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A Binary Algebra Describing Crystal Structures with Closely-Packed Anions*

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A description of structures with close-packed anions is given in terms of simple, interpenetrating component lattice arrays. Each component array is denoted by a set of binary digits, from which the spatial relationship of these arrays can be derived. For ferrimagnetic rocksalt-like structures the magnetic dipole–dipole energy is minimized subject to exchange restraints, and it is shown that dipole patterns so obtained match those found by neutron-diffraction, and are not necessarily parallel and antiparallel to a single direction. Spinel and olivine structures are found to be ordered mixtures of some component arrays found in rocksalt structures and some found in sphalerite structures.

1. Introduction

Rocksalt, sphalerite, spinel and olivine structures all contain close-packed anion arrays, or anion structures which can be expressed as simply distorted forms of a close-packed lattice array. Goodenough & Loeb (1955) and Goodenough (1955) have investigated the motivating forces determining the positions of cations relative to this close-packed anion structure, and some causes of the distortions. These motivating forces are derived from a number of free-energy terms, namely electrical, covalent, exchange, magnetic, and entropic free energies (Goodenough & Loeb, 1955). To evaluate the interactions between the various crystal elements, the following analytical description of the spatial relationships was developed. Each structure is analysed in terms of a number of component arrays whose unit-cell dimensions are an integral number times those of the structure under consideration, the integer being unity or greater. As is the case in Fourier analysis, certain regularities become apparent only when more than one period of the structure under analysis is examined.

Loeb & Goodenough (1957) have used the algebra developed here to show that magnetic dipole interactions in antiferrimagnetics are anisotropic, i.e. the interaction energy depends on the orientations of the dipoles with respect to the crystal axes.

2. Coordinate system

The locations of the ions and the orientations of the dipoles are expressed in a Cartesian system of coordinates with origin on an anion. The unit of distance is chosen as one-half the smallest distance between anions, which, for the rocksalt structure, is the shortest cation–anion distance.

3. The rocksalt structure; antiferromagnetics

In the rocksalt structure, the coordinates of the anions, as defined in § 2, satisfy equation (1), and those of the cations satisfy equation (2):

$$x+y+z = 2K\,, \tag{1}$$

$$x+y+z = 2K+1\,, \tag{2}$$

where K is an integer.

For ferrimagnetic crystals, such as those of NiO, MnO and MnS, exchange (Goodenough & Loeb, 1955; Kramers, 1930, 1952; Anderson, 1950) imposes the requirement that a pair of dipoles separated by and colinear with an anion must be antiparallel. Thus when a dipole located at (x, y, z) has Cartesian components (p, q, r), then dipoles located at $(x\pm2, y, z)$, at $(x, y\pm2, z)$ and at $(x, y, z\pm2)$ all have Cartesian components $(-p, -q, -r)$, those at $(x\pm4, y, z)$, at $(x\pm2, y\pm2, z)$, at $(x\pm2, y, z\pm2)$, at $(x, y\pm2, z\pm2)$, etc., have components (p, q, r). Thus, once the orientation of any one dipole is fixed, the orientation of many other dipoles is also fixed through the exchange mechanism. It will now be investigated just how may dipoles have their direction fixed by exchange once one dipole is fixed, or, expressed differently, how many independent dipole systems there are in antiferromagnetic rocksalt structures. A translational motion described by a change of two units in any one of the coordinates involves no change in parity of the coordinates (x, y, z), but a change in parity of K (see equation (2)). Therefore exchange requirements cause all dipoles at locations whose coordinates have the same parity, to be either parallel or antiparallel to each other. Those having the same parity for x, y and z, are all parallel to each other if they have the same parity in K, and antiparallel if they have a K with different parity. According to equation (2), the sum of x, y, and z, must be odd, so that the parity of any

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one of them is necessarily opposite to that of the sum of the other two. Therefore, when the parity of two of the three coordinates of a dipole are given, the parity of the third one can be derived. Arbitrarily, we shall here consider the parities of y and z as independent; the parities of y and z then describe an independent system of dipoles, with the parity of K distinguishing the oppositely directed dipoles within such a system. It will be convenient to use a binary notation to indicate the parities of x, y, z, and K: '0' is the symbol for 'even', '1', the symbol for 'odd'. The independent dipole systems are then denoted by the binary numbers 00, 01, 11, 10, indicating the parities of y and z. It follows that there are four independent dipole systems. These are listed in Fig. 1; in this diagram the four systems are subdivided according to the parity of K, as indicated above. In analogy with Switching theory, Fig. 1 is called a 'Karnaugh map' (Karnaugh, 1953). The three digits giving the parities of, respectively, y, z, and K are combined into a binary number called the 'descriptor'. The first two digits determine the column, the third the row in the Karnaugh map. From the Karnaugh map the result of any translation through the lattice can be derived. For example, the nearest neighbors of an anion at (0, 3, 1) are the cations at

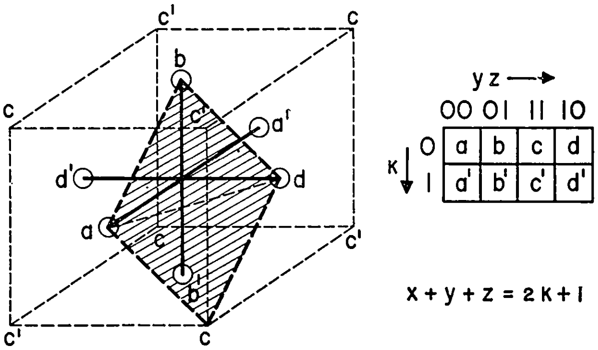
(0, 3, 2), (0, 4, 1), (1, 3, 1), (0, 3, 0), (0, 2, 1), and (−1, 3, 1)

with the following respective descriptors,

100, 010, 110, 101, 011 and 111 .

The Karnaugh map then shows that the six nearest neighbors belong respectively to the following component lattice arrays:

d, *b*, *c*, *d′*, *b′*, *c′* .



K \ yz	00	01	11	10
0	a	b	c	d
1	a'	b'	c'	d'

x + y + z = 2K + 1

Fig. 1. Geometric and Karnaugh maps for close-packed cation structure.

4. Magnetic dipole interactions in antiferromagnetic rocksalt structures

Since the orientation of a dipole is described by two parameters, the orientation of all dipoles in an antiferromagnetic rocksalt-like structure is given by eight parameters. In this section, the magnetic interaction energy between the four independent dipole systems will be computed as a function of the eight parameters, and relationships between these parameters will be found that minimize this energy.

The energy of a system of magnetic dipoles, all of magnitude, μ, is

$$E_D = \mu^2 \sum_{i<j} r_{ij}^{-3} \hat{\mu}_i . \hat{\mu}_j - 3\mu^2 \sum_{i<j} r_{ij}^{-5} (\hat{\mu}_i . \mathbf{r}_{ij})(\hat{\mu}_j . \mathbf{r}_{ij}) \,, \quad (3)$$

where $\mathbf{r}_{ij}$ is the vector from a dipole $\boldsymbol{\mu}_i$ to a dipole $\boldsymbol{\mu}_j$, and $\hat{\mu}_i$, $\hat{\mu}_j$ are unit vectors in the directions of the dipoles $\boldsymbol{\mu}_i$, $\boldsymbol{\mu}_j$. To calculate this interaction energy, it is convenient to first calculate the interactions within a cluster defined as a cation with its eighteen nearest and next-nearest cation neighbors.

If Cartesian coordinates of the dipoles are used so that

$$\hat{\mu}_i = \hat{i} p_i + \hat{j} q_i + \hat{k} r_i ; \quad p_i^2 + q_i^2 + r_i^2 = 1 \,,$$

the energy E_D is expressed as a function of the twelve variables

$$p_a, q_a, r_a ; \quad p_b, q_b, r_b ; \quad p_c, q_c, r_c ; \quad p_d, q_d, r_d \,.$$

The variables $p_{a'}$, $q_{a'}$, etc. are eliminated through the relations $p_{a'} = -p_a$, etc. Because of the relationship $p_i^2 + q_i^2 + r_i^2 = 1$, this means that the interaction energy for the cluster is expressed in terms of eight independent parameters.

To calculate the general expression for the contribution of a cluster to E_D, first consider the case of an a site in the center of the cluster. If s is the shortest anion–cation distance, the first term in equation (3) becomes

$$(\sqrt{2}.s)^{-3} \mu^2 \sum_{\substack{j \\ \text{(near} \\ \text{neighbors)}}} \hat{\mu}_a . \hat{\mu}_j = (\sqrt{2}.s)^{-3} \mu^2 \hat{\mu}_a \times [(\hat{\mu}_b + \hat{\mu}_{b'}) + (\hat{\mu}_c + \hat{\mu}_{c'}) + (\hat{\mu}_d + \hat{\mu}_{d'})] \,.$$

The next-nearest-neighbor terms do not appear since $\mu_a . \mu_{a'} = -1$, so that they only contribute terms independent of dipole orientation. Further,

$$\hat{\mu}_b = -\hat{\mu}_{b'} ; \quad \hat{\mu}_c = -\hat{\mu}_{c'} ; \quad \hat{\mu}_d = -\hat{\mu}_{d'}$$

so that the entire sum vanishes.

For the second term of equation (3) with $i = a$, Fig. 1 is conveniently used. For instance, the terms for $j = b$ and $j = b'$ become:

$$\begin{aligned} & -3\mu^2 (\sqrt{2}.s)^{-5} \{ (\hat{\mu}_a . \mathbf{r}_{ab})(\hat{\mu}_b . \mathbf{r}_{ab}) + (\hat{\mu}_a . \mathbf{r}_{ab'})(\hat{\mu}_{b'} . \mathbf{r}_{ab'}) \} \\ & = -3\mu^2 (\sqrt{2}.s)^{-3} \{ (-p_a + r_a)(-p_b + r_b) + (p_a - r_a)(p_b - r_b) \\ & \quad + (p_a + r_a)(-p_b - r_b) + (-p_a - r_a)(p_b + r_b) \} \\ & = +12\mu^2 (\sqrt{2}.s)^{-3} (p_a r_b + p_b r_a) \,. \end{aligned}$$

The interactions with c, c', d, and d' sites are similar, so that the interaction energy of the a-site dipole in the center of a cluster with the other dipoles in the cluster is

$$W_a = 12(\sqrt{2}.s)^{-3} \times \mu^2(p_a r_b + p_b r_a + q_a r_c + q_c r_a + p_a q_d + p_d q_a) . \quad (4)$$

Interactions with the next-nearest neighbors contribute a constant term, which is independent of angle. It is therefore an isotropic term and can be neglected. It merely effects the definition of zero lattice energy.

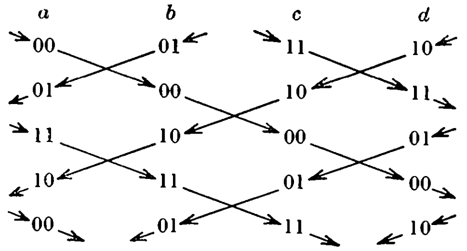
The total dipole-interaction energy for the clusters is given by

$$E_D = \tfrac{1}{2}(W_a + W_b + W_c + W_d) ,$$

where W_b, W_c, and W_d are the interaction energies of, respectively, a-, b-, c-, and d-cations with their surrounding near neighbors. The factor 1/2 accounts for the fact that each cation is counted once as the center of its own cluster and again as a surrounding dipole in another cluster.

W_b, W_c and W_d are derived from W_a by moving, successively b, c, and d into the position previously occupied by a. It is not correct to apply simple cyclic permutation to the subscripts of equation (4), for when b takes the place of a, the places previously held by b, c, and d, are not filled in order by c, d and a. The displacements must be accomplished such that the relative positions of the component lattices remain unchanged, in other words, that the parity differences* indicated in the Karnaugh map of Fig. 1 are preserved. Table 1 shows the successive positions of the component lattices when b, c, and d are removed successively into the position occupied by a.

Table 1. *The permutations used in deriving* W_b, W_c, *and* W_d *from* W_a



With the aid of these permutations it is found that:

$$W_b = 12(\sqrt{2}.s)^{-3} \times \mu^2(p_b q_c + p_c q_b + r_b q_d + p_d q_b + p_b r_a + p_a r_b) ,$$

$$W_c = 12(\sqrt{2}.s)^{-3} \times \mu^2(p_c r_d + p_d r_c + q_c r_a + q_a r_c + p_c q_b + p_b q_c) ,$$

$$W_d = 12(\sqrt{2}.s)^{-3} \times \mu^2(p_a q_d + p_a q_d + r_d q_b + r_b q_d + p_d r_c + p_c r_d) .$$

Therefore, since $p_i^2 + q_i^2 + r_i^2 = 1$, the magnetic dipole interaction energy for a cluster, E_D, is given by

$$E_D = E_0 + 3\mu^2/(\sqrt{2}.s)^{-3}\{(p_a+q_d+r_b)^2 + (p_b+q_c+r_a)^2 + (p_c+q_b+r_d)^2 + (p_d+q_a+r_c)^2\} , \quad (5)$$

where E_0 contains all terms independent of dipole orientations. Since none of the succeeding terms in the expression for E_D is negative, E_0 represents the absolute minimum of E_D.

To calculate the interaction of a dipole with the dipoles outside its own cluster, it is convenient to introduce some further definitions. Since the dipoles within a cluster have been defined by the lower-case letters $r_{ij}, a, b, \ldots$, let the clusters be defined by upper case letters so that a vector joining two clusters I, J is defined as $\mathbf{R}_{IJ}$, and the vector joining dipole i in cluster I to dipole j in cluster J is:

$$\mathbf{R}_{iIjJ} = \mathbf{R}_{IJ} + \mathbf{r}_{ij} .$$

Since the contributions to the first term in equation (2) vanish for the same reasons as in the case for intercluster interactions, the important intercluster term is

$$\begin{aligned}(\boldsymbol{\mu}_i.\mathbf{R}_{iIjJ})(\boldsymbol{\mu}_j.\mathbf{R}_{iIjJ}) &= (\boldsymbol{\mu}_i.\mathbf{R}_{IJ} + \boldsymbol{\mu}_i.\mathbf{r}_{ij}).(\boldsymbol{\mu}_j.\mathbf{R}_{IJ} + \boldsymbol{\mu}_j.\mathbf{r}_{ij}) \\ &= (\boldsymbol{\mu}_i.\mathbf{R}_{IJ})(\boldsymbol{\mu}_j.\mathbf{R}_{IJ}) + (\boldsymbol{\mu}_i.\mathbf{r}_{ij})(\boldsymbol{\mu}_j.\mathbf{r}_{ij}) \\ &\quad + (\boldsymbol{\mu}_i.\mathbf{R}_{IJ})(\boldsymbol{\mu}_j.\mathbf{r}_{ij}) + (\boldsymbol{\mu}_j.\mathbf{R}_{IJ})(\boldsymbol{\mu}_i.\mathbf{r}_{ij}) . \quad (6)\end{aligned}$$

If demagnetizing effects are neglected, an infinite crystal may be assumed. Then each cluster is spherically surrounded by identical clusters, so that each $\mathbf{R}_{IJ}$ can be paired with a $(-\mathbf{R}_{IJ})$. When equation (6) is substituted into equation (3), the summation over all clusters causes a cancellation of the third and fourth terms of equation (6). The first term in equation (6) also vanishes because for every $\boldsymbol{\mu}_j$ in a cluster there is a $\boldsymbol{\mu}_{j'} = -\boldsymbol{\mu}$ joined to $\boldsymbol{\mu}_i$ by the same $\mathbf{R}_{IJ}$. This leaves the second term in equation (6), which is identical with E_D given by equation (5) in every respect, except for s which is replaced by a larger distance. Since the magnetic dipole interaction varies as the inverse cube of the distance, the interaction between remote clusters duplicates the intracluster interaction in strongly attenuated form. The magnitude of the magnetic dipole interaction is thus found to be of the order $(\mu^2/s^3) \times 10^{22} \sim 10^6$ erg.cm.$^{-3}$. This is of the same order of magnitude as experimentally observed antiferromagnetic anisotropy energies, which can therefore be associated with the combined exchange and magnetic interaction energies between the dipoles in antiferromagnetic rocksalt structures.

The maximum value of the magnetic dipole interaction $E_{\text{max.}}$ occurs when all dipole components in equation (5) equal $1/\sqrt{3}$. The dependence of the magnetic interaction energy between *all* dipoles on the dipole orientations can therefore be written in the form given by equation (7).

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[*] Parity differences are computed according to the following rules:

$$0 \text{ minus } 1 = 1 \text{ minus } 0 = 1 ,$$
$$0 \text{ minus } 0 = 1 \text{ minus } 1 = 0 .$$

$$\frac{E_D - E_0}{E_{\mathrm{max.}} - E_0} = \frac{1}{12}\left\{(p_a+q_d+r_b)^2+(p_b+q_c+r_a)^2 + (p_c+q_b+r_d)^2+(p_d+q_a+r_c)^2\right\}. \quad (7)$$

From equation (7) it follows that the magnetic dipole energy is minimized when

$$p_a+q_d+r_b = p_b+q_c+r_a = p_c+q_b+r_d = p_d+q_a+r_c = 0\,, \quad (8)$$

subject to the restraints $p_i^2+q_i^2+r_i^2 = 1$ with $i = a, b, c, d$. Since this gives eight equations with twelve variables, there are four free parameters, or one free parameter for each simple cubic component lattice. Therefore, there is no unique solution which minimizes the dipole–dipole interactions. Refinement of the theory in the following sense may resolve the degeneracy. It has been assumed here that all dipoles are rigidly fixed in space, and can vary only their orientation. Actually, crystal distortion may occur to favor certain dipole orientations over others. Spin-orbit coupling also plays an important role in resolving degeneracy. Some important configurations for which $E_D = E_0$ are discussed below.

Let it be assumed that all the dipoles are constrained to lie within a (100) plane. Then $p_a = p_b = p_c = p_d = 0$ and

$$q_d+r_b = q_b+r_d = q_c+r_a = q_a+r_c = 0\,. \quad (9)$$

From Fig. 1, it follows that b and d, both having odd parity for $(y+z)$, have even x coordinates and lie in even (100) planes, whereas a and c have odd x and lie in odd (100) planes. Thus it is seen from equation (9) that the assumption that all dipoles lie in planes parallel to the YZ plane effectively 'uncouples' the even-x from the odd-x planes. Each set of planes can have independent low-energy configurations, which are expressed in terms of the parameters α and β in Table 2.

Table 2. *Conditions for minimum energy configurations of dipoles constrained to coordinate plane*

	q	r			q	r
b	α	$\pm\sqrt{(1-\alpha^2)}$	and	a	β	$\pm\sqrt{(1-\beta^2)}$
d	$\mp\sqrt{(1-\alpha^2)}$	$-\alpha$		c	$\mp\sqrt{(1-\beta^2)}$	$-\beta$

(10)

In Fig. 2(a) are drawn the relative positions of a, b, c, and d dipoles, as seen looking in the direction of the X axis. In Figs. 2(b), 2(c), and 2(d) are shown some typical spin configurations having different values of the parameters. Fig. 2(c) is consistent with Kaplan's findings that dipoles in a (111) plane give a minimum dipole–dipole interaction energy. However, Kaplan did not identify an optimum orientation within the (111) planes. It will now be shown that configurations in which the spins are simultaneously parallel to a coordinate plane are the only configurations in a (111) plane with minimum dipole–dipole anisotropy energy.

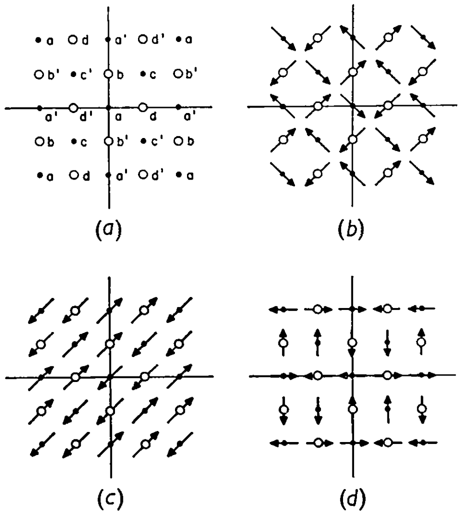

Fig. 2. Patterns giving minimum dipole–dipole interaction energies. Dots: odd (100) planes; circles: even (100) planes.

To show this, first note that if the dipoles lie in a (111) plane, then $p_i+q_i+r_i = 0$ for $i = a, b, c, d$. Kaplan's requirement that half of the near-neighbor dipoles be antiparallel to the other half is satisfied by the following:

$$\begin{array}{ccccl} & p & q & r & \\ a & u & v & -(u+v) & u^2+v^2+(u+v)^2 = 1 \\ b & u & v & -(u+v) & u^2+v^2+(u+v)^2 = 1 \\ c & -u & -v & (u+v) & u^2+v^2+(u+v)^2 = 1 \\ d & -u & -v & (u+v) & u^2+v^2+(u+v)^2 = 1 \end{array} \quad (11)$$

It follows that $E_D = E_0+12v^2(E_{\mathrm{max.}}-E_0)$, which is a minimum only if $v = 0$ and the spins are simultaneously parallel to a coordinate plane. If the signs for sublattices b and c in the above table are interchanged, the minimum value for E_D occurs only if $u = 0$, which again is consistent with the statement that the spins must be simultaneously parallel to a coordinate plane and therefore be parallel to a 110 axis. In Fig. 2(c) the dipoles are in a (111) plane directed in $[0\bar{1}1]$ and $[01\bar{1}]$ directions.

The author is indebted to Professor Frederic Keffer of the University of Pittsburgh for pointing out that Kaplan assumed that the dipoles are *all* parallel to each other in a 111 plane, but that the three antiparellel arrays discussed here imply parallel arrays respectively in $\bar{1}11$, $1\bar{1}1$ and $11\bar{1}$ planes, in which they *are* free to rotate. That this is so, can be easily seen from the Karnaugh map in Fig. 1; for instance, reflection into the XY-plane primes b and c-sites, which have odd Z-coordinates, but leaves a and d sites, having even Z-coordinates, unchanged. From equation 7 it follows that any parallel orientation in a 111-plane gives minimum dipole–dipole interaction energy.

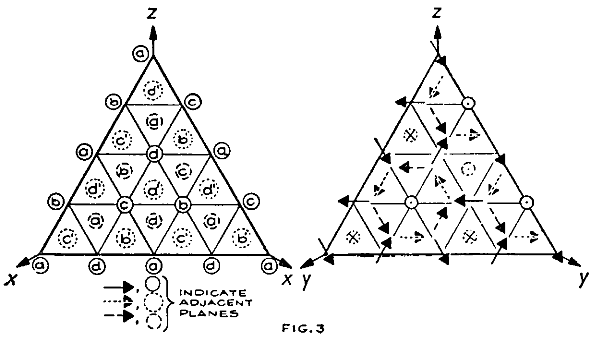

Fig. 3. A low-energy configuration, as seen along the [111] axis.

Fig. 3 represents a configuration corresponding to an energy given by

$$\frac{E_D \;-E_0}{E_{\text{max.}}-E_0}=\frac{1}{12}\,.$$

Although the dipole interaction calculated on the basis of an undistorted lattice is higher than that for the configurations shown in Fig. 2, this configuration is important because closure of field lines would favor a contraction of the crystal along the [111] axis. This contraction has been experimentally observed (Shull, Strauser & Wollan, 1951), and may bring the dipole energy down to the level of the energy of the configurations shown in Fig. 2.

5. Evaluation of neutron-diffraction data

Corliss & Hastings (private communication) have examined the spin orientations in such antiferromagnetic rocksalt structures as MnO and MnS. They divided the cation lattice array into four antiferromagnetic component structures, and expressed their results in terms of a parameter A, given by:

$$\begin{aligned} A \;=\; &(p_1q_2+q_1p_2)+(p_1r_4+r_1p_4)+(q_1r_3+r_1q_3)\\ &-(p_2r_3+r_2p_3)-(p_3q_4+q_3p_4)-(q_2r_4+r_2q_4)\,, \end{aligned} \tag{12}$$

where the subscripts 1–4 denote the four component structures. The four component structures were found to be identical to four of the component arrays shown in Fig. 1, as listed in Table 3.

Table 3. *Identification of component structures described by Corliss & Hastings with those defined in Fig. 1.*

Corliss & Hastings	1	2	3	4
This paper	c'	b	a	d

Equation (12) is then rewritten in terms of the component lattices:

Since $(p_i^2+q_i^2+r_i^2)_{i=a,b,c,d}=1$ it becomes

$$\begin{aligned} A \;=\; 2-\tfrac{1}{2}\{&(p_a+q_d+r_b)^2+(p_b+q_c+r_a)^2+(p_c+q_b+r_d)^2\\ &+(p_d+q_a+r_c)^2\}\,. \end{aligned} \tag{13}$$

From equations (7) and (13) it follows that

$$A\;=\;2\text{–}6\,\frac{E_D\;-E_0}{E_{\text{max.}}-E_0}\,.$$

It follows that $A=2$ when $E_D=E_0$. Therefore, any configuration having a minimum magnetic interaction energy would give a neutron diffraction parameter $A=2$. This is just the value observed by Corliss & Hastings, so that it is proven that the dipole arrangement in MnO and MnS, whatever it be, is a minimum magnetic energy configuration. The neutron-diffraction data do not, therefore, provide values for the free parameters α and β, so that it is not certain whether the orientation of the dipoles is actually fixed, or whether the dipoles rotate in a correlated manner, such that the minimum energy is preserved, and A always equals 2.

The configuration shown in Fig. 3 has $A=3/2$, if it is assumed that the structure is cubic. As was pointed out in the previous section, this structure is actually contracted along a [111] axis, so that the experimental value $A=2$ is not unreasonable for this configuration.

6. The sphalerite structure

The ions of sphalerite, like those of rocksalt, form two interpenetrating close-packed structures, of which one consists of anions, the other of cations. Sphalerite and rocksalt differ in the relative positions of these close-packed arrays. The rocksalt cations are surrounded by six anions at the corners of an octahedron, and the anions are similarly surrounded by cations. In sphalerite each ion is surrounded by four oppositely charged ions at the corners of a tetrahedron. The sites occupied by cations in rocksalt are called B-sites, and their occupants B-ions, while the sites occupied by cations in sphalerite are called A-sites, which may be occupied by A-ions. The coordinates of A-sites have half-integer values and satisfy either equation (11*a*) or (11*b*):

$$x+y+z\;=\;2K+\tfrac{1}{2}\,, \tag{11a}$$

$$x+y+z\;=\;2K-\tfrac{1}{2}\,. \tag{11b}$$

The coordinates of all cations in sphalerite satisfy either equation (11*a*) or equation (11*b*). For instance, a sphalerite crystal having a cation at site $(-\frac{1}{2},\,-\frac{1}{2},\,-\frac{1}{2})$, which satisfies equation (11*a*), does not have a cation at $(\frac{1}{2},\,\frac{1}{2},\,\frac{1}{2})$, which satisfies equation (11*b*). A crystal whose cations have coordinates obeying equation (11*a*) can be converted into one obeying equation (11*b*) by rotation through 90°.

7. The spinel structure

Spinels have the chemical formula $M^{\text{I}}M^{\text{II}}\text{O}_4$, where M^{I} and M^{II} stand for, generally, two types of metal ions. The oxygen ions form a, sometimes distorted, close-packed array. One-third of the cations occupy A-sites, two-thirds occupy B-sites. The spinel structure can thus be considered an ordered mixture of the rocksalt and sphalerite structures. A spinel has one-fourth as many occupied A-sites as does sphalerite, and one-half as many occupied B-sites as does rocksalt. Removal of half of the component cation arrays of the rocksalt structure can be accomplished in two essentially different ways, as shown in Table 4. Either an even or an odd number of primed arrays may be removed; every combination of four arrays reduces by rotation to one of the two combinations shown in Table 4.

Table 4. *Generation of* $M^{\mathrm{I}}M^{\mathrm{II}}O_4$ *structures from rocksalt*

(*a*) Odd number of primed lattices

	b	*c*	*d*
a'			

(*b*) Even number of primed lattices

	b		*d*
a'		*c'*	

The two resulting structures are essentially different, for the sites of lattices a', b, c and d form a tetrahedral structure (see Fig. 1), whereas a', b, c', d form planar arrays. The former structure is therefore more symmetrical, and it is the one out of which spinels are built up. The latter structure will be discussed in § 8.

When either one or three primed and unprimed arrays, adding up to half the rocksalt cations, have been removed, they must be replaced by A-cations. These A-cations occupy the center of the tetrahedra from which the B-sites were removed. If the scheme followed in Table 4(*a*) is followed, then the surroundings of the anion at the origin would be as indicated in Table 5 (see also Fig. 1).

Table 5. *Surroundings of anion at* (0, 0, 0) *in spinel*

Site	Descriptor	Component lattice	Status, according to Table 4(*a*)
1, 0, 0	000	*a*	Empty
−1, 0, 0	001	*a'*	Filled
0, 1, 0	100	*d*	Filled
0, −1, 0	101	*d'*	Empty
0, 0, 1	010	*b*	Filled
0, 0, −1	011	*b'*	Empty

The location of the nearest A-ion is at the center of the 'empty' tetrahedron, hence on a line making equal, obtuse angles with lines toward a', b and d. It is therefore at the location $(\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2})$, hence belongs to the sites whose coordinates obey the equation $x+y+z = 2K-\frac{1}{2}$.

The surroundings of the anion at, for instance, (0, −2, 0) are given in Table 6.

The nearest A-ion is at $(-\frac{1}{2}, -\frac{3}{2}, \frac{1}{2})$ the center of the 'empty' tetrahedron, and hence in the lattice whose coordinates obey the equation $x+y+z=2K+\frac{1}{2}$. The surroundings of the anion at (0, −2, 0) form a configuration that is just the mirror image of those of the anion at (0, 0, 0). Fig. 4 shows this portion of the spinel structure.

Table 6. *Surroundings of an anion at* (0, −2, 0) *in spinel*

Site	Descriptor	Component lattice	Status
1, −2, 0	001	*a'*	Filled
−1, −2, 0	000	*a*	Empty
0, −1, 0	101	*d'*	Empty
0, −3, 0	100	*d*	Filled
0, −2, 1	011	*b'*	Empty
0, −2, −1	010	*b*	Filled

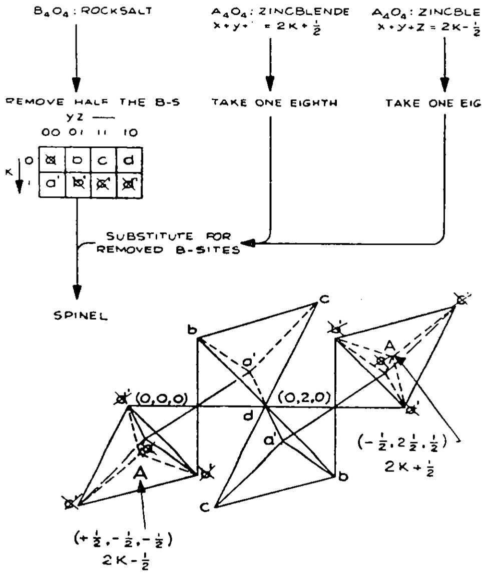

Fig. 4. Generation of spinel.

The spinel structure is therefore summarized as consisting of a close-packed anion lattice array, one or three of the unprimed and three or one of the primed component cation arrays of the rocksalt structure, and one-eighth of each of the two conjugate cation arrays that can make up the sphalerite structure. There are, therefore, six interpenetrating close-packed cation arrays in the spinel structure, each with a lattice parameter twice that of the close-packed anion arrays. Each anion is surrounded by three B-cations in mutually perpendicular directions and an A-cation in a direction making equal obtuse angles with these three directions. This configuration occurs throughout the spinel structure, in eight possible orientations, the A-ion being in one of the eight octants surrounding an anion.

Finally, in Table 7, another example is worked out, namely the surroundings of an anion at (8, 3, 1). The nearest A-ion is at $(\frac{15}{2}, \frac{5}{2}, \frac{1}{2})$; its coordinates obey the equation $x+y+z = 2K+\frac{1}{2}$.

Table 7. *Surroundings of an anion at* (8, 3, 1) *in spinel*

Site	Descriptor	Component lattice	Status, according to Table 4(*a*)
9, 3, 1	110	*c*	Filled
7, 3, 1	111	*c′*	Empty
8, 4, 1	010	*b*	Filled
8, 2, 1	011	*b′*	Empty
8, 3, 2	100	*d*	Filled
8, 3, 0	101	*d′*	Empty

8. The olivine structure

Like spinels, olivines have the chemical formula $M^{\mathrm{I}}M_2^{\mathrm{II}}\mathrm{O}_4$, and the oxygens form a distorted close-packed array. One third of the cations occupy A-sites, and two-thirds occupy B-sites, just as in the spinel structure. The distortion is such that the oxygens surrounding an A-ion are pulled very close to the A-ion, so that the olivine structure looks like an array of tetrahedra, with B-ions in the interstices. The A-ions are, in olivine, Si, and the bond between Si and O is covalent, hence very short. The difference between spinels and olivines is illustrated by Table 4, for the olivine structure is generated from rocksalt and sphalerite according to the scheme of Table 4(*b*), rather than that of Table 4(*a*) used for spinel. As explained in § 7, the resulting structure has a symmetry lower than that of spinel, with a preferred axis (one of the [111] axes of the close-packed anion lattice). This is in accord with experimental observations on olivine. As a result of the removal of B-cations according to the scheme shown in Table 4(*b*), the A-sites replacing these B-cations are located in planes parallel to those of the remaining B-sites. As examples, the surroundings of anions respectively at (0, 0, 0), (0, −2, 0) and (8, 3, 1) are shown in Tables 8, 9, and 10.

Table 8. *Surroundings of anion at* (0, 0, 0) *in olivine*

Site	Descriptor	Component lattice	Status, according to Table 4(*b*)
1, 0, 0	000	*a*	Empty
−1, 0, 0	001	*a′*	Filled
0, 1, 0	100	*d*	Filled
0, −1, 0	101	*d′*	Empty
0, 0, 1	010	*b*	Filled
0, 0, −1	011	*b′*	Empty

Table 9. *Surroundings of anion at* (0, −2, 0) *in olivine*

Site	Descriptor	Component lattice	Status, according to Table 4(*b*)
1, −2, 0	001	*a′*	Filled
−1, −2, 0	000	*a*	Empty
0, −1, 0	101	*d′*	Empty
0, −3, 0	100	*d*	Filled
0, −2, 1	011	*b′*	Empty
0, −2, −1	010	*b*	Filled

Table 10. *Surroundings of anion at* (8, 3, 1) *in olivine*

Site	Descriptor	Component lattice	Status, according to Table 4(*b*)
9, 3, 1	110	*c*	Empty
7, 3, 1	111	*c′*	Filled
8, 4, 1	010	*b*	Filled
8, 2, 1	011	*b′*	Empty
8, 3, 2	100	*d*	Filled
8, 3, 0	101	*d′*	Empty

The A-ion nearest to (0, 0, 0) is located at $(\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2})$; its coordinates satisfy the equation $x+y+z = 2K-\frac{1}{2}$.

The A-ion nearest to (0, −2, 0) is located at $(-\frac{1}{2}, -\frac{3}{2}, \frac{1}{2})$; its coordinates satisfy the equation $2K+\frac{1}{2}$.

The A-ion nearest (8, 3, 1) is at $(\frac{17}{2}, \frac{5}{2}, \frac{1}{2})$; its coordinates satisfy the equation $x+y+z = 2K-\frac{1}{2}$. It is observed that the immediate surroundings of anions at (0, 0, 0) and at (0, −2, 0) are the same in spinel as they are in olivine, but that for the anion at (8, 3, 1) the configurations of the surrounding ions differ in orientation.

9. Conclusions

Through various applications it has been shown that a description of crystals in terms of interpenetrating arrays is convenient when interactions between various crystal elements are to be evaluated, particularly when the spatial relationships between these lattices enter into these interactions.

The binary algebra describing these lattices has been useful in showing that dipole arrangements observed in antiferromagnets correspond to a minimum magnetic dipole interaction energy. Furthermore, it has given a better insight into the spinel and olivine structures.

This algebra has several advantages over pictorial unit-cell descriptions. Most of the interactions considered extend beyond the boundaries of a unit cell, and therefore cannot be contained in a unit-cell representation. Moreover, a single unit cell is usually chosen relative to one of the component lattices. For example, the drawing in Fig. 1 shows twice as many c-lattice elements as it does a-, b- and d-elements. By contrast, the Karnaugh map shown in the same figure represents the eight lattices in a perfectly symmetrical manner. As a consequence, the difficulty of counting fractional ions at corners, edges and faces is avoided, and a more direct connection between the chemical formula and crystal structure is established. The symmetry and flexibility of the Karnaugh representation allows a grouping together of various configurations, such as tetrahedra, squares and others that may be of interest, which is very difficult to do in the case of the unit-cell representation, since most of these configurations overlap several adjacent unit cells. The recent observations that some metallic crystals and metal-oxide crystals contain the same cation structures indicated that a separate description of the various cation lattices without reference to the anion structure is quite useful.

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The Crystal and Molecular Structure of 9:10-Dihydro-1:2:5:6-Dibenzanthracene

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The structure of 9:10-dihydro-1:2:5:6-dibenzanthracene has been determined by two-dimensional Fourier syntheses. The cell is monoclinic with $a = 9{\cdot}49$, $b = 6{\cdot}77$, $c = 11{\cdot}38$ Å, $\beta = 91° 29'$; 2 molecules ($C_{22}H_{16}$) per unit cell; space group = $P2_1/a$. Atomic coordinates were obtained from F_o and $(F_o - F_c)$ Fourier syntheses on the three principal zones. The molecule is essentially planar (r.m.s. deviation of carbon atoms from mean plane is 0·039 Å); the mean length of the C–C single bond in the central ring is 1·503 Å, the mean bond length of the aromatic rings is 1·401 Å and the mean angle in the aromatic rings is 120° 0'.

Introduction

This compound (Fig. 1) is of interest because it is slightly carcinogenic and is derived from the more strongly carcinogenic parent compound, 1:2:5:6-dibenzanthracene. It is of interest also because of its relation to 9:10-dihydroanthracene. The latter compound was shown by Ferrier & Iball (1954) to have a bent molecule in which two planar halves are inclined to each other at 145°. Beckett & Mulley (1955) subsequently gave some theoretical reasons, based on chemical evidence, why 9:10-disubstituted anthracenes should have bent molecules, and they postulated structures for the *cis*- and *trans*- isomers which can occur when the substituents are different. The present work will show that 9:10-dihydro-1:2:5:6-dibenzanthracene has a *planar* molecule which is not in accord with predictions from normal stereochemical considerations.

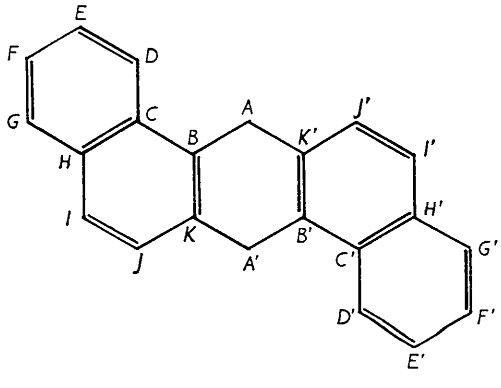

Fig. 1. 9:10-Dihydro-1:2:5:6-dibenzanthracene ($C_{22}H_{16}$).

A preliminary crystallographic study was carried out by Iball (1938), who gave the unit cells and space groups of two crystal forms, both monoclinic. He showed that one form [Form (ii)] had a space group in which the molecules must possess a centre of symmetry, and from this deduced that the molecule must be planar. It is this form which is the subject of the present investigation. The crystals (from a sample kindly provided by Dr J. W. Cook) were the same as were used in the earlier investigation.

Crystal data

The crystals are monoclinic six-sided plates parallel to (001). In the earlier work (Iball, 1938) the unit cell chosen was as follows:

$$a = 9{\cdot}51,\ b = 6{\cdot}77,\ c = 24{\cdot}43\ \text{Å},\ \beta = 111{\cdot}4° .$$

The crystals have negative birefringence with β parallel to b and γ approximately parallel to c. The space group with the above cell is $B2_1/c$, and this