3} &= [-K+2M+4P-(K_0-2M_\gamma)\,(1-3a_{1j}^2)]\,\psi,\\
T_7 &= (3K-6M+4P)\,\psi,\\
T_8 &= (-3K-6M-4P)\,\psi.
\end{aligned}\right\} \qquad (5{\cdot}9)$$

We find that T_7 corresponds to type 1 order (see figure 19); T_1, T_2, and T_3 to type 2 order (see figure 20, which corresponds to T_3); T_4, T_5 and T_6, to type 3 order (see figure 21, which corresponds to T_6); and T_8 to ferromagnetic order. All types of order are 'proper' ones.

Ferromagnetic and type 1 *order.* T_7 and T_8 are independent of the anisotropy parameters, and there is no preferred direction.

Type 2 *order.* If $K_0+2M_\gamma<0$ the preferred direction for T_3 is along the Z axis, while if $K_0+2M_\gamma>0$ it may be anywhere in the XY plane.

Type 3 *order.* If $K_0-2M_\gamma>0$ the preferred direction for T_6 is along the Z axis, and for $K_0-2M_\gamma<0$ somewhere in the XY plane.

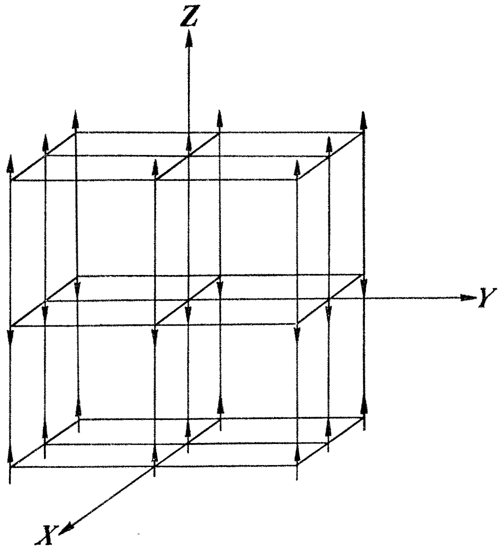

Figure 21. Type 3 order for the s.c. case.

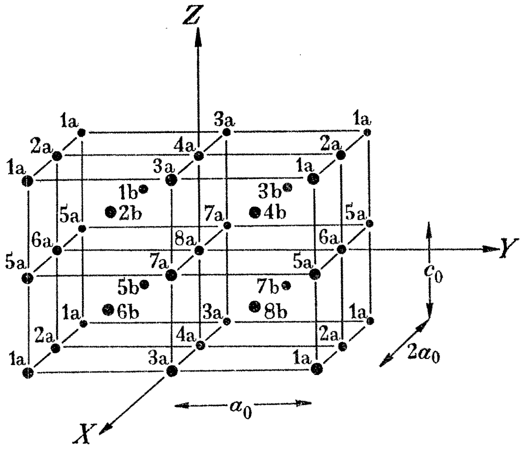

Figure 22. The 16 sublattices of the b.c.t. magnetic lattice.

6. The body-centred tetragonal magnetic lattice

Many antiferromagnetics, such as MnF_2, have their magnetic ions upon a body-centred tetragonal (b.c.t.) lattice. The lattice structure of the crystals themselves is often the rutile structure. In the present section we shall discuss the isolated b.c.t. magnetic lattice, and in the next section we shall consider the modifications to be introduced when the anions change the structure from the b.c.t. to the rutile one.

The b.c.t. magnetic lattice is shown in figure 22. We have now sixteen sublattices and will take first, second, and third neighbours into account. We must tread rather warily here. In most of the antiferromagnetics with a b.c.t. magnetic lattice, the ratio of c_0 to a_0, that is, of the distances between atoms along the Z and along the X or Y axes (see figure 22) lies between 0·6 and 0·8. Consider now a central atom on an 8a site. There are two first neighbours on 4a sites, eight second neighbours on the 1b, 2b, 3b, 4b, 5b, 6b, 7b, and 8b sublattices, and four third neighbours: two each on the 6a and 7a sublattices. The fourth neighbours are the eight atoms on the 2a and 3a sublattices, but these are only fractionally nearer to the central atom than the next 8a atoms along the Z axis. These latter atoms could only be included, if we introduced more than sixteen sublattices, and we decided therefore to neglect both fourth and fifth neighbours.

The total exchange interaction deriving from first-order interactions is given by the equation

$$V_1^{8a} = 4J_1 S_{x'}^{8a} S_{x'}^{4a} + 4J_2 S_{y'}^{8a} S_{y'}^{4a} + 4J_2 S_{z'}^{8a} S_{z'}^{4a}, \qquad (6{\cdot}1)$$

where the x', y', and z' directions are along the $(0,0,1)$, $(1,0,0)$, and $(0,1,0)$ directions. We have used here the fact that in the b.c.t. lattice the Z axis is a fourfold axis of symmetry.

The second-neighbour-exchange parameters K_1, K_2, and K_3 are introduced such that we have, for instance,

$$V_{8a,4b} = 2K_1 S_{x'}^{8a} S_{x'}^{4b} + 2K_2 S_{y'}^{8a} S_{y'}^{4b} + 2K_3 S_{z'}^{8a} S_{z'}^{4b}, \qquad (6{\cdot}2)$$

where the x', y', and z' directions are parallel to the unit vectors (P, P, Pw), $2^{-\frac{1}{2}}(-1, +1, 0)$, and $(Q, Q, -2Q/w)$ (see figure 23), where

$$w = \frac{c_0}{a_0}, \quad P = \frac{1}{\surd(2+w^2)}, \quad Q = \frac{w}{\surd(4+2w^2)}. \tag{6·3}$$

The third-neighbour-exchange parameters M_1, M_2, and M_3 are associated with the following directions: M_1 with the line connecting the central atom with the third neighbour considered, M_3 with the Z direction, while M_2 is associated with a direction perpendicular to the first two directions.

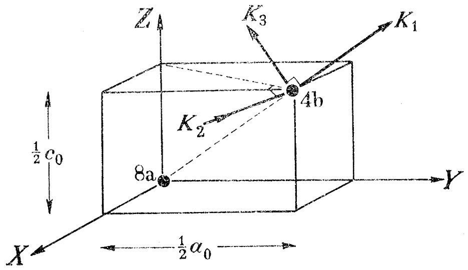

FIGURE 23. Second-neighbour interactions in the b.c.t. case.

The total exchange energy V' attributable to the central 8a atom is given by the equation (cf. (4·3))

$$V'^{8\mathrm{a}} = S^{8\mathrm{a}}[\nu S^{4\mathrm{a}} + \delta S^{7\mathrm{a}} + \delta' S^{6\mathrm{a}} + \rho_1(S^{1\mathrm{b}} + S^{8\mathrm{b}}) \\ + \rho_2(S^{4\mathrm{b}} + S^{5\mathrm{b}}) + \rho_3(S^{3\mathrm{b}} + S^{6\mathrm{b}}) + \rho_4(S^{2\mathrm{b}} + S^{7\mathrm{b}})], \tag{6·4}$$

where we have again transformed to Σ', put all y and z components equal to zero, and dropped the index x everywhere, and where

$$\nu = 4[a_{13}^2 J_1 + (a_{11}^2 + a_{12}^2)\, J_2], \tag{6·5}$$

$$\delta = 4[a_{11}^2 M_1 + a_{12}^2 M_2 + a_{13}^2 M_3], \tag{6·6}$$

$$\delta' = 4[a_{12}^2 M_1 + a_{11}^2 M_2 + a_{13}^2 M_3], \tag{6·7}$$

$$\rho_1 = 2K_1 P^2(a_{11} + a_{12} - wa_{13})^2 + K_2(a_{11} - a_{12})^2 + 2K_3 Q^2(a_{11} + a_{12} + 2a_{13}/w)^2, \tag{6·8}$$

$$\rho_2 = 2K_1 P^2(a_{11} + a_{12} + wa_{13})^2 + K_2(a_{11} - a_{12})^2 + 2K_3 Q^2(a_{11} + a_{12} - 2a_{13}/w)^2, \tag{6·9}$$

$$\rho_3 = 2K_1 P^2(a_{11} - a_{12} - wa_{13})^2 + K_2(a_{11} + a_{12})^2 + 2K_3 Q^2(a_{11} - a_{12} + 2a_{13}/w)^2, \tag{6·10}$$

$$\rho_4 = 2K_1 P^2(a_{11} - a_{12} + wa_{13})^2 + K_2(a_{11} + a_{12})^2 + 2K_3 Q^2(a_{11} - a_{12} - 2a_{13}/w)^2. \tag{6·11}$$

To $V'^{8\mathrm{a}}$ we must add an additional term deriving from the anisotropy effect due to the crystalline field. The anisotropy energy $E_{\mathrm{c.f.}}$ ascribable to the 8a atom will be of the form

$$E_{\mathrm{c.f.}} = 2[Da_{13}^2 - \tfrac{1}{2}D(a_{11}^2 + a_{12}^2)]\,(S_x^{8\mathrm{a}})^2 = \tfrac{1}{2}\lambda(S_x^{8\mathrm{a}})^2 \tag{6·12}$$

with

$$\lambda = 2D(3a_{13}^2 - 1). \tag{6·13}$$

In adding this term to $V'^{8\mathrm{a}}$ we must bear in mind that $E_{\mathrm{c.f.}}$ occurs once only while the exchange energy terms all occur twice. To make allowance for that we must thus add $\lambda(S^{8\mathrm{a}})^2$ to $V'^{8\mathrm{a}}$, and get thus

$$V^{8\mathrm{a}} = V'^{8\mathrm{a}} + \lambda(S^{8\mathrm{a}})^2, \tag{6·14}$$

where we have again dropped the subscript x.

Putting again
$$J_1 = J + J_0, \quad J_2 = J + J_i, \quad J_0 + 2J_i = 0; \tag{6·15}$$
$$K_1 = K + K_\alpha, \quad K_2 = K + K_\beta, \quad K_3 = K + K_\gamma, \quad K_\alpha + K_\beta + K_\gamma = 0; \tag{6·16}$$
$$M_1 = M + M_\alpha, \quad M_2 = M + M_\beta, \quad M_3 = M + M_\gamma, \quad M_\alpha + M_\beta + M_\gamma = 0, \tag{6·17}$$
and proceeding as before, we now find an anisotropic Weiss constant
$$\Theta = [J + 4K + 2M - (\tfrac{1}{2}D + \tfrac{1}{2}J_0 + M_\gamma + 4P^2K_\gamma + 2P^2w^2K_\alpha)\,(1 - 3a_{13}^2)]\,\psi. \tag{6·18}$$
We notice that Θ now is anisotropic and that the susceptibility above T_C should thus depend on the direction in which it is measured. From (6·18) we expect the susceptibility to vary in magnitude from one extreme along the c_0 (Z) axis to the other extreme in the XY plane. Whether the extremes are maxima or minima depends on the sign of the factor of $(1 - 3a_{13}^2)$.

$$\begin{vmatrix}
\phi+\lambda & \delta & \delta' & 0 & \nu & 0 & 0 & 0 & \rho_1 & \rho_4 & \rho_3 & \rho_2 & \rho_2 & \rho_3 & \rho_4 & \rho_1 \\
\delta & \phi+\lambda & 0 & \delta' & 0 & \nu & 0 & 0 & \rho_4 & \rho_1 & \rho_2 & \rho_3 & \rho_3 & \rho_2 & \rho_1 & \rho_4 \\
\delta' & 0 & \phi+\lambda & \delta & 0 & 0 & \nu & 0 & \rho_3 & \rho_2 & \rho_1 & \rho_4 & \rho_4 & \rho_1 & \rho_2 & \rho_3 \\
0 & \delta' & \delta & \phi+\lambda & 0 & 0 & 0 & \nu & \rho_2 & \rho_3 & \rho_4 & \rho_1 & \rho_1 & \rho_4 & \rho_3 & \rho_2 \\
\nu & 0 & 0 & 0 & \phi+\lambda & \delta & \delta' & 0 & \rho_2 & \rho_3 & \rho_4 & \rho_1 & \rho_1 & \rho_4 & \rho_3 & \rho_2 \\
0 & \nu & 0 & 0 & \delta & \phi+\lambda & 0 & \delta' & \rho_3 & \rho_2 & \rho_1 & \rho_4 & \rho_4 & \rho_1 & \rho_2 & \rho_3 \\
0 & 0 & \nu & 0 & \delta' & 0 & \phi+\lambda & \delta & \rho_4 & \rho_1 & \rho_2 & \rho_3 & \rho_3 & \rho_2 & \rho_1 & \rho_4 \\
0 & 0 & 0 & \nu & 0 & \delta' & \delta & \phi+\lambda & \rho_1 & \rho_4 & \rho_3 & \rho_2 & \rho_2 & \rho_3 & \rho_4 & \rho_1 \\
\rho_1 & \rho_4 & \rho_3 & \rho_2 & \rho_2 & \rho_3 & \rho_4 & \rho_1 & \phi+\lambda & \delta & \delta' & 0 & \nu & 0 & 0 & 0 \\
\rho_4 & \rho_1 & \rho_2 & \rho_3 & \rho_3 & \rho_2 & \rho_1 & \rho_4 & \delta & \phi+\lambda & 0 & \delta' & 0 & \nu & 0 & 0 \\
\rho_3 & \rho_2 & \rho_1 & \rho_4 & \rho_4 & \rho_1 & \rho_2 & \rho_3 & \delta' & 0 & \phi+\lambda & \delta & 0 & 0 & \nu & 0 \\
\rho_2 & \rho_3 & \rho_4 & \rho_1 & \rho_1 & \rho_4 & \rho_3 & \rho_2 & 0 & \delta' & \delta & \phi+\lambda & 0 & 0 & 0 & \nu \\
\rho_2 & \rho_3 & \rho_4 & \rho_1 & \rho_1 & \rho_4 & \rho_3 & \rho_2 & \nu & 0 & 0 & 0 & \phi+\lambda & \delta & \delta' & 0 \\
\rho_3 & \rho_2 & \rho_1 & \rho_4 & \rho_4 & \rho_1 & \rho_2 & \rho_3 & 0 & \nu & 0 & 0 & \delta & \phi+\lambda & 0 & \delta' \\
\rho_4 & \rho_1 & \rho_2 & \rho_3 & \rho_3 & \rho_2 & \rho_1 & \rho_4 & 0 & 0 & \nu & 0 & \delta' & 0 & \phi+\lambda & \delta \\
\rho_1 & \rho_4 & \rho_3 & \rho_2 & \rho_2 & \rho_3 & \rho_4 & \rho_1 & 0 & 0 & 0 & \nu & 0 & \delta' & \delta & \phi+\lambda
\end{vmatrix}$$

FIGURE 24. The determinant of the secular equation for the b.c.t. case.

To find the transition temperatures we must solve a secular equation
$$D_{\text{b.c.t.}} = 0, \tag{6·19}$$
where the 16×16 determinant $D_{\text{b.c.t.}}$ is the one given in figure 24. Once again the determinant can be factorized and the different factors occurring are the following ones
$$\left.\begin{array}{rl}
(1) & \phi+\delta+\delta'+\nu+2(\rho_1+\rho_2+\rho_3+\rho_4)+\lambda, \\
(2) & \phi+\delta+\delta'+\nu-2(\rho_1+\rho_2+\rho_3+\rho_4)+\lambda, \\
(3) & \phi+\delta-\delta'-\nu+2(-\rho_1+\rho_2+\rho_3-\rho_4)+\lambda, \\
(4) & \phi-\delta+\delta'-\nu+2(\rho_1-\rho_2+\rho_3-\rho_4)+\lambda, \\
(5) & \phi-\delta-\delta'+\nu+2(\rho_1+\rho_2-\rho_3-\rho_4)+\lambda, \\
(6) & \phi+\delta-\delta'-\nu-2(-\rho_1+\rho_2+\rho_3-\rho_4)+\lambda, \\
(7) & \phi-\delta+\delta'-\nu-2(\rho_1-\rho_2+\rho_3-\rho_4)+\lambda, \\
(8) & \phi-\delta-\delta'+\nu-2(\rho_1+\rho_2-\rho_3-\rho_4)+\lambda, \\
(9) & \phi-\delta-\delta'-\nu+\lambda, \\
(10) & \phi-\delta+\delta'+\nu+\lambda, \\
(11) & \phi+\delta-\delta'+\nu+\lambda, \\
(12) & \phi+\delta+\delta'-\nu+\lambda.
\end{array}\right\} \tag{6·20}$$

The last four factors occur twice in $D_{\text{b.c.t.}}$. For the T_i we find

$$\left.\begin{aligned}
T_1 &= [-J-4K-2M+(\tfrac{1}{2}D-J_i+M_\gamma+4P^2K_\gamma+2P^2w^2K_\alpha)\,(1-3a_{13}^2)]\,\psi,\\
T_2 &= [-J+4K-2M+(\tfrac{1}{2}D-J_i+M_\gamma-4P^2K_\gamma-2P^2w^2K_\alpha)\,(1-3a_{13}^2)]\,\psi,\\
T_3 &= [J+(\tfrac{1}{2}D+J_i)\,(1-3a_{13}^2)+(M_1-M_2)\,(a_{12}^2-a_{11}^2)-8wP^2(K_1-K_3)\,a_{12}a_{13}]\,\psi,\\
T_4 &= [J+(\tfrac{1}{2}D+J_i)\,(1-3a_{13}^2)+(M_1-M_2)\,(a_{11}^2-a_{12}^2)+8wP^2(K_1-K_3)\,a_{11}a_{13}]\,\psi,\\
T_5 &= [-J+2M+(\tfrac{1}{2}D-J_i-M_\gamma)\,(1-3a_{13}^2)-\{8P^2(K_1-K_2)+4wP^2(K_3-K_2)\}\,a_{11}a_{12}]\,\psi,\\
T_6 &= [J+(\tfrac{1}{2}D+J_i)\,(1-3a_{13}^2)+(M_1-M_2)\,(a_{12}^2-a_{11}^2)+8wP^2(K_1-K_3)\,a_{12}a_{13}]\,\psi,\\
T_7 &= [J+(\tfrac{1}{2}D+J_i)\,(1-3a_{13}^2)+(M_1-M_2)\,(a_{11}^2-a_{12}^2)-8wP^2(K_1-K_3)\,a_{11}a_{13}]\,\psi,\\
T_8 &= [-J+2M+(\tfrac{1}{2}D-J_i-M_\gamma)\,(1-3a_{13}^2)+\{8P^2(K_1-K_2)+4wP^2(K_3-K_2)\}\,a_{11}a_{12}]\,\psi,\\
T_9 &= [J+2M+(\tfrac{1}{2}D+J_i-M_\gamma)\,(1-3a_{13}^2)]\,\psi,\\
T_{10} &= [-J+(M_1-M_2)\,(a_{11}^2-a_{12}^2)+(\tfrac{1}{2}D-J_i)\,(1-3a_{13}^2)]\,\psi,\\
T_{11} &= [-J-(M_1-M_2)\,(a_{11}^2-a_{12}^2)+(\tfrac{1}{2}D-J_i)\,(1-3a_{13}^2)]\,\psi,\\
T_{12} &= [J-2M+(\tfrac{1}{2}D+J_i+M_\gamma)\,(1-3a_{13}^2)]\,\psi.
\end{aligned}\right\} \tag{6·21}$$

We find that T_1 corresponds to ferromagnetic order; T_2 to type 1 order (see figure 25); T_9 to type 2 order (see figure 26); T_3, T_4, T_6, and T_7 to type 3A order (see figure 27, which corresponds to T_4); T_5 and T_8 to type 3B order (see figure 28, which corresponds to T_5); T_{10} and T_{11} to type 4A order (see figure 29, which corresponds to T_{10}); and T_{12} to type 4B order (see figure 30).

Ferromagnetic order. If $\frac{1}{2}D-J_i+M_\gamma+4P^2K_\gamma+2P^2w^2K_\alpha$ is negative, the preferred direction **n** will be along the Z axis, and if this expression is positive, **n** may be anywhere in the XY plane.

Type 1 *order.* If $\frac{1}{2}D-J_i+M_\gamma-4P^2K_\gamma-2P^2w^2K_\alpha$ is negative, **n** will be along the Z axis, and if this expression is positive, **n** may be anywhere in the XY plane. The order is always a proper one.

Type 2 *order.* If $\frac{1}{2}D-\frac{1}{2}J_0-M_\gamma$ is negative, **n** is along the Z axis, and if it is positive, **n** may be anywhere in the XY plane. In the latter case, the ordering need not be a proper one, but the a and b sublattices must be antiferromagnetically ordered within themselves.

Type 3A *order.* One can easily find the values of a_{11}, a_{12}, and a_{13} which make the corresponding T_i a maximum, but they are complicated expressions in the anisotropy parameters, and we shall not write them down explicitly. The order is a proper one.

Type 3B *order.* We shall consider T_5. If $\frac{1}{2}D-J_i-M_\gamma > 0$, **n** will be along the $(1, 1, 0)$ or $(1, -1, 0)$ direction, depending upon whether $8P^2(K_1-K_2)+4w^2P^2(K_3-K_2)$ is negative or positive, respectively. If $\frac{1}{2}D-J_i-M_\gamma < 0$, **n** will be along the Z axis or along an XY face diagonal depending upon whether $6\,|\frac{1}{2}D-J_i-M_\gamma|$ is larger or smaller than

$$|8P^2(K_1-K_2)+4w^2P^2(K_3-K_2)|,$$

respectively. The order is a proper one.

Type 4A order. We shall consider T_{10}. If $\frac{1}{2}D+\frac{1}{2}J_0 > 0$ and $M_1 > M_2$, **n** will be along the X axis. If $\frac{1}{2}D+\frac{1}{2}J_0 > 0$ and $M_1 < M_2$, **n** is along the Y axis. If

$$\tfrac{1}{2}D+\tfrac{1}{2}J_0 < 0 \quad \text{and} \quad |3J_0/2| > |M_1-M_2|,$$

n is along the Z-axis, and finally, if

$$\tfrac{1}{2}D+\tfrac{1}{2}J_0<0 \quad \text{and} \quad |3J_0/2|<|M_1-M_2|,$$

n is along the X or the Y axis according to whether K_1-K_2 is positive or negative, respectively. This type order is not necessarily a proper one, but the a and b sublattices must be antiferromagnetically ordered within themselves.

Type 4B *order*. If $\frac{1}{2}D+J_i+M_\gamma<0$, **n** is along the Z axis, and if $\frac{1}{2}D+J_i+M_\gamma>0$, **n** may be anywhere in the XY plane. The order is again not necessarily a proper one, but the a and b sublattices must be antiferromagnetically ordered within themselves.

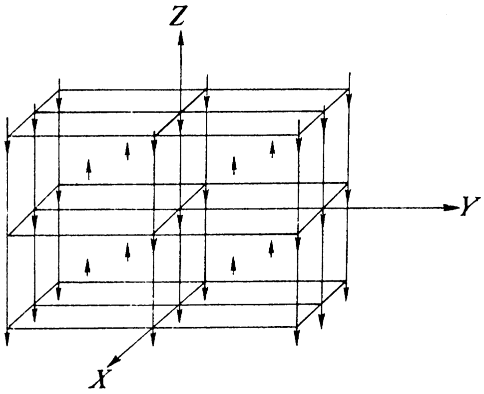

FIGURE 25. Type 1 order for the b.c.t. case.

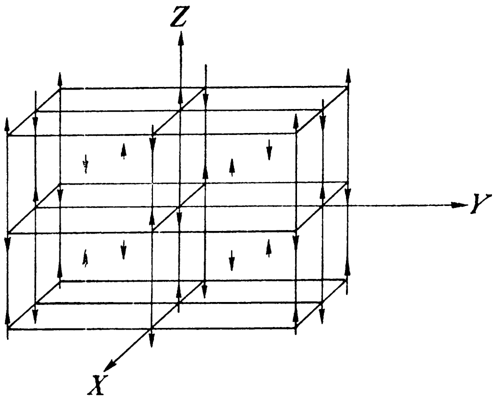

FIGURE 26. Type 2 order for the b.c.t. case.

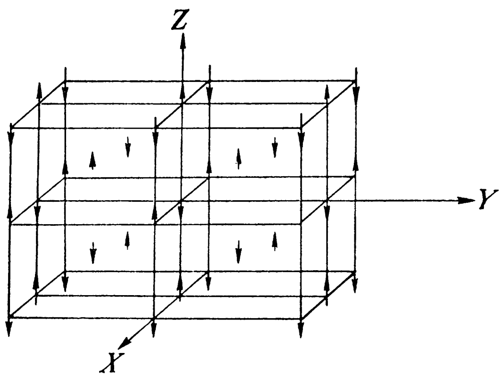

FIGURE 27. Type 3A order for the b.c.t. case.

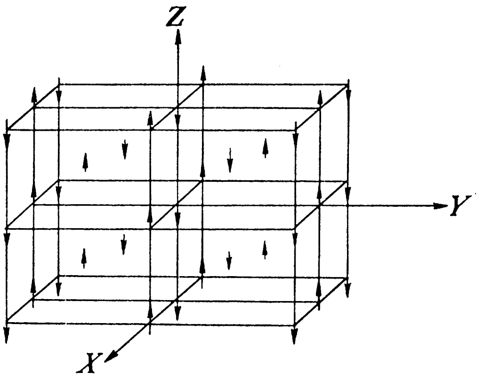

FIGURE 28. Type 3B order for the b.c.t. case.

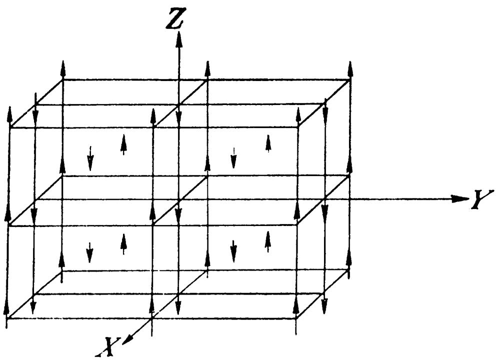

FIGURE 29. Type 4A order for the b.c.t. case.

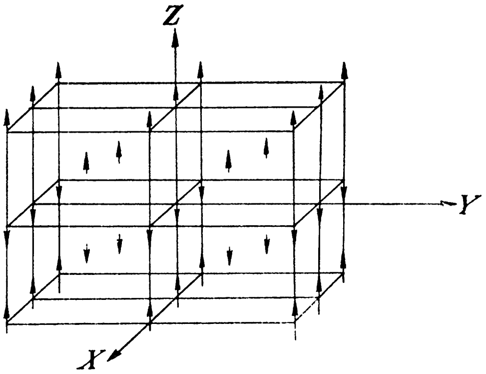

FIGURE 30. Type 4B order for the b.c.t. case.

In conclusion we may draw attention to the fact that type 3B and type 4A order are unlikely to occur unless some of the exchange interactions are ferromagnetic rather than antiferromagnetic.

7. THE RUTILE CRYSTAL STRUCTURE

A considerable amount of experimental work has been carried out upon antiferromagnetics with the rutile crystal structure. The magnetic atoms in that case are upon a b.c.t. lattice, and the magnetic system should therefore behave not very differently from an isolated b.c.t. magnetic lattice. Figure 31 shows the rutile structure and figure 32 the sixteen sublattices which we shall again introduce. We shall now try to take into account possible superexchange interactions and to discuss how the presence of anions will modify the results obtained in the previous section.

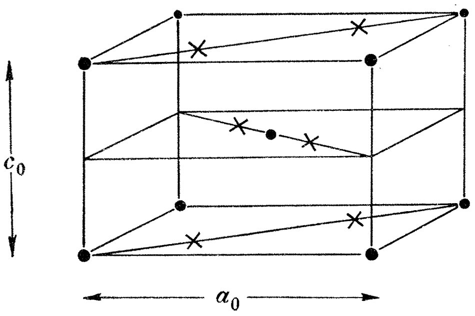

FIGURE 31. The rutile crystal structure. Circles represent the magnetic cations and crosses the non-magnetic anions.

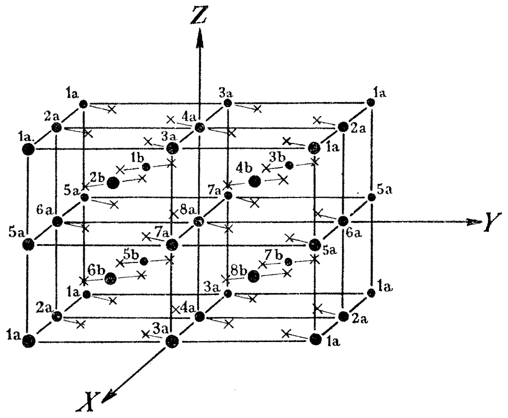

FIGURE 32. The sixteen sublattices of the rutile lattice.

We shall again take into account only such exchange interactions which can be expressed in the form (1·15). As before, our main task is to try to choose the most suitable set of axes for each interaction, where we now must take into account the positions of the anions as well as those of the magnetic cations.

We first of all consider a central atom upon the 8a sublattice (figure 32). For the first-neighbour interactions the magnetic lattice singles out the Z axis, but the anions now allow us to single out the $(1, 1, 0)$ and $(1, -1, 0)$ directions. We take thus our x', y', and z' axes along the $(0, 0, 1)$, $(1, 1, 0)$ and $(1, -1, 0)$ directions and associate three different exchange parameters J_1, J_2, and J_3 with these directions. We note that the presence of the anions has forced us to introduce three instead of two exchange parameters. In Σ' we get for the first-neighbour interaction the expression

$$V_1^{8a} = \sigma S^{8a} S^{4a}, \tag{7·1}$$

where we have used the molecular field approximation and have dropped the subscript x, and where

$$\sigma = 4J_1 a_{13}^2 + 2J_2(a_{11} + a_{12})^2 + 2J_3(a_{11} - a_{12})^2. \tag{7·2}$$

We shall also use again the notation

$$J_1 = J + J_\alpha, \quad J_2 = J + J_\beta, \quad J_3 = J + J_\gamma, \quad J_\alpha + J_\beta + J_\gamma = 0. \tag{7·3}$$

There is some evidence that our representation of the second-neighbour interactions for the isolated magnetic lattice need not be changed very much. Keffer (1952) has shown that these second-neighbour interactions are probably largely of the dipole type. We shall, however, add to (6·2) a further anisotropy expression as follows

$$V_{8\mathrm{a},4\mathrm{b}} = 2K_1 S_{x'}^{8\mathrm{a}} S_{x'}^{4\mathrm{b}} + 2K_2 S_{y'}^{8\mathrm{a}} S_{y'}^{4\mathrm{b}} + 2K_3 S_{z'}^{8\mathrm{a}} S_{z'}^{4\mathrm{b}} + 2L_\alpha S_{x''}^{8\mathrm{a}} S_{x''}^{4\mathrm{b}} + 2L_\beta S_{y''}^{8\mathrm{a}} S_{y''}^{4\mathrm{b}} + 2L_\gamma S_{z''}^{8\mathrm{a}} S_{z''}^{4\mathrm{b}}, \tag{7·4}$$

where the x', y', z' directions are the same as those used in (6·2), where the x'', y'', z'' directions, which are singled out by the anions, are the same as the x', y', z' directions for the first-neighbour interactions, and where

$$L_\alpha + L_\beta + L_\gamma = 0. \tag{7·5}$$

In Σ' we get in the molecular-field approximation

$$V_{8\mathrm{a},4\mathrm{b}} = [2K_1 P^2(a_{11}+a_{12}+wa_{13})^2 + K_2(a_{11}-a_{12})^2 + 2K_3 Q^2(a_{11}+a_{12}-2a_{13}/w)^2 \\ + 2L_\alpha a_{13}^2 + L_\beta(a_{11}+a_{12})^2 + L_\gamma(a_{11}-a_{12})^2]\, S^{8\mathrm{a}} S^{4\mathrm{b}}. \tag{7·6}$$

If we examine the possible paths for superexchange in the rutile lattice, we see that it is to be expected that the third-neighbour interactions will be small compared to the nearer-neighbour exchanges; we shall therefore neglect the anisotropic parts of the third-neighbour interactions. The total interaction of the central 8a atom with its neighbours is now

$$V^{8\mathrm{a}} = S^{8\mathrm{a}}[\sigma S^{4\mathrm{a}} + \delta(S^{7\mathrm{a}}+S^{6\mathrm{a}}) + \rho_1'(S^{1\mathrm{b}}+S^{8\mathrm{b}}) + \rho_2'(S^{4\mathrm{b}}+S^{5\mathrm{b}}) \\ + \rho_3'(S^{3\mathrm{b}}+S^{6\mathrm{b}}) + \rho_4'(S^{2\mathrm{b}}+S^{7\mathrm{b}}) + \mu S^{8\mathrm{a}}], \tag{7·7}$$

where σ is given by (7·2), $\delta = 4M$, and

$$\rho_1' = \rho_1 + 2L_\alpha a_{13}^2 + L_\beta(a_{11}+a_{12})^2 + L_\gamma(a_{11}-a_{12})^2, \tag{7·8}$$

$$\rho_2' = \rho_2 + 2L_\alpha a_{13}^2 + L_\beta(a_{11}+a_{12})^2 + L_\gamma(a_{11}-a_{12})^2, \tag{7·9}$$

$$\rho_3' = \rho_3 + 2L_\alpha a_{13}^2 + L_\beta(a_{11}-a_{12})^2 + L_\gamma(a_{11}+a_{12})^2, \tag{7·10}$$

$$\rho_4' = \rho_4 + 2L_\alpha a_{13}^2 + L_\beta(a_{11}-a_{12})^2 + L_\gamma(a_{11}+a_{12})^2, \tag{7·11}$$

with ρ_i given by (6·8) to (6·11). In (7·7) we have included the anisotropy part of the interaction of the central atom with the crystalline field. This energy $E_{\mathrm{c.f.}}$ has essentially the same symmetry as the first-neighbour exchange energy,

$$E_{\mathrm{c.f.}} = 2[DS_{x'}^2 + D'S_{y'}^2 + D''S_{z'}^2], \tag{7·12}$$

where the x', y', z' axes are the same for the first-neighbour interactions. In Σ' we get in the molecular-field approximation

$$E_{\mathrm{c.f.}} = [D(3a_{13}^2-1) + 2Ea_{11}a_{12}]\,(S^{8\mathrm{a}})^2, \tag{7·13}$$

where

$$E = D' - D'', \quad D + D' + D'' = 0. \tag{7·14}$$

The term involving $S^{8\mathrm{a}}$ in (7·7) arises from (7·13) if we take the extra factor 2 mentioned in the previous section into account and write

$$\mu = 2D(3a_{13}^2-1) + 4Ea_{11}a_{12}. \tag{7·15}$$

Before we can write down the secular determinant we must take into account that the atoms on the a sublattices see a different molecular field from those upon the b sublattices. For a 4b atom as a central atom we get, for instance, instead of (7·7)

$$V^{4\mathrm{b}} = S^{4\mathrm{b}}[\sigma' S^{8\mathrm{b}} + \delta(S^{2\mathrm{b}}+S^{3\mathrm{b}}) + \rho_1'(S^{4\mathrm{a}}+S^{5\mathrm{a}}) + \rho_2'(S^{1\mathrm{a}}+S^{8\mathrm{a}}) \\ + \rho_3'(S^{2\mathrm{a}}+S^{7\mathrm{a}}) + \rho_4'(S^{3\mathrm{a}}+S^{6\mathrm{a}}) + \mu' S^{4\mathrm{b}}], \tag{7·16}$$

where now
$$\sigma' = 4J_1 a_{13}^2 + 2J_2(a_{11}-a_{12})^2 + 2J_3(a_{11}+a_{12})^2, \tag{7·17}$$
$$\mu' = 2D(3a_{13}^2-1) - 4Ea_{11}a_{12}. \tag{7·18}$$

The secular determinant can now be determined and is given by figure 33. This determinant has 8 linear factors, leaving an 8×8 determinant which we shall discuss later on in this section. The eight linear factors are the following ones

$$\left.\begin{array}{ll} (1) & \phi+\sigma+\mu, \\ (2) & \phi+\sigma'+\mu', \\ (3) & \phi+2\delta-\sigma+\mu, \\ (4) & \phi+2\delta-\sigma'+\mu', \\ (5) & \phi-2\delta-\sigma+\mu, \\ (6) & \phi-2\delta-\sigma'+\mu', \end{array}\right\} \tag{7·19}$$

where the first two factors each occur twice.

$$\begin{vmatrix}
\phi+\mu' & \delta & \delta & 0 & \sigma' & 0 & 0 & 0 & \rho'_1 & \rho'_4 & \rho'_3 & \rho'_2 & \rho'_2 & \rho'_3 & \rho'_4 & \rho'_1 \\
\delta & \phi+\mu' & 0 & \delta & 0 & \sigma' & 0 & 0 & \rho'_4 & \rho'_1 & \rho'_2 & \rho'_3 & \rho'_3 & \rho'_2 & \rho'_1 & \rho'_4 \\
\delta & 0 & \phi+\mu' & \delta & 0 & 0 & \sigma' & 0 & \rho'_3 & \rho'_2 & \rho'_1 & \rho'_4 & \rho'_4 & \rho'_1 & \rho'_2 & \rho'_3 \\
0 & \delta & \delta & \phi+\mu' & 0 & 0 & 0 & \sigma' & \rho'_2 & \rho'_3 & \rho'_4 & \rho'_1 & \rho'_1 & \rho'_4 & \rho'_3 & \rho'_2 \\
\sigma' & 0 & 0 & 0 & \phi+\mu' & \delta & \delta & 0 & \rho'_2 & \rho'_3 & \rho'_4 & \rho'_1 & \rho'_1 & \rho'_4 & \rho'_3 & \rho'_2 \\
0 & \sigma' & 0 & 0 & \delta & \phi+\mu' & 0 & \delta & \rho'_3 & \rho'_2 & \rho'_1 & \rho'_4 & \rho'_4 & \rho'_1 & \rho'_2 & \rho'_3 \\
0 & 0 & \sigma' & 0 & \delta & 0 & \phi+\mu' & \delta & \rho'_4 & \rho'_1 & \rho'_2 & \rho'_3 & \rho'_3 & \rho'_2 & \rho'_1 & \rho'_4 \\
0 & 0 & 0 & \sigma' & 0 & \delta & \delta & \phi+\mu' & \rho'_1 & \rho'_4 & \rho'_3 & \rho'_2 & \rho'_2 & \rho'_3 & \rho'_4 & \rho'_1 \\
\rho'_1 & \rho'_4 & \rho'_3 & \rho'_2 & \rho'_2 & \rho'_3 & \rho'_4 & \rho'_1 & \phi+\mu & \delta & \delta & 0 & \sigma & 0 & 0 & 0 \\
\rho'_4 & \rho'_1 & \rho'_2 & \rho'_3 & \rho'_3 & \rho'_2 & \rho'_1 & \rho'_4 & \delta & \phi+\mu & 0 & \delta & 0 & \sigma & 0 & 0 \\
\rho'_3 & \rho'_2 & \rho'_1 & \rho'_4 & \rho'_4 & \rho'_1 & \rho'_2 & \rho'_3 & \delta & 0 & \phi+\mu & \delta & 0 & 0 & \sigma & 0 \\
\rho'_2 & \rho'_3 & \rho'_4 & \rho'_1 & \rho'_1 & \rho'_4 & \rho'_3 & \rho'_2 & 0 & \delta & \delta & \phi+\mu & 0 & 0 & 0 & \sigma \\
\rho'_2 & \rho'_3 & \rho'_4 & \rho'_1 & \rho'_1 & \rho'_4 & \rho'_3 & \rho'_2 & \sigma & 0 & 0 & 0 & \phi+\mu & \delta & \delta & 0 \\
\rho'_3 & \rho'_2 & \rho'_1 & \rho'_4 & \rho'_4 & \rho'_1 & \rho'_2 & \rho'_3 & 0 & \sigma & 0 & 0 & \delta & \phi+\mu & 0 & \delta \\
\rho'_4 & \rho'_1 & \rho'_2 & \rho'_3 & \rho'_3 & \rho'_2 & \rho'_1 & \rho'_4 & 0 & 0 & \sigma & 0 & \delta & 0 & \phi+\mu & \delta \\
\rho'_1 & \rho'_4 & \rho'_3 & \rho'_2 & \rho'_2 & \rho'_3 & \rho'_4 & \rho'_1 & 0 & 0 & 0 & \sigma & 0 & \delta & \delta & \phi+\mu
\end{vmatrix}$$

FIGURE 33. The determinant of the secular equation for the rutile case.

These factors correspond to the following transition temperatures

$$\left.\begin{aligned}
T_1 &= [-J-(J_\beta-J_\gamma+E)\,a_{11}a_{12}+(\tfrac{1}{2}D+\tfrac{1}{2}J_\alpha)\,(1-3a_{13}^2)]\,\psi, \\
T_2 &= [-J+(J_\beta-J_\gamma+E)\,a_{11}a_{12}+(\tfrac{1}{2}D+\tfrac{1}{2}J_\alpha)\,(1-3a_{13}^2)]\,\psi, \\
T_3 &= [J-2M+(J_\beta-J_\gamma-E)\,a_{11}a_{12}+(\tfrac{1}{2}D-\tfrac{1}{2}J_\alpha)\,(1-3a_{13}^2)]\,\psi, \\
T_4 &= [J-2M-(J_\beta-J_\gamma-E)\,a_{11}a_{12}+(\tfrac{1}{2}D-\tfrac{1}{2}J_\alpha)\,(1-3a_{13}^2)]\,\psi, \\
T_5 &= [J+2M+(J_\beta-J_\gamma-E)\,a_{11}a_{12}+(\tfrac{1}{2}D-\tfrac{1}{2}J_\alpha)\,(1-3a_{13}^2)]\,\psi, \\
T_6 &= [J+2M-(J_\beta-J_\gamma-E)\,a_{11}a_{12}+(\tfrac{1}{2}D-\tfrac{1}{2}J_\alpha)\,(1-3a_{13}^2)]\,\psi.
\end{aligned}\right\} \tag{7·20}$$

Here T_1 and T_2 correspond to type 4A order, T_3 and T_4 to type 4B order, and T_5 and T_6 to type 2 order, where the types of order are the ones defined in the previous section. For each of these types of order one possible direction of ordering is along the Z axis; the other possible direction is either the $(1, 1, 0)$ or the $(1, -1, 0)$ direction. Moreover, in the latter case the directions of ordering of the a- and b-sublattice spins will be at right angles to one another, that is, if the a spins are along the $(1, 1, 0)$ direction, the b spins will be along the

(1, −1, 0) direction, or the other way round. This effect did not occur in the b.c.t. case (the angle between the a and b sublattices for the equivalent case was arbitrary) and is produced by the inclusion of the anions. We shall call such an ordering *rutile type diagonal ordering*.

Type 2 *order*. The a-sublattice spins have an exchange interaction energy due to their surroundings which is proportional to

$$J+2M+(\tfrac{1}{2}D-\tfrac{1}{2}J_\alpha)\,(1-3a_{13}^2)+(J_\beta-J_\gamma-E)\,a_{11}a_{12}, \tag{7·21}$$

and the corresponding expression for the b-sublattice spins is proportional to

$$J+2M+(\tfrac{1}{2}D-\tfrac{1}{2}J_\alpha)\,(1-3a_{13}^2)-(J_\beta-J_\gamma-E)\,a_{11}a_{12}. \tag{7·22}$$

If $D-J_\alpha<0$ and $3\,|D-J_\alpha|>|J_\beta-J_\gamma-E|$ both (7·21) and (7·22) are maximum when $a_{13}^2=1$: both a and b spins will be directed along the Z axis.

If either $D-J_\alpha>0$, or $D-J_\alpha<0$ but $3\,|D-J_\alpha|<|J_\beta-J_\gamma-E|$, (7·21) is maximum for $a_{11}=a_{12}=2^{-\frac{1}{2}}$, if $J_\beta-J_\gamma-E>0$ and for $a_{11}=-a_{12}=-2^{-\frac{1}{2}}$, if $J_\beta-J_\gamma-E<0$; the a and b spins point to their anion neighbours, if $J_\beta-J_\gamma-E>0$, and at right angles to them, if $J_\beta-J_\gamma-E<0$; this means that we have rutile type diagonal ordering.

Type 4A *order*. We find by similar arguments, that if

$$D+J_\alpha<0 \quad\text{and}\quad 3\,|D+J_\alpha|>|J_\beta-J_\gamma+E|,$$

both a and b spins will be directed along the Z axis. If $D+J_\alpha>0$, or $D+J_\alpha<0$ but $3\,|D+J_\alpha|<|J_\beta-J_\gamma+E|$ we have rutile type diagonal ordering; the spins will point to their anion neighbours, if $J_\beta-J_\gamma+E<0$.

Type 4*B order*. The situation is exactly the same as for the type 2 order.

We must now discuss the 8 × 8 determinant which is left after the factors (7·19) have been removed. As this determinant can not be written as a product of linear terms we cannot, for any general direction in space, find ferromagnetic or type 1, 3A, or 3B order where all spins in the lattice are parallel or antiparallel as we did for the b.c.t. case. We notice, however, that if $\sigma=\sigma'$ and $\mu=\mu'$, that is, if either $E=0$ and $J_\beta=J_\gamma$, or $a_{11}=a_{12}=0$, we could factorize the determinant in linear factors.

The 8 × 8 determinant can be factorized as a product of four 2 × 2 determinants, and the remaining secular equation is of the form

$$\begin{vmatrix} A & R \\ R & A' \end{vmatrix}\begin{vmatrix} B & U \\ U & B' \end{vmatrix}\begin{vmatrix} C & V \\ V & C' \end{vmatrix}\begin{vmatrix} C & W \\ W & C' \end{vmatrix}=0, \tag{7·23}$$

$$A=\phi+\mu+\sigma+2\delta, \quad A'=\phi+\mu'+\sigma'+2\delta; \tag{7·24}$$

$$B=\phi+\mu+\sigma-2\delta, \quad B'=\phi+\mu'+\sigma'-2\delta; \tag{7·25}$$

$$C=\phi+\mu-\sigma, \qquad C'=\phi+\mu'-\sigma'; \tag{7·26}$$

$$R=2(\rho_1+\rho_2+\rho_3+\rho_4); \tag{7·27}$$

$$U=2(\rho_1+\rho_2-\rho_3-\rho_4); \tag{7·28}$$

$$V=2(\rho_1-\rho_2+\rho_3-\rho_4); \tag{7·29}$$

$$W=2(-\rho_1+\rho_2+\rho_3-\rho_4). \tag{7·30}$$

We note that if $\mu = \mu'$ and $\sigma = \sigma'$, the left-hand side of (7·23) reduces to the product of the first 8 factors (6·20). We can thus expect the determinant involving A to lead to type 1 or ferromagnetic order approximately, the determinant involving B to type 3B order approximately, and the determinants involving C to type 3A order approximately.

Type 1 *order*. The solution $R = \surd(AA')$ leads to a transition temperature

$$T_7 = [4K - J - 2M + (\tfrac{1}{2}D - J_i - 4P^2K_\gamma - 2P^2w^2K_\alpha - 2L_\alpha)\,(1 - 3a_{13}^2) + 2Ka_{11}^2\,a_{12}^2\chi^2]\,\psi, \quad (7·31)$$

where

$$\chi = \frac{J_\beta - J_\gamma + E}{4K}, \quad (7·32)$$

and where we have assumed $|\chi|$ to be small compared to unity so that we can expand the square root in powers of χ. This assumption is almost certainly justified for the rutile salts; for the particular case of NiF_2 the antiferromagnetic ordering found experimentally indicates, as we shall see in the next section, that $\chi \sim \frac{1}{16}$.

Let us now assume that there is an angle $\pi - \theta$ between the spins on the a sublattices and those on the b sublattices, and that θ is a small angle. This entails that the system Σ' is no longer uniquely defined, but will be different for the a and the b sublattices. Let the a_{ij} refer to the system Σ'_{a} corresponding to the a sublattices and the b_{ij} to the system Σ'_{b} corresponding to the b sublattices. If $a_{ij} = b_{ij}$, θ would vanish. Having found T_7 we can then solve the simultaneous linear equations for the S^i and then find equations relating θ to the a_{ij} and b_{ij}. The result is that θ must satisfy the following two equations

$$\left.\begin{aligned} 1 - \cos\theta &= -a_{11}a_{12}\chi, \\ 1 - \cos\theta &= b_{11}b_{12}\chi. \end{aligned}\right\} \quad (7·33)$$

If $\frac{1}{2}D - J_i - 4P^2K_\gamma - 2P^2w^2K_\alpha - 2L_\alpha < 0$, T_7 is a maximum if $a_{13} = b_{13} = 1$. In that case $\theta = 0$, and the order is a proper type 1 order with **n** along the Z axis.

If $\frac{1}{2}D - J_i - 4P^2K_\gamma - 2P^2w^2K_\alpha - 2L_\alpha > 0$, T_7 is a maximum if $a_{13} = b_{13} = 0$, and (7·33) is solved by:

$$\left.\begin{array}{llll} \text{either} & a_{11} = b_{11} = 0, \quad \text{or} \quad a_{12} = b_{12} = 0, & & \theta = 0; \\ \text{or} & a_{11} = -b_{11} = -\frac{1}{2}\chi, \quad a_{12} = b_{12} = 1, & \left.\vphantom{\begin{array}{l}a\\a\end{array}}\right\} & |\theta| = |\chi|. \\ \text{or} & a_{12} = -b_{12} = -\frac{1}{2}\chi, \quad a_{11} = b_{11} = 1, & & \end{array}\right\} \quad (7·34)$$

The second alternative leads to a larger total energy and corresponds thus to stable order. We must note, however, that we have obtained this result from the original assumption that the exchange-interaction energies were of the form (7·7) and this would only be true if the order were a proper one, which it is not. However, as long as θ is small, equations such as (7·7) are close to the correct ones, and the result obtained in this way for θ should be a good approximation.

In this type of order we have the spins on the a and b sublattices all inclined at the same small angle $\frac{1}{2}\theta$ to either the X or the Y axis. It is a distorted type 1 order, and there are four equivalent spin arrangements which are shown in figure 34, depending on whether χ is positive or negative and whether the spins are pointing approximately in the X or the direction.

We note that for this type of order for temperatures below T_C there should be a small resultant ferromagnetic moment along either the X or the Y axis; this moment should be $\frac{1}{2}|\chi|$ times the saturation magnetic moment.

Ferromagnetic order. The solution $R = -\surd(AA')$ leads to

$$T_8 = [-J-4K-2M+(\tfrac{1}{2}D+\tfrac{1}{2}J_\alpha+4P^2K_\gamma+2P^2w^2K_\alpha+2L_\alpha)(1-3a_{13}^2)-2Ka_{11}^2a_{12}^2\chi^2]\,\psi, \tag{7·35}$$

where we have again expanded in powers of χ. The situation is similar to the one for type 1 order, and we find the following results.

If $\frac{1}{2}D+\frac{1}{2}J_\alpha+4P^2K_\gamma+2P^2w^2K_\alpha+2L_\alpha < 0$, all spins will be alined along the Z axis.

If $\frac{1}{2}D+\frac{1}{2}J_\alpha+4P^2K_\gamma+2P^2w^2K_\alpha+2L_\alpha > 0$, we get a distorted order, where the spins on the a and the b sublattices will be inclined to one another at an angle θ and to the X (or Y) axis at an angle $\frac{1}{2}\theta$, where again $\theta = |\chi|$.

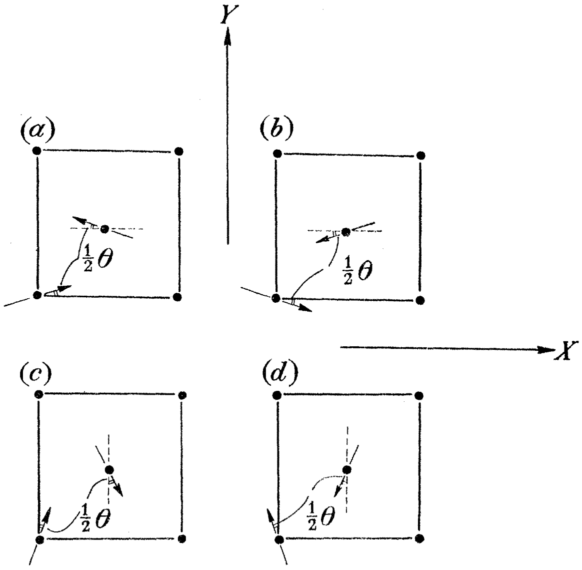

FIGURE 34. Four equivalent arrangements for a type 1 order of the rutile crystal spins in the XY plane. Centre atoms are on a b sublattice, corner atoms on an a sublattice. The angle θ is given by the equation $\theta = |\chi|$. Figure 34*a* corresponds to $a_{11} \doteqdot 1$, χ negative; figure 34*b* to $a_{11} \doteqdot 1$, χ positive; figure 34*c* to $a_{12} \doteqdot 1$, χ negative; figure 34*d* to $a_{12} \doteqdot 1$, χ positive.

Type 3A *order.* The solutions $V = \pm\surd(CC')$, $W = \pm\surd(CC')$ lead to the transition temperatures

$$T_9 = [J+(\tfrac{1}{2}D-\tfrac{1}{2}J_\alpha)(1-3a_{13}^2)\pm 4\surd\{4w^2P^4(K_3-K_1)^2a_{11}^2a_{13}^2+a_{11}^2a_{12}^2K^2\chi^2\}]\,\psi, \tag{7·36}$$

$$T_{10} = J+(\tfrac{1}{2}D-\tfrac{1}{2}J_\alpha)(1-3a_{13}^2)\pm 4\surd\{4w^2P^4(K_3-K_1)^2a_{12}^2a_{13}^2+a_{11}^2a_{12}^2K^2\chi^2\}\,\psi. \tag{7·37}$$

There are three possible configurations; which of these will be the stable one will depend on the signs and magnitudes of the various anisotropy parameters. The three possibilities are the following ones for T_9: the first one is formed by putting $a_{12} = 0$ and making $(\frac{1}{2}D-\frac{1}{2}J_\alpha)(1-3a_{13}^2)-8wP^2(K_3-K_1)\,a_{11}a_{13}$ a maximum; the second one is found by putting $a_{12} = 0$ and making $(\frac{1}{2}D-\frac{1}{2}J_\alpha)(1-3a_{13}^2)+8wP^2(K_3-K_1)\,a_{11}a_{13}$ a maximum; the third one is the rutile type diagonal ordering in the XY plane. In the first two cases the order is a proper one, but **n** is a complicated function of the anisotropy parameters.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Type 3B *order.* The solutions $U = \pm\sqrt{BB'}$ correspond to the transition temperatures

$$T_{11} = \{-J+2M+(\tfrac{1}{2}D+\tfrac{1}{2}J_\alpha)\,(1-3a_{13}^2)\\ \pm 2a_{11}a_{12}\sqrt{[4K^2\chi^2+\{4P^2(K_1-K_2)-2w^2P^2(K_2-K_3)+2(L_\beta-L_\gamma)\}^2]}\}\,\psi. \quad (7{\cdot}38)$$

This type of order has not yet been found in nature. If $D+J_\alpha < 0$ both a and b sublattices are alined along the Z axis. If $D+J_\alpha > 0$, ordering takes place in the XY plane. The a sublattices and the b sublattices will each be properly antiferromagnetically ordered, but if $\chi \neq 0$ they will not have the same preferred direction of alinement. In the limiting case of negligible second-neighbour anisotropy, the ordering approaches the rutile type diagonal ordering. In other cases the angle between the spins on the a and the b sublattices will be a function of the anisotropy parameters which can be found in the usual way.

8. Comparison with experimental data on rutile structure antiferromagnetics

A considerable amount of experimental work (Erickson 1952, 1953; Shulman 1961) has been carried out on the following rutile structure antiferromagnetics: MnF_2, FeF_2, CoF_2, NiF_2, and MnO_2. Of these MnF_2, FeF_2, and CoF_2 show type 1 order with the Z axis as the preferred direction, and MnO_2 shows type 2 order with the preferred directions along the XY face diagonals with probably the a and b sublattices mutually perpendicular. All these arrangements were found as possible types of order for rutile structure antiferromagnets. We must mention here the work of Yoshimori (1959) who has found a screw-type ordering for MnO_2 with a pitch of several times c_0. He claims that this order has been found experimentally. We have found that this type of order is, indeed, the most stable one for certain ranges of J and K; it is not included in our results as it necessarily involves magnetic unit cells larger than the ones considered here.

The most interesting case to date is, perhaps, that of NiF_2. This crystal appears to have a type 1 order but with the preferred direction in the XY plane and a small residual ferromagnetic moment in the X or Y direction below the antiferromagnetic transition temperature (Matarrese & Stout 1954; Shulman 1961). From these data one can calculate χ and the result is that $\chi \sim \frac{1}{16}$ as mentioned in the previous section (giving $\frac{1}{2}\theta \sim 1{\cdot}8^\circ$).

Moriya (1960) has also treated the NiF_2 problem theoretically. He arrives at essentially the same spin arrangement as we have found. He neglects dipole- and pseudo-dipole interactions, and although we have shown that this restriction is unnecessary to find the NiF_2-type ordering, it is probably true that for NiF_2 the main anisotropy effect is due to the crystalline field.

Other antiferromagnetic salts, the spin arrangements of which have recently been determined, are $CrCl_2$ and CrF_2 (Cable, Wilkinson & Wollan 1960). Neither of these salts have their magnetic atoms on a b.c.t. lattice, but both show the rutile anion positions. The chlorine atoms in $CrCl_2$ are on an ortho-rhombic lattice. Since in this case the lattice is very close to a b.c.t. one, we may with some justification apply our results to it. This salt shows type 3A order with rutile type diagonal ordering which is again one of the arrangements found in the previous section.

Although CrF_2 is actually monoclinic it is only slightly distorted from proper rutile structure. It shows type 1 order with the preferred direction definitely not along the Z axis, but otherwise undetermined. This would suggest an arrangement similar to that of NiF_2 and a small residual ferromagnetic moment below its antiferromagnetic transition temperature.

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