

## Arrangements of Point Charges Having Zero Electric-Field Gradient

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The general conditions are investigated under which an assembly of point charges will produce a zero electric-field gradient (ZEF) at a reference point  $s_0(0,0,0)$ . It is shown that for equal charges it is necessary that they form a configuration of cubic or icosahedral symmetry about  $s_0$ . Unequal charges must be located at the vertices of a *centrosymmetric* polyhedron of symmetry  $m\bar{3}m$ ,  $m\bar{3}$  or  $5\bar{3}m$  in such a way that the sum of the charge values in a pair of charges related by the centre of symmetry of the polyhedron be the same for all the pairs. Configurations of this kind are self-dual (SD) with respect to interchange of vertices by inversion in the centre of symmetry of the polyhedron. Self-dual configurations containing two kinds of charges (SD2C) are listed for polyhedra of up to 20 vertices and enumerated for *all* the centrosymmetric cubic and icosahedral Archimedean polyhedra and their duals. The method of enumeration without construction is described. The conditions under which such discrete ZEF configurations can be embedded in three-dimensional crystal structures to give ZEF structures are also investigated and a number of examples of such embeddings are given. The potential usefulness of such structures as Mössbauer null matrices is briefly discussed.

Certain properties of atoms in ionic crystals depend on the electric field gradient (EFG) at the atom or its nucleus. For example, the quadrupole splitting in the Mössbauer spectrum of  $^{57}\text{Fe}$  or  $^{119}\text{Sn}$  depends on the EFG at the Mössbauer-active nucleus. When the EFG is zero (ZEF), the quadrupole splitting is zero. The EFG is the resultant of two contributions, one due to the asymmetry of the electronic charge-density distribution in the Mössbauer-active atom  $M^*$  and the other, to charges on ions surrounding  $M^*$ . When the charge-density distribution about the  $M^*$  nucleus is of 'spherical' symmetry, the EFG from this source is zero (*cf.* for example, Collins & Travis, 1967); a case in point would be  $^{57}\text{Fe}^{3+}$  (high-spin) in a purely ionic crystal. In the following we shall investigate the conditions under which the second contribution, the EFG due to ionic charges surrounding  $M^*$ , is zero. This problem in electrostatics does not appear to have received a general treatment before. The charges will be considered to be point charges throughout; the coordinate system is Cartesian.

Let  $M^*$  be situated at a site  $s_0(0,0,0)$ . A number  $n$  of point charges of values  $u_i$  located at  $s_i(x_i, y_i, z_i)$  will produce at  $s_0$  an EFG given by the tensor

$$\mathbf{EFG} = \begin{pmatrix} \sum U_{xx}^{(i)} & \sum U_{xy}^{(i)} & \sum U_{xz}^{(i)} \\ \sum U_{xy}^{(i)} & \sum U_{yy}^{(i)} & \sum U_{yz}^{(i)} \\ \sum U_{xz}^{(i)} & \sum U_{yz}^{(i)} & \sum U_{zz}^{(i)} \end{pmatrix}, \quad \text{tr } \mathbf{EFG} = 0,$$

where  $U_{xx}^{(i)} = u_i r_i^{-5} (3x_i^2 - r_i^2)$  etc.,  $U_{xy}^{(i)} = 3u_i r_i^{-5} x_i y_i$  etc.,  $r_i = (x_i^2 + y_i^2 + z_i^2)^{1/2}$ , and the summation is over the  $n$  sites.

Only two of the three eigenvalues of this real symmetric matrix,  $|v_{zz}| \geq |v_{yy}| \geq |v_{xx}|$ , are needed to define the gradient  $\mathbf{EFG} = v_{zz}(1 + \eta^2/3)^{1/2}$ ,  $\eta = (v_{yy} - v_{xx})/v_{zz}$ ,  $0 \leq \eta \leq 1$ , because of  $v_{xx} + v_{yy} + v_{zz} = 0$ . For the EFG at  $s_0$  to be zero,  $v_{zz}$  must be zero and consequently  $v_{xx} = v_{yy} = v_{zz} = 0$ . For the three eigenvalues to be zero, the **EFG** matrix must be null.

For each particular value of  $r_i = (\varepsilon_i^2 + \eta_i^2 + \lambda_i^2)^{1/2}$ , the nullity of **EFG** is satisfied, nontrivially, by subsets  $\mathcal{S}_j$  (or their sums) of the complete set  $\mathcal{S}$  of the  $n_i$  coordinate triplets formed by letter and sign permutations of  $\varepsilon_i, \eta_i, \lambda_i$  (the condition for  $u_i$  is discussed below). The number  $n_j$  of elements in  $\mathcal{S}_j$  is a factor of  $n_i$ . Each subset  $\mathcal{S}_j$  consists of one half of the full set of sign permutations performed on the cyclic permutations  $(\varepsilon_i \eta_i \lambda_i)$  or  $(\varepsilon_i \lambda_i \eta_i)$ , subject to the restriction that the coordinate triplets in a subset must not be related by complete sign inversion, *i.e.* the sites represented by them must not be centrosymmetric with respect to  $s_0$ . These subsets are the minimum subsets of  $\mathcal{S}$  that will yield  $\mathbf{EFG} = 0$ .

The subsets  $\mathcal{S}_j(\varepsilon_i \eta_i \lambda_i)$  and  $\mathcal{S}_j^*(\varepsilon_i \lambda_i \eta_i)$  are related by interchange of two of the axes of reference (=reflexion in a  $45^\circ$  plane). Each subset  $\mathcal{S}_j(\varepsilon_i \eta_i \lambda_i)$  has associated with it a complementary subset  $\mathcal{S}_j^*(\varepsilon_i \eta_i \lambda_i)$  consisting of the other half of the full set of sign permutations of the cyclic permutations  $(\varepsilon_i \eta_i \lambda_i)$ , and likewise for  $\mathcal{S}_j^*$  and  $\mathcal{S}_j$ . When  $|\varepsilon_i| \neq |\eta_i| \neq |\lambda_i|$ , the two complementary pairs of subsets are mutually exclusive and  $\mathcal{S}_j + \mathcal{S}_j^* + \mathcal{S}_j + \mathcal{S}_j^* = \mathcal{S}$ . If  $k$  ( $1 \leq j \leq k$ ) is the total number of such distinct decompositions of

$\mathcal{S}$ , the total number of subsets satisfying the nullity of EFG is  $4k$ . When two of  $|\varepsilon_i|, |\eta_i|, |\lambda_i|$  are equal, the permutations  $(\varepsilon_i \eta_i \lambda_i)$  and  $(\varepsilon_i \lambda_i \eta_i)$  are no longer distinct and  $\mathcal{S}_j = \mathcal{S}_j^\dagger$ . Hence  $\mathcal{S} = \mathcal{S}_j + \mathcal{S}_j^*$  and the total number of subsets for which EFG = (0) is  $2k$ .

The charge values associated with the coordinate triplets of a particular subset are identical, but the values  $u_{ij}(\mathcal{S}_j), u_{ij}(\mathcal{S}_j^*), u_{ij}(\mathcal{S}_j^\dagger), u_{ij}(\mathcal{S}_j^{\dagger*})$  may all be different and so can  $u_{ij}$  for different values of  $j$ . The condition EFG = (0) is satisfied by each subset separately, regardless of the charge value of  $u_{ij}(\mathcal{S}_j)$ , and consequently it is also satisfied by any sum of the subsets, including  $\mathcal{S}$ .

*Example 1.* Let  $\varepsilon=2, \eta=1, \lambda=0$ . A possible ZEEG subset would be, for example,

$$\begin{aligned} \mathcal{S}_1 &= 2, 1, 0; 1, 0, 2; 0, 2, 1; 2, -1, 0; -1, 0, 2; \\ &\quad 0, 2, -1 \\ \mathcal{S}_1^* &= -2, -1, 0; -1, 0, -2; 0, -2, -1; -2, 1, 0; \\ &\quad 1, 0, -2; 0, -2, 1 \\ \mathcal{S}_1^\dagger &= 1, 2, 0; 2, 0, 1; 0, 1, 2; -1, 2, 0; 2, 0, -1; \\ &\quad 0, -1, 2 \\ \mathcal{S}_1^{\dagger*} &= -1, -2, 0; -2, 0, -1; 0, -1, -2; \\ &\quad 1, -2, 0; -2, 0, 1; 0, 1, -2. \end{aligned}$$

The subsets  $\mathcal{S}_j$  of coordinate triplets correspond to sets of vertices of a polyhedron  $\mathcal{P}$  of  $V$  vertices and symmetry  $m3m, m3$  or  $53m$  inscribed in a sphere of radius  $r_i$  with centre at  $s_0$ .<sup>‡</sup> The vertices in such a set are permutable by the symmetry operations of a noncentrosymmetric subgroup of the point group of  $\mathcal{P}$ . If the  $n_i$  charges have the same value,

(1) every configuration on  $\mathcal{P}$  consisting of  $V/2$  vertices and with no two vertices related by the centre of symmetry of  $\mathcal{P}$ , is a representation of  $\mathcal{S}_j$  and hence a ZEEG configuration. The representations  $\mathcal{S}_j$  and  $\mathcal{S}_j^*$  are *self-dual* (SD) relative to interchange of the vertices by inversion in  $s_0$ .<sup>§</sup>

(2) The combination of every such configuration with its own complement is a representation of  $\mathcal{S}_j + \mathcal{S}_j^*$  and hence a centrosymmetric ZEEG configuration; it is in fact  $\mathcal{P}$  with all the vertices occupied by equal charges and hence its symmetry is  $m3m, m3$  or  $53m$ .

(3) The representation of  $\mathcal{S}_j + \mathcal{S}_j^* + \mathcal{S}_j^\dagger + \mathcal{S}_j^{\dagger*} = \mathcal{S}$  is the vertices of a polyhedron  $\mathcal{T} \supset \mathcal{P}$  of symmetry  $m3m$  or  $53m$  and having  $2V$  vertices. If  $\mathcal{S}_j = \mathcal{S}_j^\dagger$ ,  $\mathcal{T} = \mathcal{P}$ .

(4) Configurations representing mixed sums, e.g.  $\mathcal{S}_j + \mathcal{S}_j^\dagger$  or  $\mathcal{S}_j^* + \mathcal{S}_j^{\dagger*} + \mathcal{S}_j^{\dagger*}$ , are noncentrosymmetric and embedded in  $\mathcal{T}$ .

<sup>‡</sup> In the Cartesian coordinate system the equivalence of vertices of polyhedra of symmetry  $53m$  and  $V \geq 20$  cannot be expressed by permutations of a single triplet  $\varepsilon, \eta, \lambda$  and two or more distinct triplets are required (cf. p. 23 and Table 1). However, the subsets  $\mathcal{S}_j$  are formed from permutations of both, or all, such triplets. The apparent composite character of such polyhedra simply reflects the unsuitability of the Cartesian system to describe symmetry operations of order 5.

<sup>§</sup> Duality in this context is not the familiar face-vertex duality of polyhedra; this latter is referred to in Table 4 by  $\mathcal{D}$ .

*Example 2.* In Example 1  $\mathcal{P}$  is an icosahedron of symmetry  $m3$  (=dual of a crystallographic pentagon-dodecahedron) and  $V=12$ ;  $\mathcal{T}$  is a truncated octahedron ( $m3m, V=24$ ).  $\mathcal{S}_1 + \mathcal{S}_1^*$  and  $\mathcal{S}_1^\dagger + \mathcal{S}_1^{\dagger*}$  correspond to two different orientations of  $\mathcal{P}$ ,  $\mathcal{S}$  corresponds to  $\mathcal{T}$ . Representations of the subsets  $\mathcal{S}_1, \mathcal{S}_1^*, \mathcal{S}_1^\dagger, \mathcal{S}_1^{\dagger*}$  are configurations of symmetry 3 on  $\mathcal{P}$  and can be brought to coincidence by rotation and reflexion.  $\mathcal{S}_1 + \mathcal{S}_1^\dagger$  and  $\mathcal{S}_1^\dagger + \mathcal{S}_1^{\dagger*}$  have symmetry  $3m$  and can be rotated into each other.  $\mathcal{S}_1 + \mathcal{S}_1^{\dagger*}$  and  $\mathcal{S}_1^* + \mathcal{S}_1^\dagger$  have symmetry 32;  $\mathcal{S}_1 + \mathcal{S}_1^* + \mathcal{S}_1^\dagger, \mathcal{S}_1 + \mathcal{S}_1^* + \mathcal{S}_1^{\dagger*}, \mathcal{S}_1 + \mathcal{S}_1^\dagger + \mathcal{S}_1^{\dagger*}$  and  $\mathcal{S}_1^* + \mathcal{S}_1^\dagger + \mathcal{S}_1^{\dagger*}$  have symmetry 3 and differ only by rotation and reflexion. The point groups 3, 32, and  $3m$  are noncentrosymmetric subgroups of  $m3m$ . Each contains two rotations of order three, consistent with the cyclic permutation of three different values of the coordinate numbers  $\varepsilon, \eta, \lambda$ .

The representations of  $\mathcal{S}_j + \mathcal{S}_j^*$  and  $\mathcal{S}$ , and the cubic representations of  $\mathcal{S}$ , correspond to all the vertices of a cubic or icosahedral polyhedron being occupied by equal charges. The cubic arrangements of this kind are well known to yield ZEEG. The less obvious ZEEG configurations are those under (1) that correspond to the noncentrosymmetric *non-cubic* representations of  $\mathcal{S}_j$ :

*Example 3.* The configuration  $abcd$  on the cube (Table 1) is ZEEG, even though only the four corners of one of the cube faces contain equal charges and the other corners are unoccupied.

When  $u_{ij}(\mathcal{S}_j) \neq u_{ij}(\mathcal{S}_j^*)$ , the arrangement of charges corresponding to  $\mathcal{S}_j + \mathcal{S}_j^*$  is no longer centrosymmetric with respect to charge inversion in  $s_0$ , but the vertex coordinates are. This configuration  $\mathcal{C}$  is then *self-dual* relative to both vertex and charge inversion. When charge inversion  $u_{ij} \leftrightarrow u_{ij}^*$  is admitted as a symmetry operation, the symmetry of  $\mathcal{C}$  is described by a dichromatic point group  $\mathbf{G}(\mathcal{C})$ . This group derives from a proper subgroup of  $m3m$  or  $53m$  by changing some of the symmetry operations of the subgroup to colour-changing (antisymmetry) operations, e.g.  $2 \rightarrow 2'$  or  $m \rightarrow m'$ . Otherwise the symmetry of  $\mathcal{C}$  is described by the maximal monochromatic subgroup  $\mathbf{M}$  of  $\mathbf{G}$  (cf. for example, Birss, 1964).  $\mathbf{M}$  is a proper noncentrosymmetric subgroup of  $m3m$  or  $53m$  and a subgroup of index 2 in  $\mathbf{G}$ , hence invariant. The group  $\mathbf{G}$  can be decomposed according to  $\mathbf{G} = \mathbf{M} + \mathbf{M} \times \bar{1}'$ . The elements of the coset  $\mathbf{M} \times \bar{1}'$  are the symmetry operations that will convert  $\mathcal{C}$  into its dual (chromatic inversion  $\bar{1}'$  and one or several of the following:  $m', 2', 3', 4', 5', 3', 5'$ ).

On a particular  $\mathcal{P}$  each  $\mathcal{S}_j(u_{ij})$  corresponds to a ZEEG configuration of equal charges  $u_{ij}$ . Hence  $\mathcal{S}_j(u_{ij}) + \mathcal{S}_j^*(u_{ij}^*)$  also yields a ZEEG configuration. In this configuration every centrosymmetric pair of charges is of the type  $(u_{ij}, u_{ij}^*)$ . The contribution made to  $\sum U_{xx}(\mathcal{P})$  by a charge  $u_{ij}$  at  $(x, y, z)$  is  $u_{ij}K_1(xx)$ ; that

Table 1. *Vertex coordinates for polyhedra of V up to 20 in standard orientations*

The coordinates have been normalized by placing all the vertices on a sphere of unit radius.

## Octahedron

$$a(0,0,1) = -d, b(1,0,0) = -e, c(0,1,0) = -f$$

Cube,  $\varepsilon = \sqrt{3}/3$ 

$$a(\varepsilon, \varepsilon, \varepsilon) = -e, b(-\varepsilon, \varepsilon, \varepsilon) = -f, c(-\varepsilon, -\varepsilon, \varepsilon) = -g, d(\varepsilon, -\varepsilon, \varepsilon) = -h$$

Cuboctahedron,  $\varepsilon = \sqrt{2}/2$ 

$$a(\varepsilon, 0, \varepsilon) = -g, b(0, \varepsilon, \varepsilon) = -h, c(-\varepsilon, 0, \varepsilon) = -i, d(0, -\varepsilon, \varepsilon) = -j, e(\varepsilon, \varepsilon, 0) = -k, f(-\varepsilon, \varepsilon, 0) = -m$$

Icosahedron,  $\varepsilon = [(5 - \sqrt{5})/10]^{1/2}$ ,  $\eta = [(5 + \sqrt{5})/10]^{1/2}$ 

$$a(\varepsilon, 0, \eta) = -g, b(0, \eta, \varepsilon) = -h, c(-\varepsilon, 0, \eta) = -i, d(0, -\eta, \varepsilon) = -j, e(\eta, -\varepsilon, 0) = -k, f(\eta, \varepsilon, 0) = -m$$

Tetrahexahedron,  $\varepsilon = \sqrt{3}/3$ 

$$a(\varepsilon, \varepsilon, \varepsilon) = -e, b(-\varepsilon, \varepsilon, \varepsilon) = -f, c(-\varepsilon, -\varepsilon, \varepsilon) = -g, d(\varepsilon, -\varepsilon, \varepsilon) = -h, i(0, 0, 1) = -m, j(1, 0, 0) = -n, k(0, 1, 0) = -p$$

Augmented cuboctahedron,  $V=18$ ,  $\varepsilon = \sqrt{2}/2$ 

$$a(\varepsilon, 0, \varepsilon) = -g, b(0, \varepsilon, \varepsilon) = -h, c(-\varepsilon, 0, \varepsilon) = -i, d(0, -\varepsilon, \varepsilon) = -j, e(\varepsilon, \varepsilon, 0) = -k, f(-\varepsilon, \varepsilon, 0) = -m, n(0, 0, 1) = -r, p(1, 0, 0) = -s, q(0, 1, 0) = -t$$

Augmented cuboctahedron,  $V=20$ ,  $\varepsilon = \sqrt{2}/2$ ,  $\eta = \sqrt{3}/3$ 

$$a(\varepsilon, 0, \varepsilon) = -g, b(0, \varepsilon, \varepsilon) = -h, c(-\varepsilon, 0, \varepsilon) = -i, d(0, -\varepsilon, \varepsilon) = -j, e(\varepsilon, \varepsilon, 0) = -k, f(-\varepsilon, \varepsilon, 0) = -m, n(\eta, \eta, \eta) = -s, p(-\eta, \eta, \eta) = -t, q(-\eta, -\eta, \eta) = -u, r(\eta, -\eta, \eta) = -v$$

Dodecahedron,  $(2/\sqrt{3})\varepsilon = 2$ ,  $(2/\sqrt{3})\eta = \sqrt{5} + 1$ ,  $(2/\sqrt{3})\lambda = \sqrt{5} - 1$ 

$$a(\varepsilon, \varepsilon, \varepsilon) = -e, b(\varepsilon, -\varepsilon, \varepsilon) = -f, c(\varepsilon, -\varepsilon, -\varepsilon) = -g, d(\varepsilon, \varepsilon, -\varepsilon) = -h, i(\eta, 0, \lambda) = -q, j(\eta, 0, -\lambda) = -r, k(\lambda, \eta, 0) = -s, m(-\lambda, \eta, 0) = -t, n(0, \lambda, -\eta) = u, p(0, -\lambda, -\eta) = -v$$

made by a charge  $u_{ij}^*$  at  $(-x, -y, -z)$  is  $u_{ij}^* K_1(xx)$ , and similarly for  $\sum U_{xy}^{(\mathcal{P})}$ ,  $\sum U_{xy}^{(\mathcal{P}^*)}$  etc.  $\sum U_{xx}^{(\mathcal{P})}$  can thus be written as  $\sum_g (u_{ij} + u_{ij}^*) K_g(xx) = 0$ , where  $g = 1, 2, \dots, V/2$ ,

and similarly for  $\sum U_{yy}^{(\mathcal{P})}$  etc. Consequently the two charges in a centrosymmetric pair can have any values provided their sum is the same as that for any other centrosymmetric charge pair in  $\mathcal{S}_j(u_{ij}) + \mathcal{S}_j^*(u_{ij}^*)$ , so that in a subset  $\text{sum } \mathcal{S}_j + \mathcal{S}_j^*$  there can be up to  $V$  different kinds of charges provided the sums of their values in centrosymmetric pairs are identical.†

In the case of  $\mathcal{S}_j + \mathcal{S}_j^* + \mathcal{S}_j^* + \mathcal{S}_j^* = \mathcal{S}$  each of the four subsets of the decomposition can have a different charge value associated with it, which gives rise to a ZEFGE arrangement of four kinds of charge (=four-colouring of the vertices of  $\mathcal{S}$ ) without any relation between  $u_{ij} + u_{ij}^*$  and  $u_{ij}^* + u_{ij}^*$  having to exist.

*Example 4.* In Example 3 the charges at the vertices  $a, b, c, d$  may be thought of as having the value  $+2$  and

† Use has been made of this fact in an analysis of the origin of the quadrupole splitting in the Mössbauer spectrum of cubic (disordered)  $\text{LiFeO}_2$  (Ayasse, 1972; Knop, Ayasse, Meads, Parker & Woodhams, 1975).

the unoccupied vertices  $e, f, g, h$  as carrying zero charge. This arrangement is equivalent to one in which all eight vertices of the cube are occupied by charges of value  $+1$ . Another possible equivalent arrangement is  $a(3) - e(-1)$ ,  $b(-2) - f(4)$ ,  $c(1) - g(1)$ ,  $d(0) - h(2)$ .

The representations of  $\mathcal{S}_j$  can thus always be regarded as SD configurations of two kinds of charges corresponding to subset sums  $\mathcal{S}_j(u_{ij}) + \mathcal{S}_j^*(u_{ij}^*)$  in which  $u_{ij}^* = 0$  and need not be treated separately. The nonzero charges are distributed among the vertices of centrosymmetric polyhedra  $\mathcal{P}_i$  of  $V_i$  vertices and symmetry  $m3m$ ,  $m3$  or  $53m$ ; not all the vertices of a polyhedron need be occupied by nonzero charges. The polyhedra  $\mathcal{P}_i$  are 'concentric', i.e. they share the geometric centre of gravity in  $s_0$ . When  $s_0$  and  $s$  are points of a crystallographic lattice, only arrangements of cubic symmetry are admissible. The point-group symmetry of the polyhedra is then governed by the site symmetry at  $s_0$ . True icosahedral ZEFGE configurations could exist in large rigid polyhedral ions or molecules containing charge maxima on the individual constituent atoms ('localized' charge), or in similar charge assemblies that are not lattice-bound in the crystallographic sense, and would then be of importance in certain types of nuclear resonance experiments.

### Construction of ZEFGE configurations

The conditions necessary for the construction of ZEFGE configurations follow immediately from the preceding:

(5) The configuration  $\mathcal{C}$  must be embedded in a centrosymmetric isogonal, i.e. platonic ( $\mathcal{P}$ ) or Archimedean ( $\mathcal{A}$ , excluding prisms and antiprisms), polyhedron  $\mathcal{P}$  of  $V$  vertices inscribed in a sphere, or in a number of such polyhedra inscribed in concentric spheres. The isohedral duals of  $\mathcal{A}$  (the Catalan polyhedra,  $\mathcal{A}^*$ ), whose vertex coordinates cannot be generated from a single triplet of coordinate numbers  $\varepsilon, \eta, \lambda$ , must be treated as combinations of isogonal polyhedra properly oriented relative to one another.

(6) For  $2n \leq V$  kinds of charges  $A_i$ ,  $i = 1, 2, \dots, 2n$ , the configuration  $\mathcal{C}$  must be self-dual, i.e. one in which pairs of vertices related by the centre of symmetry of  $\mathcal{P}$  are occupied by pairs of different charges  $(A_1, A_{2n})$ ,  $(A_2, A_{2n-1})$  etc., satisfying the condition  $A_1 + A_{2n} = A_2 + A_{2n-1} = \dots = A_n + A_{n+1}$ . All centrosymmetric charge pairs are then polar, hence the point group of  $\mathcal{C}$  is a noncentrosymmetric subgroup of the point group of  $\mathcal{P}$ .

(7)  $2n + 1$  kinds of charges  $A_i$  cannot all be different because of  $A_1 + A_{2n+1} = A_2 + A_{2n} = \dots = A_{n-1} + A_{n+3} = A_n + A_{n+2} = 2A_{n+1}$ , and neutral charge pairs  $(A_{n+1}, A_{n+1})$  will be present.  $\mathcal{C}$  is then SD relative to the non-neutral charge pairs.

A configuration is regarded as distinct if it cannot be brought to coincidence, by rotation or reflexion or both, with a configuration already listed.

Because of the considerable complexity of the sub-

ject only the case of two kinds of charge will be treated in detail. Here the charge composition of  $\mathcal{C}$  is restricted to  $A_{V/2}B_{V/2}$ .

For small values of  $V$  construction of all the SD 2-colour (SD2C) configurations on  $\mathcal{P}$  and elimination of duplicates can be accomplished relatively easily by inspection of drawings or models, but for large values of  $V$  this procedure is prohibitive unless adapted to computer search by exhaustion. When dealing with composite SD configurations a reduction of effort can be attained as follows. A vector sum  $\mathcal{L}_i$ ,  $i=1, 2, \dots, z$ , of the radius vectors (from  $s_0$ ) of all the vertices containing one kind of charge is formed for each of the  $z$  constituent SD configurations  $\mathcal{C}_i$ . Leaving  $\mathcal{L}_1$  stationary, the other  $z-1$  vector sums are permuted over all the permissible orientations on  $\mathcal{P}_1$ . This is equivalent to reducing each  $\mathcal{C}_i$  to a point on  $\mathcal{P}_1$  and forming all the distinct configurations of the  $z$  points.

In a later section we shall examine some of the properties of the SD2C configurations on polyhedra of  $V \leq 20$ . However, as a check on the completeness of our listing,<sup>‡</sup> and to form an idea of what would be involved in extending the construction of such configurations beyond  $V=20$ , we shall first seek the total number  $N_1$  of distinct SD configurations  $A_{V/2}B_{V/2}$  on polyhedra  $\mathcal{P}$ , i.e. the number of distinct decompositions  $\mathcal{S}_j + \mathcal{S}_j^*$ . For convenience of description we shall formulate the problem in terms of two colours (black and white) instead of two kinds of charges. Two related enumeration problems will be considered at the same time:

(a) What is the total number  $N_2$  of distinct *self-complementary* (SC) two-colourings of the vertices of  $\mathcal{P}$  in which the configuration is unchanged on interchanging the colours? Since all SD configurations are SC,  $N_2 \geq N_1$ .

(b) What is the total number  $N_3$  of distinct two-colourings of  $\mathcal{P}$  with an equal number of vertices of each colour?

All these questions are answered below using the enumeration theory developed by Redfield and by Pólya (cf. Harary & Palmer, 1973; Palmer & Robinson 1975). Evaluation of  $N_3$  on convex polyhedra in general has been dealt with by Knop, Barker & White (1975), who have tabulated the values of  $N_3$  also for the various subgroup symmetries of the polyhedra discussed in the present paper.

### Enumeration of SD two-colourings

Let  $p$  be a positive integer and consider the points on the sphere of radius  $\sqrt{p}$  whose coordinates are all integers. These points correspond to the integer solutions of

$$x^2 + y^2 + z^2 = p. \quad (1)$$

Each such point  $(x_i, y_i, z_i)$  has an opposite or dual vertex  $(-x_i, -y_i, -z_i)$  that is also a solution. When  $p=1$ , two of the variables must be zero while the other is  $+1$  or  $-1$ . Hence there are six solutions and the rotations or reflexions of the sphere which permute these six solutions constitute a representation of the octahedral group of order 48 and degree six. Solutions which have two coordinates equal to zero are called type I solutions. There are five other different types, each of which has associated with it a different isogonal polyhedron and a different transitive representation of the octahedral group (Table 2).

Table 2. *The six types of solution for  $p=1$*

Type	Polyhedron	$V$	Typical vertex
I	Octahedron	6	$(\varepsilon, 0, 0)$
II	Cuboctahedron	12	$(\varepsilon, \varepsilon, 0)$
III	Cube	8	$(\varepsilon, \varepsilon, \varepsilon)$
IV	Truncated octahedron	24	$(\varepsilon, \eta, 0)$
V	Truncated cube	24	$(\varepsilon, \varepsilon, \eta)$
VI	Truncated cuboctahedron	48	$(\varepsilon, \eta, \lambda)$

In Table 3 we display all the different terms in the cycle indices of these six representations of the octahedral group. The variables  $s_k$  correspond to *SD cycles* in which  $k/2$  opposite pairs of points are permuted; the term  $t_k^2$  corresponds to a pair of cycles, each permuting the  $k$  opposite points of the other. A few simple observations facilitate the compilation of the entries for the reflections. They can all be obtained from the corresponding rotation entry by the following rules: (i)  $t_{2k+1}^2$  always becomes  $s_{2(2k+1)}^2$  and *vice versa*; (ii)  $t_{2k}^2$  and  $s_{4k}^4$  are always unchanged.

Table 3. *The cycle indices of the six types of representations of the octahedral group of order 48*

Stewart's (1970) book has a section whose content includes essentially the information listed here under types I, II and III.

Number of permutations	Type					
	I	II	III	IV	V	VI
	Rotations					
1	$t_1^6$	$t_1^{12}$	$t_1^8$	$t_1^{24}$	$t_1^{24}$	$t_1^{48}$
6	$s_2^3 t_1^2$	$s_4^3 t_1^4$	$t_4^2$	$s_4^2 t_4^4$	$t_6^2$	$t_4^{12}$
3	$s_2^2 t_1^2$	$s_2^2 t_1^2$	$t_4^4$	$s_2^2 t_2^8$	$t_2^{12}$	$t_2^{24}$
8	$t_3^2$	$t_3^4$	$t_2^2 t_3^2$	$t_3^6$	$t_3^8$	$t_3^{16}$
6	$s_2^2 t_2^2$	$s_2^2 t_2^2$	$s_2^2 t_2^2$	$t_2^{12}$	$s_2^2 t_2^{10}$	$t_2^{24}$
	Reflections					
1	$s_2^3$	$s_2^6$	$s_2^4$	$s_2^{12}$	$s_2^{12}$	$s_2^{24}$
6	$s_2^2 s_4$	$s_4^2 t_4^2$	$t_4^4$	$s_4^2 t_4^4$	$t_6^2$	$t_4^{12}$
3	$s_2 t_1^4$	$t_4^4 t_2^2$	$t_4^4$	$t_4^8 t_2^8$	$t_2^{12}$	$t_2^{24}$
8	$s_6^2$	$s_6^2$	$s_2^2 s_6^2$	$s_6^4$	$s_6^4$	$s_6^8$
6	$t_2^2 t_2^2$	$s_2^2 t_2^2 t_2^2$	$t_2^2 t_2^2$	$t_2^{12}$	$t_2^4 t_2^{10}$	$t_2^{24}$

Table 3 can be used to calculate  $N_1$ ,  $N_2$ , and  $N_3$  for any combination of the six different types of solutions of equation (1). This is important when the polyhedron is isohedral ( $\mathcal{I}^*$ ) or when it is desired to consider combinations of concentric isogonal polyhedra that do not produce an isogonal polyhedron.

<sup>‡</sup> The configurations listed in Table 7 were obtained without recourse to computer search.

*Example 5.* Consider the lattice points which are solutions of the equation  $x^2 + y^2 + z^2 \leq 3$ . There is one solution of type I, one of type II, and one of type III. Using Table 3 to express the cycle index of the octahedral group represented as a permutation group on the points of solution I (*octahedron*) gives the following result:  $(\frac{1}{48}) [t_1^6 + 6s_4^1 t_1^2 + 3s_2^2 t_1^2 + 8t_3^2 + 6s_2^1 t_2^2 + s_2^2 + 6s_2^1 s_4^1 + 3s_2^1 t_1^4 + 8s_6^1 + 6t_1^2 t_2^2]$ ; the divisor 48 is the order of the group. In applying the enumeration theorem for SD2C configurations, we set  $s_k = 0$  and  $t_k = \sqrt{2}$  and obtain  $N_1 = (\frac{1}{48}) (2^3 + 8 \times 2 + 6 \times 2 \times 2) = 1$ , *i.e.* there is only one SD2C configuration on the octahedron. The three solutions can be combined to produce a type I + II + III Catalan polyhedron of  $V = 26$ , the *hexoctahedron*. Each term of the cycle index for this combination is a product of the corresponding terms for types I, II, and III:  $(\frac{1}{48}) [(t_1^6) (t_1^2) (t_1^2) + 6(s_4^1 t_1^2) (s_4^1 t_1^2) (t_1^2) + 3(s_2^2 t_1^2) (s_2^2 t_1^2) (\dots)]$ . Setting  $s_k = 0$  and  $t_k = \sqrt{2}$  gives  $N_1 = 176$ .

Table 4. *The vertices of the polyhedra of symmetry 53m*

Type	Polyhedron	V	Typical vertex
VII	Icosahedron	12	$(\varepsilon, \eta, 0)$
VIII	Dodecahedron†	20	$(\varepsilon, \varepsilon, \varepsilon), (\eta, \lambda, 0)$
IX	Icosidodecahedron	30	$(\varepsilon, \varepsilon^{-1}, \eta), (\lambda, 0, 0)$
X	Truncated icosahedron	60	
XI	Truncated icosidodecahedron	120	

† The vertex coordinates of the *crystallographic* pentagon-dodecahedron ( $m3$ ) are of the same type but the polyhedron has two kinds of edges. For illustrations of the icosahedral solids see Nowacki (1933).

Table 5. *The cycle indices of representations of the icosahedral group of order 120*

Number of permutations	VII	VIII	Type IX	X	XI
Rotations					
1	$t_1^{12}$	$t_1^{20}$	$t_1^{30}$	$t_1^{60}$	$t_1^{120}$
24	$t_1^2 t_5^2$	$t_2^5$	$t_3^6$	$t_5^2$	$t_5^4$
20	$t_3^4$	$t_1^2 t_3^6$	$t_3^{10}$	$t_3^{20}$	$t_3^{40}$
15	$s_2^2 t_2^4$	$s_2^2 t_2^8$	$t_2^{12} s_2^2 t_2^{12}$	$s_2^2 t_2^{28}$	$t_2^{60}$
Reflexions					
1	$s_2^6$	$s_2^{10}$	$s_2^{15}$	$s_2^{30}$	$s_2^{60}$
24	$s_2^2 s_5^{10}$	$s_3^{10}$	$s_3^{10}$	$s_5^{10}$	$s_5^{10}$
20	$s_2^2 s_6^4$	$s_2^2 s_6^3$	$s_6^5$	$s_6^{10}$	$s_6^{20}$
15	$t_1^4 t_2^4$	$t_1^4 t_2^8$	$s_2^2 t_1^4 t_2^{12}$	$t_1^4 t_2^{28}$	$t_2^{60}$

The same approach applies to colouring the vertices of the polyhedra of symmetry  $53m$  (Tables 4, 5). Once the terms for the rotations are found, the same rules (i) and (ii) can be used to obtain entries for the reflexions. In complete analogy with the cubic polyhedra, the cycle-index terms for a polyhedron of a composite type are obtained simply by multiplying the corresponding terms for the constituent types. For example, the terms for the tricosahedron ( $V = 32$ ) are obtained by multiplying the corresponding terms for VII and VIII in Table 5; the terms for the trapezoidal hexcontahedron ( $V = 62$ ) are found by multiplying the corresponding terms for VII, VIII and IX. This 'aufbau' principle can be extended indefinitely to con-

Table 6. *The numbers of distinct self-dual ( $N_1$ ), self-complementary ( $N_2$ ), and all ( $N_3$ ) configurations on centrosymmetric polyhedra with  $V/2$  black and  $V/2$  white vertices*

V	Polyhedron <sup>1</sup>	Type	$N_1$	$N_2$	$N_3$	$100N_1/N_3$
6	Octahedron ( $\mathcal{P}l$ )	I	1	2	2	50
8	Cube ( $\mathcal{P}l$ ; $\mathcal{D}$ [octahedron])	III	3	6	6	50
12	Cuboctahedron ( $\mathcal{A}$ )	II	3	8	30	10
12	Icosahedron ( $\mathcal{P}l$ )	VII	4	10	18	22.22
14	Tetrahexahedron <sup>2</sup> ( $\mathcal{A}^*$ ; $\mathcal{D}$ [truncated octahedron])	I, III	8	22	102	7.84
18	Augmented cuboctahedron	I, II	12	16	1154	1.04
20	Dodecahedron ( $\mathcal{P}l$ ; $\mathcal{D}$ [icosahedron])	VIII	20	140	1648	1.21
20	Augmented cuboctahedron	II, III	28	96	4078	0.69
20	Pentagonal dodecahedron ( $m3$ )		56	176	7820	0.72
24	Truncated cube <sup>3</sup> ( $\mathcal{A}$ )	V	114	1128	56846	0.20
24	Truncated octahedron ( $\mathcal{A}$ )	IV	120	1384	57168	0.21
26	Hexoctahedron <sup>4</sup> ( $\mathcal{A}^*$ ; $\mathcal{D}$ [trunc. cuboctahedron])	I, II, III	176	192	219952	0.08
30	Icosidodecahedron ( $\mathcal{A}$ )	IX	280	280	1295266	0.02
32	Tricosahedron <sup>5</sup> ( $\mathcal{A}^*$ ; $\mathcal{D}$ [trunc. dodecahedron])	VII, VIII	688	8752	5024564	0.01
48	Truncated cuboctahedron ( $\mathcal{A}$ )	VI	351120	6642048	<sup>10</sup>	<sup>10</sup>
60	Truncated icosahedron <sup>6</sup> ( $\mathcal{A}$ )	X	8956224	143165760	<sup>10</sup>	<sup>10</sup>
62	Trapezoidal hexcontahedron <sup>7</sup> ( $\mathcal{A}^*$ ; $\mathcal{D}$ [rhombicosidodecahedron])	VII, VIII, IX	17896064	17896064	<sup>10</sup>	<sup>10</sup>
120	Truncated icosidodecahedron ( $\mathcal{A}$ )	XI	<sup>8</sup>	<sup>9</sup>	<sup>10</sup>	<sup>10</sup>

<sup>1</sup> $\mathcal{P}l$ , Platonic;  $\mathcal{A}$ , Archimedean;  $\mathcal{A}^*$ , Catalan;  $\mathcal{D}$ , dual polyhedron. <sup>2</sup>Or trisoctahedron ( $\mathcal{A}^*$ ;  $\mathcal{D}$ [truncated cube]) or rhombic dodecahedron ( $\mathcal{A}^*$ ;  $\mathcal{D}$ [cuboctahedron]). <sup>3</sup>Or rhombicuboctahedron ( $\mathcal{A}$ ). <sup>4</sup>Or deltoid trapezohedron ( $\mathcal{A}^*$ ;  $\mathcal{D}$ [rhombicuboctahedron]). <sup>5</sup>Or rhombic triacontahedron ( $\mathcal{A}^*$ ;  $\mathcal{D}$ [icosidodecahedron]) or pentakisidodecahedron ( $\mathcal{A}^*$ ;  $\mathcal{D}$ [truncated icosahedron]). <sup>6</sup>Or truncated dodecahedron ( $\mathcal{A}$ ) or rhombicosidodecahedron ( $\mathcal{A}$ ). <sup>7</sup>Or hecatonicosahedron (hexicosahedron;  $\mathcal{A}^*$ ;  $\mathcal{D}$ [truncated icosidodecahedron]). <sup>8</sup>9,607,679,473,668,096. <sup>9</sup>297,838,055,356,944,384. <sup>10</sup>See text for expressions permitting these very large or very small numbers to be estimated.

Table 7. Self-dual two-colour configurations  $\mathcal{C}$  on some polyhedra, their dichromatic ( $\mathbf{G}$ ) and one-colour ( $\mathbf{M}$ ) symmetries and connectivity symbols (C.S.)

$\mathcal{C}$	$\mathbf{G}$	$\mathbf{M}$	C.S.	$\mathcal{C}$	$\mathbf{G}$	$\mathbf{M}$	C.S.
Octahedron							
1. $abc$	$\bar{3}'m$	$3m$	0300-3				
Cube							
1. $abcd$	$4/m'mm$	$4mm$	0400-4	3. $acfh$	$m'3m$	$\bar{4}3m$	0004-0
2. $abch$	$\bar{3}'m$	$3m$	1030-3				
Cuboctahedron							
1. $abcdef$	$2'/m$	$m$	12300-8	3. $abcjkm$	$2'/m$	$m$	00321-4
2. $abcejm$	$\bar{3}'$	$3$	03030-6				
Icosahedron							
1. $abcdef$	$\bar{3}'m$	$5m$	105000-10	3. $abcejm$	$\bar{3}'m$	$3m$	003030-6
2. $abcdem$	$\bar{3}'m$	$3m$	030300-9	4. $abdikm$	$\bar{3}'m$	$5m$	000501-5
Tetrahexahedron*							
1. $abcdijk$	$2'/m$	$m$	0131200-12	5. $abchjkm$	$2'/m$	$m$	0013030-8
2. $abcdjkm$	$2'/m$	$m$	0012301-8	6. $abchjmp$	$\bar{3}'m$	$3m$	0001330-6
3. $abchijk$	$2'/m$	$m$	0112210-10	7. $acfhijk$	$\bar{3}'m$	$3m$	0001330-6
4. $abchikn$	$\bar{3}'m$	$3m$	1006000-12	8. $acfhikn$	$\bar{3}'m$	$3m$	0000601-6
Augmented cuboctahedron, $V=18$							
1. $abcdefnpq$	$\bar{1}'$	$1$	1133100-17	7. $abcejmnst$	$\bar{1}'$	$1$	0023130-11
2. $abcdefnpt$	$\bar{1}'$	$1$	0231210-15	8. $abcejmrst$	$\bar{3}'$	$3$	0003330-9
3. $abcdefpqr$	$\bar{1}'$	$1$	0123201-13	9. $abcejmnpq$	$\bar{1}'$	$1$	0022320-11
4. $abcdefprt$	$\bar{1}'$	$1$	0023211-11	10. $abcejmnpt$	$\bar{1}'$	$1$	0014301-11
5. $abcejmnpq$	$\bar{3}'$	$3$	0303300-15	11. $abcejmpqr$	$\bar{1}'$	$1$	0002421-8
6. $abcejmnpt$	$\bar{1}'$	$1$	0123120-13	12. $abcejmprt$	$\bar{1}'$	$1$	0002502-8
Augmented cuboctahedron, $V=20$							
1. $abcdefnpqr$	$2'/m$	$m$	1214200-18	15. $abcejmpqrs$	$\bar{1}'$	$1$	0022321-11
2. $abcdefnpqv$	$\bar{1}'$	$1$	1124110-17	16. $abcejmprsu$	$\bar{3}'$	$3$	0030601-12
3. $abcdefnpuv$	$2'/m$	$m$	1042120-16	17. $abcejmstuv$	$\bar{3}'$	$3$	0003331-9
4. $abcdefnqrt$	$\bar{1}'$	$1$	0222301-15	18. $abcejmstuv$	$\bar{1}'$	$1$	0013231-10
5. $abcdefnqtv$	$\bar{1}'$	$1$	0124111-14	19. $abcejmnpqr$	$2'/m$	$m$	0030601-12
6. $abcdefnrtu$	$\bar{1}'$	$1$	0213211-14	20. $abcejmnpqv$	$\bar{1}'$	$1$	0012430-11
7. $abcdefntuv$	$\bar{1}'$	$1$	0123121-13	21. $abcejmnpuv$	$2'/m$	$m$	0012340-10
8. $abcdefqrst$	$2'/m$	$m$	0040402-12	22. $abcejmnqrt$	$\bar{1}'$	$1$	0013411-11
9. $abcdefqstv$	$\bar{1}'$	$1$	0023212-11	23. $abcejmnqtv$	$\bar{1}'$	$1$	0003430-10
10. $abcdefstuv$	$2'/m$	$m$	0014122-10	24. $abcejmnrtu$	$\bar{1}'$	$1$	0012340-10
11. $abcejmnpqr$	$\bar{1}'$	$1$	0212320-14	25. $abcejmntuv$	$\bar{1}'$	$1$	0002440-9
12. $abcejmnpqv$	$\bar{1}'$	$1$	0122230-13	26. $abcejmqrst$	$2'/m$	$m$	0004321-10
13. $abcejmnpqu$	$\bar{3}'$	$3$	0301600-15	27. $abcejmqstv$	$\bar{1}'$	$1$	0002440-9
14. $abcejmnqtv$	$\bar{3}'$	$3$	0031330-12	28. $abcejmstuv$	$2'/m$	$m$	0000640-8
Dodecahedron (platonic)							
1. $abcdijkmnp$	$2'/m$	$m$	4420-11	11. $abcdimnrsv$	$2'/m$	$m$	0244-4
2. $abcdijkmnu$	$\bar{3}'m$	$5m$	5050-10	12. $abcdimrsuv$	$\bar{3}'m$	$5m$	0505-5
3. $abcdijkmpu$	$2'/m$	$m$	3430-10	13. $abcdkmpqr$	$\bar{1}'$	$1$	1351-7
4. $abcdijknpt$	$\bar{3}'m$	$3m$	4600-12	14. $abcdknpqrt$	$2'/m$	$m$	0640-8
5. $abcdijmnpv$	$2'/m$	$m$	2422-8	15. $abcdnqrstv$	$\bar{3}'m$	$3m$	1090-6
6. $abcdikmnpv$	$\bar{1}'$	$1$	1531-8	16. $abchijkmpu$	$\bar{3}'$	$3$	1630-9
7. $abcdikmnrw$	$2'/m$	$m$	2242-7	17. $abchijmnsu$	$2'/m$	$m$	1252-6
8. $abcdiknprt$	$\bar{3}'m$	$3m$	0901-9	18. $abchikmnpv$	$2'/m$	$m$	0460-7
9. $abcdikrtuv$	$2'/m$	$m$	2521-9	19. $abchimnpvs$	$\bar{3}'$	$3$	0361-6
10. $abcdimnpvs$	$2'/m$	$m$	0343-5	20. $abchjmnqsv$	$\bar{3}'m$	$3m$	0064-3

\* The connectivity symbols for the rhombic dodecahedron and the trisectahedron, which are vertex-isomorphic with the tetrahexahedron, are

Rhombic dodecahedron	Trisectahedron
1. 0011410-8	1021210-11
2. 0000322-4	0020221-7
3. 0002221-6	0202120-10
4. 0004300-9	0301300-12
5. 0001231-5	0102211-8
6. 0000061-3	0000061-3
7. 0001330-6	0031030-9
8. 0000601-6	0030301-9

centric centrosymmetric polyhedral shells of charges in structural arrangements based on the cubic Bravais lattices (see below). Here of course it is appropriate to speak of assemblies of points rather than of convex polyhedra. The contribution to the EFG at  $s_0$  due to charges in each separate shell must each be zero.

The number  $N_2$  of self-complementary configurations is obtained from the cycle index of a polyhedron by the substitutions  $s_{2n} = t_{2n} = 2$ ,  $s_{2n+1} = t_{2n+1} = 0$ . The number  $N_3$  of all two-coloured configurations is found by substituting for  $s_n$  and  $t_n$  the generating function  $1 + x^n$ ; it is equal to the coefficient of the  $x^{V/2}$  term in the expanded cycle-index polynomial.

The values of  $N_1$ ,  $N_2$ , and  $N_3$  for the  $\mathcal{P}l$ ,  $\mathcal{A}$  and  $\mathcal{A}^*$  polyhedra are listed in Table 6. For the icosidodecahedron and the trapezoidal hexecontahedron the interesting result is obtained that  $N_1 = N_2$ , i.e. all the two-coloured SC configurations are SD, while for other polyhedra  $N_2$  may exceed  $N_1$  many times.

The fraction  $N_1/N_3$  decreases steadily with increasing  $V$ : for  $V=26$  only about eight in  $10^4$  distinct black-white configurations are SD. The consequences of this decrease for the properties of point-charge assemblies on crystallographic lattices are discussed below.

As  $V$  increases, the terms following  $t_1^V$  in the cycle-index polynomial for  $N_1$  become rapidly unimportant.  $N_1$  can thus be estimated from the expressions  $\ln N_1(\text{cubic}) \simeq V/2 - \ln 48$  and  $\ln N_1(\text{icosahedral}) \simeq V/2 - \ln 120$ , the accuracy of the estimate increasing asymptotically with  $V$ . Similarly, the fraction  $N_1/N_3$  can be estimated from the expressions  $\ln(N_1/N_3) \simeq V/2 - \ln {}_{V/2}C_V - \ln 48$  and  $\ln(N_1/N_3) \simeq V/2 - \ln {}_{V/2}C_V - \ln 120$ .

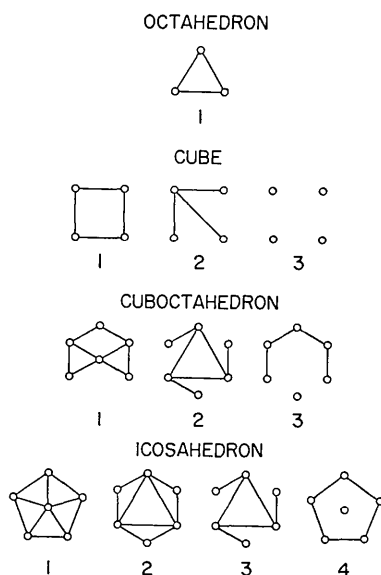


Fig. 1. Mapping of the SD2C configurations on the octahedron, cube, cuboctahedron and icosahedron (Table 7) into topologically equivalent graphs  $\mathcal{G}$ . The points of each graph correspond to vertices of one colour.

### Extension to more than two colours

The number  $N_1$  of distinct SD multicharge configurations is given by the number of distinct charge permutations over the black (or the white) vertices of the two-coloured configurations (Table 7). It is obtained from the cycle index of the two-coloured configuration of symmetry  $\mathbf{M}$  by substituting for  $s_n$  and  $t_n$  the generating function  $\alpha^n + \beta^n + \gamma^n + \dots$ , where the number of terms is the number of distinct types of charge pairs, and determining the coefficient of the appropriate term in the expanded cycle-index polynomial. The values of these coefficients are available for a large variety of  $V$  values and symmetries (Knop, Barker & White, 1975).

For three and four colours each set of vertices of the same colour will be an SD configuration if and only if the three or four-colouring corresponds to a decomposition  $\mathcal{S} = \mathcal{S}_j + \mathcal{S}_j^* + \mathcal{S}_j^{\dagger} + \mathcal{S}_j^{\ddagger}$ ; for three-colourings one of the two complementary pairs of subsets must satisfy  $\mathcal{S}_j = \mathcal{S}_j^*$ .

### Properties of SD configurations on some of the polyhedra

Before listing the distinct SD2C configurations for the first few values of  $V$  it is necessary to identify the vertices of the suitably oriented polyhedra (Table 1). The identifying letters are used to indicate vertices of one colour and the resulting grouping of letters is reduced to the lowest equivalent lexicographic permutation (Table 7); permutations obtained from the configuration by rotation or reflection or both are regarded as equivalent. Each SD2C configuration listed is also mapped into a topologically equivalent planar graph  $\mathcal{G}$  (Figs. 1–5)† corresponding to vertices of one colour.§ The graph is described by a connectivity symbol. For

† Figs. 3 and 4, and Tables 8, 10 and 11 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30597 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

§ This mapping is not unique: the graph for configurations Nos. 6 and 7 on the tetrahedron is an example of homomorphism. Configurations Nos. 16 and 19 on the augmented cuboctahedron ( $V=20$ ) have identical connectivity symbols, and likewise Nos. 21 and 24, and 25 and 27. With polyhedra other than isogonal, several different polyhedra may have the same number of vertices but the valencies of the vertices will differ. The rhombic dodecahedron, the tetrahedron, and the trisoctahedron all have  $V=14$ , but their vertex valencies are, respectively, 4 and 3, 6 and 4, and 8 and 3. Adjacency of vertices along edges, for a given  $V$ , is then not uniquely defined and the topologically equivalent graphs (and connectivity symbols) of the SD2C configurations will be different (Fig. 2). However,  $N_1, N_2, N_3, \mathbf{M}, \mathbf{G}$ , and the Coulombic energy depend only on the relative positions of the point charges at the vertices and not on the number and type of edges, the latter being in the present context merely an artifice to aid visualization; any one of the  $V$ -equivalent polyhedra can be used for verbal reference. The equivalent polyhedra are listed in the footnotes of Table 6.

example, 12300-8 for the configuration  $abcdef$  on the cuboctahedron stand for  $4^13^22^31^00^0-8$ , which indicates that  $\mathcal{G}$  contains one tetravalent node, two trivalent, three divalent, no end points and no isolated points; the nodes are connected by eight edges which correspond with edges of the black half of the configuration on the cuboctahedron. Finally the symmetry groups  $\mathbf{G}(\mathcal{G})$  and  $\mathbf{M}(\mathcal{G})$  are also listed.

With the exception of configuration no. 3 on the cube the  $\mathbf{M}$  symmetries of the SD2C configurations are of one of the following types for all the polyhedra listed in Table 7:  $1, m, 3, 3m, 4mm, 5m$ . For the composite polyhedra [tetrahexahedron=I+III, augmented cuboctahedron=I+II ( $V=18$ ) or II+III ( $V=20$ ), etc.] this lack of variety is the result of superimposing two or more constituent SD configurations properly oriented relative to one another: the  $\mathbf{M}$  symmetry of the resulting composite configuration is at most the intersection of the  $\mathbf{M}$  symmetries of the constituent configurations.

For  $n$  similarly oriented 'nested' polyhedra of the same type the set of combinations of  $n$  SD configurations of the same type will contain  $2^{n-1}$  composite configurations of the same unreduced  $\mathbf{M}$  symmetry as the  $n$  constituent configurations. Thus with two similarly oriented concentric cubes ( $V=16$ ) 19 SD2C configurations are possible, two of which have  $\mathbf{M}=\bar{4}3m$ . These are the *syn* and *anti* combinations of the configurations  $acfh-acfh$ . They are examples of the rare situation where the  $\mathbf{G}$  symmetry of an SD configuration containing more than one kind of charge is cubic, and of the even rarer situation where both  $\mathbf{G}$  and  $\mathbf{M}$  are cubic. Similar situations obtain with the truncated cube, the rhombicuboctahedron and the truncated cuboctahedron. The last-named case is particularly interesting in that a polyhedron which is a solution to equation (1) yields two SD2C configurations of cubic  $\mathbf{M}$  symmetry,  $\bar{4}3m$  and  $432$ , so that for two concentric truncated cuboctahedra in similar orientations, in addition to the combinations  $\bar{4}3m-\bar{4}3m$  (two of  $\mathbf{M}=\bar{4}3m$ ) and  $432-432$  (two of  $\mathbf{M}=432$ ), two other combinations exist,  $\bar{4}3m-432$  and  $432-\bar{4}3m$ , both of symmetry  $\mathbf{M}=23$ . Similar situations exist for other combinations of configurations of cubic  $\mathbf{M}$  symmetry. For cubic  $\mathbf{M}$  symmetry to obtain, the black vertices of  $\mathcal{G}$  must all be *inside* the octants of the axial reference system and not in the axial planes.

When  $\mathcal{G}$  is totally disconnected, *i.e.* when no two of its points are adjacent (along an edge of  $\mathcal{G}$ ), its chromatic number  $\chi(\mathcal{G})=1$ .<sup>†</sup> Stated differently,  $\mathcal{G}$  is one-chromatic: *one* colour suffices for each of the points of  $\mathcal{G}$  to have no adjacent points of the same colour. There is only one such graph among those shown here, that of configuration No. 3 on the cube. Graphs with  $\chi=2$

<sup>†</sup> For a more precise definition and criteria of chromaticity see Harary (1969). In particular, (1)  $\chi(\mathcal{G})\leq 2$  if and only if  $\mathcal{G}$  has no odd cycles; (2) every planar graph has  $\chi(\mathcal{G})\leq 5$  (the Four Colour Conjecture asserts that  $\chi(\mathcal{G})\leq 4$ ); and (3) every planar graph with fewer than four triangles has  $\chi(\mathcal{G})\leq 3$ .

are more numerous, 20 out of the total of 79 in Figs. 1-5 (Table 8).<sup>§</sup>

<sup>§</sup> Table 8 has been deposited. See footnote <sup>‡</sup> on p. 25.

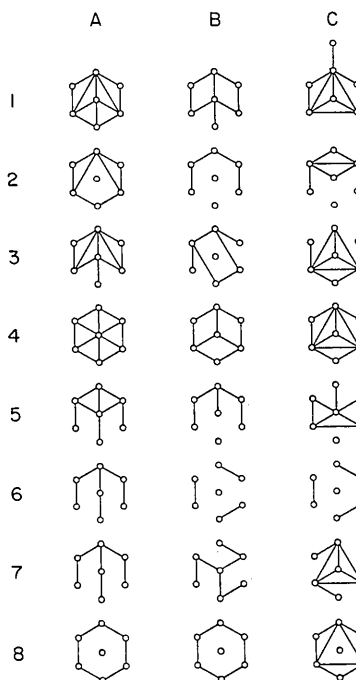


Fig. 2. Mapping of the SD2C configurations on the three cubic convex polyhedra of  $V=14$  (Table 7) into topologically equivalent graphs  $\mathcal{G}$ . A, tetrahexahedron; B, rhombic dodecahedron; C, trisoctahedron.

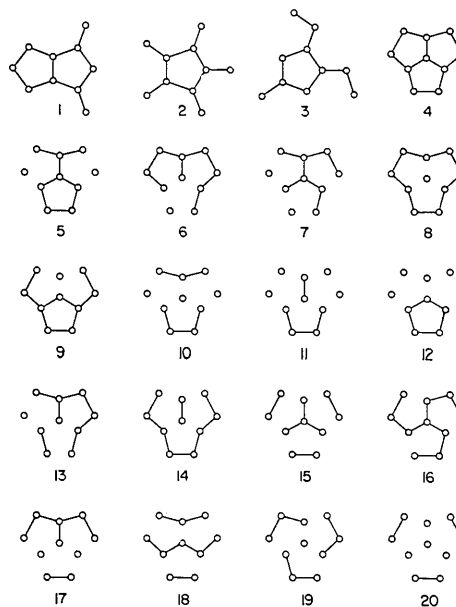


Fig. 5. Mapping of the SD2C configurations on the (platonic) dodecahedron (Table 7) into topologically equivalent graphs  $\mathcal{G}$ .



The chromatic number  $\chi(\mathcal{G})$  is of interest for the following reason. When  $\chi=1$ , the black and white vertices of the configuration alternate; the nearest neighbours of a charge  $A$  on  $\mathcal{P}$  are charges  $B$  and *vice versa*. When  $\chi=2$  and the charges are  $A, B, C, D$  (arranged in centrosymmetric pairs  $A, D$  and  $B, C$ ), the points of  $\mathcal{G}$  correspond to vertices of  $\mathcal{P}$  of more than one colour. One or several four-colour arrangements on  $\mathcal{P}$  then exist in which no charge has a charge of the same kind as its nearest neighbour. When  $\chi=3$ , the minimum number of colours required to colour  $\mathcal{G}$  in such a manner is three; this corresponds to six kinds of charges arranged in three types of centrosymmetric charge pairs. For a given composition, *i.e.* for a given number  $q$  of distinct centrosymmetric charge pairs, arrangements of this kind are possible only for SD configurations for which  $\chi(\mathcal{G}) \leq q$ . Such arrangements on *isogonal* polyhedra<sup>‡</sup> permit the charge density on the surface of  $\mathcal{P}$  to be more evenly distributed than any other arrangements, and the Coulombic energies of such configurations will be low.

As would be expected, SD2C configurations whose graphs are trees of  $V$  points are rare (Table 8).

#### Embedding of ZFEG configurations: ZFEG structures

Under certain conditions cubic ZFEG charge configurations can be embedded in compatible point-charge crystal structures. The centres of coordination polyhedra containing the ZFEG configurations and defined by lattice points, form one or several three-dimensional lattice complexes LC. For *homogeneous* (*i.e.* containing charges of one kind only) ZFEG configurations to be so embeddable it is necessary that the site symmetry at points of LC be cubic. This requirement can be satisfied in all the cubic space groups except  $P2_13$ ,  $I2_13$ ,  $Pa3$ ,  $Ia3$ ,  $P4_132$ ,  $P4_332$ ,  $I4_132$ ,  $I4_3d$  and  $Ia3d$ , possible lattice complexes being  $Pm3m(a)$ ,  $Fm3m(a)$ ,  $Im3m(a)$ ,  $Fd3m(a)$  (*cf. Internationale Tabellen zur Bestimmung von Kristallstrukturen*, 1935). The resulting arrangement of point charges is a structure of infinite extension which has ZFEG at all points of LC, *i.e.* a ZFEG structure in LC. Representations of such abstract arrangements would be, for example, idealized structures of the NaCl or CsCl types, both of which are ZFEG in both the cation and the anion LC.

Cubic *two-colour* ZFEG charge configurations can only be embedded if the site symmetry at the centres of the coordination polyhedra (*i.e.* at points of LC) is *centrosymmetric* cubic,  $m3m$  or  $m3$ . Hence only the

space-group symmetries  $S$  in Table 9 are admissible for the *undifferentiated* structure.

Table 9. *Admissible space-group symmetries S for the undifferentiated structure*

Site symmetry	S	Point-position	LC
$m3m$	$Pm3m$	1(a); 1(b)	$Pm3m(a)$
	$Fm3m$	4(a); 4(b)	$Fm3m(a)$
	$Im3m$	2(a)	$Im3m(a)$
$m3$	$Pm3n$	2(a)	$Im3m(a)$
	$Fm3c$	8(b)	$Pm3m(a)$
	$Pm3$	1(a); 1(b)	$Pm3m(a)$
	$Fm3$	4(a); 4(b)	$Fm3m(a)$
	$Im3$	2(a)	$Im3m(a)$

Embedding a SD2C configuration on a compatible polyhedron in a lattice having one of these  $S$  symmetries results in a structure of dichromatic space-group symmetry  $G_s$  containing a LC whose points have the symmetry  $\mathcal{G}_s$  containing a LC whose points have the site symmetry  $\bar{1}$ . Points of this complex are therefore grey, and the symmetry of LC is restricted to  $P2/m(a)$ ,  $C2/m(a)$ ,  $Pm3m(a)$ ,  $Cmmm(a)$ ,  $Fmmm(a)$ ,  $Immm(a)$ ,  $Fddd(c)$ ,  $P4/m3m(a)$ ,  $I4/m3m(a)$ ,  $I4/amd(c)$ ,  $R\bar{3}m(a, d)$ ,  $Pm3m(a)$ ,  $Fm3m(a)$ ,  $Im3m(a, b)$ ,  $Fd3m(a, c)$ ; additional symmetries are admissible as a result of special choice of parameter values (*cf. Internationale Tabellen*, 1935). The *geometry* of LC, as distinct from the symmetry of the charge arrangement, is of course always cubic.

The symmetry of a two-colour ZFEG structure can also be described by the monochromatic subgroup  $M_s$  of index two in  $G_s$ . This subgroup is related to a monochromatic group  $G_{s,m}$  isomorphic with  $G_s$ :  $M_s \times a_2$  is equal to  $G_{s,m}$  if  $a_2$  is a symmetry operation and to  $G_s$  if  $a_2$  is an antisymmetry (= colour) operation. The pairs  $G_{s,m}|M_s$  defining  $G_s$  have been tabulated by Koptsik (1966) (Tables 10 and  $\pi 8-\pi 12$ ).  $G_{s,m}$  is the group which results when a structure of symmetry  $M_s$  disorders relative to the charges connected by the  $\bar{1}$  anticentres of LC.

*Example 6.* The solitary SD2C configuration  $abc$  on the octahedron is of symmetry  $M=3m$ ,  $G=\bar{3}'m$ . It can be embedded in a structure containing sites of symmetry  $\bar{3}m$  (corresponding to  $G_{s,m}$ ) on a LC of one of the above admissible types. Thus we have to find a space group  $G_{s,m}$  containing sites of symmetry  $\bar{3}m$  on a lattice complex  $LC(\bar{3}m)$  and a corresponding space group  $M_s$  containing sites of symmetry  $3m$  on a  $LC(3m)$  of the same type. Of the possible space groups (*cf. Internationale Tabellen*, 1935, chaps. VII and VIII),

$G_{s,m}$	$Pn3m$	$Fd3m$	$Im3m$	$R\bar{3}m$
$LC(\bar{3}m)$	$Fm3m(a)$	$Fd3m(a)$	$Pm3m(a)$	$R\bar{3}m(a)$

only  $R\bar{3}m$  has a subgroup  $M_s$  containing a  $LC(3m)$  of the same type as that occurring in  $G_{s,m}$ . This is  $R3m$ ,  $LC=R\bar{3}m(a)$  in point-position 1(a). The configuration  $abc$  can thus only exist in a structure of symmetry  $G_{s,m}|M_s=R\bar{3}m|R3m$ , *i.e.*  $G_s=R\bar{3}'m$  ( $\pi 166$ ).

<sup>‡</sup> Where several non-isogonal polyhedra (*cf.* footnote §, p. 25) correspond to the same value of  $V$ , the adjacency of vertices, and the chromatic numbers of the topologically equivalent graphs  $\mathcal{G}$ , refer to the polyhedron with the smallest number of edges. For  $V=14$  the appropriate  $\mathcal{P}$  is the rhombic dodecahedron (Fig. 2), for  $V=26$  the deltoid trapezohedron, for  $V=32$  the rhombic triacontahedron, and for  $V=62$  the trapezoidal hexecontahedron. All of these have  $\chi=2$ .

Similarly, the only  $G_{s,m}|M_s$  combination corresponding to the SD2C configuration on the cube  $acfh$  ( $m3m|\bar{4}3m$ ) in which  $LC(m3m)$  is of the same type as  $LC(\bar{4}3m)$ , is  $Fm3m|F\bar{4}3m$ ,  $G_s = Fm3m'$  ( $\mathbb{U}_{225}^{119}$ ),  $LC = Fm3m(a)$ , point-positions 4(a) and 4(b) of  $Fm3m$ . Obviously as the site symmetry of  $\mathcal{C}$  decreases, the number of possible  $G_{s,m}|M_s$  pairs increases and the configuration can be embedded in a prescribed undifferentiated structure in more than one distinct ways. The possibility of admissible LCs being generated from special parameter values must not be left out of account.

**Example 7.** Consider embeddings of the SD2C configurations on the cube in a structure of the fluorite type, of composition  $MXX'$  and having ZEFG in  $M$ . For the undifferentiated ( $X=X'$ ) structure,  $M_s = G_s = Fm3m$ :  $M$  in 4(a),  $X+X'$  in 8(c); the LC in 4(a) is  $Fm3m(a)$ . Three such embeddings are shown in Table 10<sup>‡</sup> and Fig. 6 (top). In the embedding of  $acfh$  the sites 4(a), 4(c) and 4(d) do not contain centres of symmetry. However, their symmetry is cubic,  $\bar{4}3m$ , and so the arrangement has ZEFG not only in  $M$  but also in  $X$  and  $X'$ . Since  $X$  and  $X'$  are segregated on their own lattice complexes,  $M_s$  describes the symmetry of the arrangement adequately, without recourse to  $G_s$ ;  $G_{s,m} = Fm3m$  corresponds to a disordered  $X+X'$  population. Representations of this arrangement are the structures of the ternary alloy phases of type  $C_1b$ , FeSbTi and FeSbV (Krip'yakevich & Markiv, 1963; Gladyshevskii, Markiv, Kuz'ma & Cherkashin, 1963): Fe in 4(a), Sb in 4(c), Ti (or V) in 4(d), a triply ZEFG structure.

**Example 8.** The fluorite structure  $MXX'$  can be 'filled' by placing additional metal atoms in 4(b) to yield  $M_2XX'$  (Fig. 6, bottom). The new structure has ZEFG in  $M$ . For the undifferentiated ( $X=X'$ ) structure,  $M_s = G_s = Fm3m$ :  $M$  in 4(a) and 4(b),  $X+X'$  in 8(c); LC in 4(a) and 4(b),  $Fm3m(a)$ . This unit cell may be considered as an octuple unit cell of the CsCl =  $M(X_{1/2}X'_{1/2})$  type. The arrangement for  $acfh$  resembles that in Example 7 in that it has ZEFG in all four types of sites, 4(a), 4(b), 4(c) and 4(d), all of symmetry  $\bar{4}3m$ , and is therefore fully described by  $M_s$  (Table 10). The arrangement described by  $G_{s,m} = Fm3m$  corresponds to disorder relative to  $X$  and  $X'$ , but if  $X=X'$ , the idealized  $L2_1$  (AlMnCu<sub>2</sub>)-type structure results. For example, SnTiFe<sub>2</sub> and SnVFe<sub>2</sub> have been reported (Krip'yakevich & Markiv, 1963; Gladyshevskii *et al.*, 1963) to contain Sn in 4(a), Ti (or V) in 4(b), and Fe in 8(c), again a triply ZEFG structure. The BiF<sub>3</sub> arrangement (AlFe<sub>3</sub>, SiFe<sub>3</sub>, SnNi<sub>3</sub>) is of the same type except that the sites 4(b) and 8(c) of  $G_s$  are occupied by atoms of the same element, *i.e.* the formulae are properly written as AlFeFe<sub>2</sub> *etc.*

**Example 9.** Consider embeddings of the SD2C configurations on the cube, the octahedron and the cuboctahedron in a perovskite structure (Table 11,<sup>‡</sup> Fig. 7). The undifferentiated structure,  $ABX_3$ , is taken to consist of eight simple perovskite unit cells ( $Pm3m$ ,  $Z=1$ ):  $M_s = G_s = Fm3m$ . Origin in  $A$ :  $A$  in 4(a) and 4(b),  $B$  in 8(c),  $X$  in 24(d). Origin in  $B$ :  $A$  in 8(c),  $B$  in 4(a) and 4(b),  $X$  in 24(e)  $\{\frac{1}{4}00\}$ . The arrangement of charges in Fig. 7-3 corresponds to the idealized structure of Cs<sub>2</sub>Ag<sup>I</sup>Au<sup>III</sup>Cl<sub>6</sub> and Cs<sub>2</sub>Au<sup>I</sup>Au<sup>III</sup>Cl<sub>6</sub>:  $a_{cubic} = a_{tetra.}/\sqrt{2} = c_{tetra.}$ ,  $A = Cs$ ,  $B = Ag$  or  $Au^I$ ,  $B' = Au^{III}$ ,  $X = Cl(1) = Cl(2)$  (*cf.* also the cubic or pseudocubic compounds Cs<sub>4</sub>M(AuCl<sub>6</sub>)<sub>2</sub>,  $M = Cu, Zn, Cd, Hg$ ) (Wyckoff, 1963–1965). In the arrangements of Figs. 7-3 and 7-6 both the  $A$  and  $B$  sites are split into two point-positions. Ordering in  $AA'BB'X_6$  perovskite structures is therefore in principle always possible (KBaTiNbO<sub>4</sub>?, CaBaGeZrO<sub>4</sub>?). The arrangement of charges shown in Fig. 7-6 corresponds to the idealized perovskite superstructure of the (NH<sub>4</sub>)<sub>3</sub>FeF<sub>6</sub> type:  $A = A' = NH_4(1)$ ,  $B[4(a)] = Fe$ ,  $B[4(b)] = NH_4(2)$ ,  $X = F$ .

### ZEFG in disordered structures

Consider an idealized structure of the CsCl type and of composition  $MX$ . One of the two interpenetrating p.c. lattices is occupied by point charges  $M$  and the other, by point charges  $X$ . Each  $M$  charge is surrounded by 6  $M$  charges at a distance  $r_1$ , 12  $M$  charges at  $r_2$ , 8  $M$  charges at  $r_3$  *etc.* These charges form concentric poly-

§ Table 11 has been deposited. See footnote ‡ on p. 25.

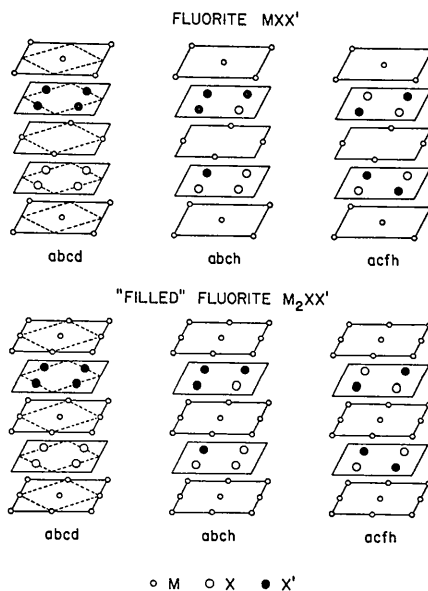


Fig. 6. Some ZEFG arrangements produced by embedding SD2C configurations on the cube in the cubic fluorite ( $MXX'$ ) and 'filled' fluorite ( $M_2XX'$ ) structures. A unit cell one quarter the size of the fluorite cell can be chosen for the  $M_2XX'$  arrangement based on  $abcd$ .

‡ Table 10 has been deposited. See footnote ‡ on p. 25.

hedra  $\mathcal{P}_i$  of symmetry  $m3m$  about  $M$  and embedded in a p.c. lattice. Each  $M$  atom is also surrounded by 8  $X$  at a distance  $r_1$ , 24  $X$  at  $r_2$ , 24  $X$  at  $r_3$  etc. These concentric polyhedra  $\mathcal{P}_i$  of symmetry  $m3m$  are embedded in the b.c.c. lattice containing the  $M$  and  $X$  atoms. This structure is thus a ZEFG structure with respect to both  $M$  and  $X$ .

However, when the composition is changed to  $MX'_{1/2}X''_{1/2}$  and the charges  $X'$  and  $X''$  replacing  $X$  are distributed at random, the probability that the vertices of a polyhedron  $\mathcal{P}_i$  of  $V_i$  vertices will be occupied by  $n$  charges  $X'$  and  $V_i - n$  charges  $X''$  is  $P(V_i, n) = \binom{V_i}{n} 2^{-V_i}$ . Consequently only a fraction  $2^{-V_i+1}$  of the  $M$  atoms will be surrounded by polyhedra  $\mathcal{P}_i$  of composition  $X'_{V_i}$  or  $X''_{V_i}$ , and  $2^{-V_i} \times V_i C_{V_i/2}$  of the  $M$

atoms by polyhedra  $\mathcal{P}_i$  of composition  $X'_{V_i/2}X''_{V_i/2}$ . All the other polyhedra  $\mathcal{P}_i$  (accounting for a fraction  $1 - 2^{-V_i+1} - 2^{-V_i} \times V_i C_{V_i/2}$  of the total) will have compositions that preclude the possibility of a ZEFG at their respective  $M$  atoms. Thus for the above structure and  $V_1=8$  ( $\mathcal{P}_1$ =cube), the fraction of  $M$  atoms at which the charge on  $\mathcal{P}_1$  produce ZEFG, is  $2^{-8}[2 + (N_1/N_3) \times 8C_4] = 37/256$  ( $\sim 14.5\%$ ); for  $V_2=24$  ( $\mathcal{P}_2$ =rhombicuboctahedron),  $2^{-24}[2 + (N_1/N_3) \times 24C_{12}] = 0.000323$  ( $\sim 0.032\%$ ); the fraction of  $M$  atoms at which the charges on  $\mathcal{P}_1$  and  $\mathcal{P}_2$  produce ZEFG is less than  $0.005\%$  of the total.

The fraction  $2^{-V} \times V C_{V/2}$  decreases with increasing  $V$  approximately as  $(2/\pi V)^{1/2}$ . However, the steady decrease of  $N_1/N_3$  with increasing  $V$  is much more

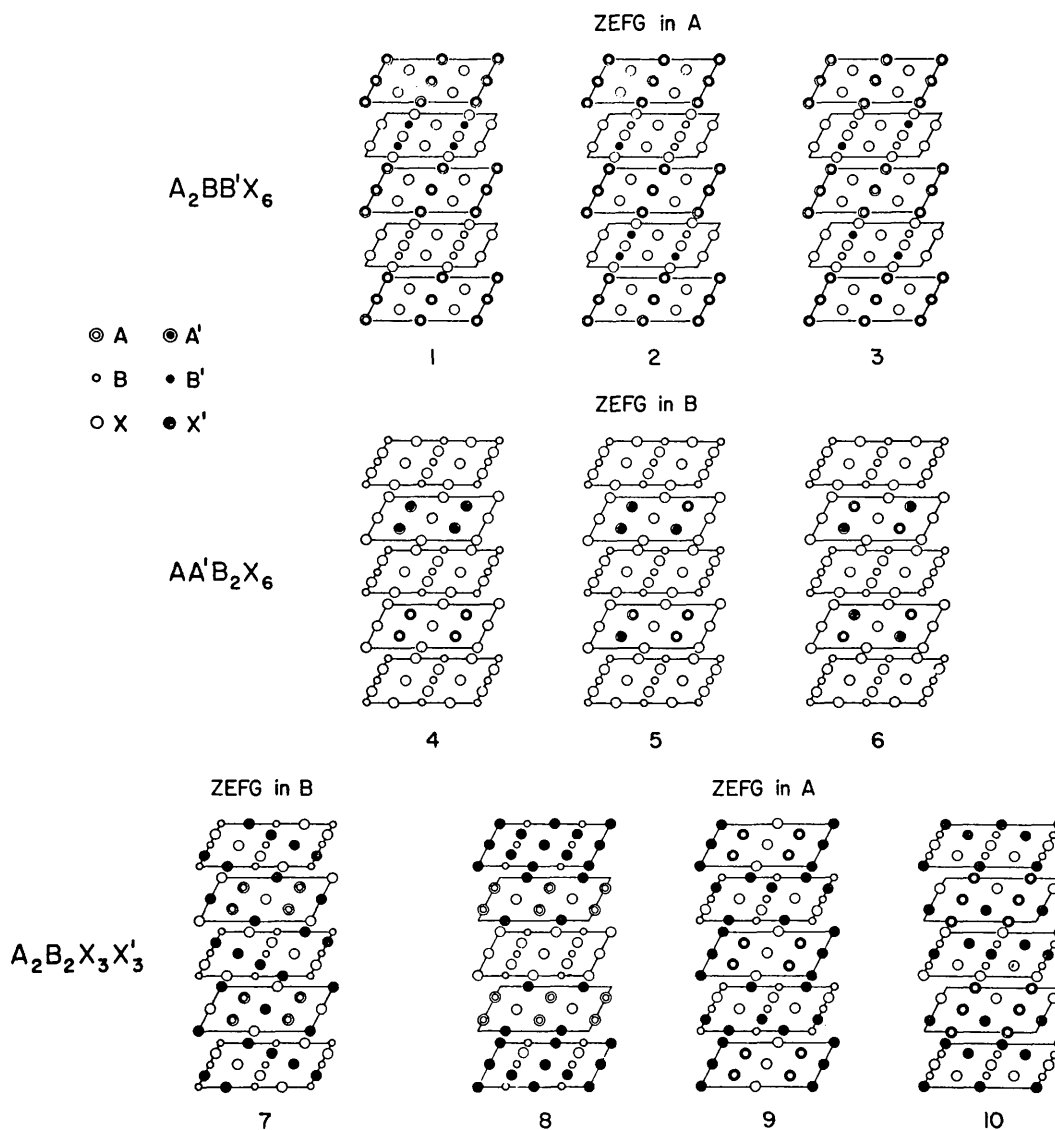


Fig. 7. Some ZEFG arrangements produced by embedding SD2C configurations on the cube (1-6), octahedron (7) and cuboctahedron (8-10) in the cubic perovskite structure. Unit cells smaller than the octuple perovskite unit cell shown can be chosen for some of the arrangements.

rapid: for  $V=26$  only about eight in  $10^4$  distinct  $X_{13}X'_{13}$  configurations are SD (Table 6), so that the term  $(N_1/N_3) \times 2^{-26} \times {}_{26}C_{13}$  is less than  $0.0001 \sim 0.01\%$ . Moreover,  $\sum V_i$  in crystallographic lattices or lattice complexes increases with the radius of the outermost polyhedral shell, i.e.  $\sum V_i$  is the number of lattice points of a cubic lattice that are inside and on the spherical shell of radius  $\sqrt{p}=f(i)$ ,  $i$  being the number of consecutive shells (Table 12).

Table 12. Number of sites surrounding a site  $s_0$ 

$i$	P.c.	Lattice type*			
		B.c.c.	NaCl(I)	NaCl(II)	CaF <sub>2</sub> (II <sub>X</sub> )
1	6	8	12	6	4
2	18	32	18	14	16
3	26	56	42	38	28
4	32	88	54	68	44
5	56	136	78	92	68

\* Based on a tabulation by Wiley & Seman (1970). NaCl-type structures:  $M(s_0)-M$ , NaCl(I);  $M(s_0)-X$ , NaCl(II). CsCl-type structures:  $M(s_0)-M$ , p.c.;  $M(s_0)-X$ , b.c.c. CaF<sub>2</sub>-type structures:  $M(s_0)-M$ , CaF<sub>2</sub>(I<sub>M</sub>) = NaCl(I);  $M(s_0)-X$ , CaF<sub>2</sub>(II<sub>M</sub>) = b.c.c.;  $X(s_0)-X$ , CaF<sub>2</sub>(I<sub>X</sub>) = p.c.;  $X(s_0)-M$ , CaF<sub>2</sub>(II<sub>X</sub>).

The fraction of homogeneous configurations  $X'_V$  and  $X''_V$  decreases exponentially with increasing  $V$ : for  $V=12$  it is less than 0.05% of all the  $X'_n X''_{12-n}$  ( $0 \leq n \leq 12$ ) configurations, and for  $V > 12$  it is negligible.

It is seen that even a completely disordered form of a ZEFG structure contains SD charge configurations that produce ZEFG at their centres, but the fraction of such configurations becomes unimportant after the second coordination shell. This must be considered in conjunction with the fact that the EFG produced at  $s_0$  by a charge  $u$  falls off with the inverse cube of the distance  $r$  of  $u$  from  $s_0$ . The values of properties which depend linearly on EFG will thus be reduced in the ratio  $(r_i/r_{i+1})^3$  when going from  $\mathcal{P}_i$  to  $\mathcal{P}_{i+1}$  (Table 13).

Table 13. Ratios  $(r_i/r_{i+1})^3$  for different lattices

Lattice	$(r_2/r_1)^3$	$(r_3/r_1)^3$	$(r_4/r_1)^3$
PC or NaCl(I)	$2^{3/2} \sim 2.83$	$3^{3/2} \sim 5.20$	$2^3 = 8$
NaCl(II)	$3^{3/2} \sim 5.20$	$5^{3/2} \sim 11.18$	$3^3 = 27$
BCC or CaF <sub>2</sub> (II <sub>X</sub> )	$(\frac{1}{3})^{3/2} \sim 7.02$	$(\frac{1}{3})^{3/2} \sim 15.94$	$3^3 = 27$

One of the consequences of the existence of ZEFG configurations in disordered cubic ionic crystals is that, on the point-charge model, there will always be a certain non-zero calculated intensity of the Mössbauer absorption at zero quadrupole splitting from SD configurations of the type  $X'_{V/2} X''_{V/2}$ , but only the smallest coordination polyhedra about  $M^*$  will contribute significantly. The situation in cubic (disordered) LiFeO<sub>2</sub> has been analyzed from this point of view by Knop, Ayasse, Meads, Parker & Woodhams (1975).

### Pseudo ZEFG structures

In a structure that does not contain a cubic lattice complex of site symmetry  $\bar{1}$  the requirement for EFG

to be zero can still be satisfied, *locally*, if the space group of the structure contains symmetry operations that will produce a SD2C configuration of point charges, provided the lattice complex is dimensionally cubic. Such an arrangement of charges  $A$  and  $B$  obtains, for example, in a structure of composition  $AB$  and specified by  $\mathbf{M}_s = P4/nmm$ ,  $c/a = \sqrt{2}$ ,  $A$  in  $2(a)$  and  $2(c)$   $\{0\frac{1}{2}\frac{3}{4}\}$ ,  $B$  in  $2(b)$  and  $2(c)$   $\{0\frac{1}{2}\frac{1}{4}\}$ ,  $\mathbf{G}_s = P_c4/nmm$  ( $\mathbb{W}_{129}^{420}$ ) (Table 14). This arrangement may be regarded as a short-range ZEFG structure in  $2(a)$  and  $2(b)$  but ZEFG in  $2(c)$ .

Table 14. Arrangement of charges in structure of composition  $AB$ 

This arrangement may be regarded as a short-range ZEFG structure in  $2(a)$  and  $2(b)$

Nearest neighbours	$r$	Configuration	EFG
Site $s_0$ in $2(a)$ or $2(b)$ , $\bar{4}2m$ , $LC = P4/nmm$ ( $a$ )			
First	$\sqrt{3}$	Cube $A_4B_4$ ( $acfh$ )	0
Second	$\sqrt{4}$	Octahedron $A_4B_2$ or $A_2B_4$	$\neq 0$
Third	$\sqrt{8}$	Cuboctahedron $A_8B_4$ or $A_4B_8$	$\neq 0$
Site $s_0$ in $2(c)$ , $4mm$ , $LC = P4/nmm$ ( $c$ )†			
First	$\sqrt{3}$	Cube $A_4B_4$ ( $abcd$ )	0
Second	$\sqrt{4}$	Octahedron $A_6$ or $B_6$	0
Third	$\sqrt{8}$	Cuboctahedron $A_{12}$ or $B_{12}$	0

† This LC is in reality  $P4/mmm(a)$ , as a result of a special choice of the parameter  $z$ .

Evidently the greater the  $r_2/r_1$  ratio, the greater the ZEFG effectivity, at  $s_0$ , of the first coordination polyhedron. In the present case the ratio is not very favourable,  $\sqrt{(\frac{4}{3})}$  giving  $(\frac{4}{3})^{3/2} \sim 1.54$ . However, as shown in the preceding section, in the b.c.c. lattice  $r_2/r_1 = \sqrt{(\frac{1}{3})}$  and  $(r_2/r_1)^3 \sim 7.02$ , so that in a pseudo ZEFG structure based on this lattice the dominance of the first coordination polyhedron in determining the EFG at  $s_0$  would be assured.

### A practical aspect: ZEFG structures as Mössbauer null matrices

In the point-charge model of crystals consisting of atoms with localized charges any ZEFG structure is a null matrix for Mössbauer-active atoms  $M^*$  in ZEFG sites. In other words, the contribution of the lattice term  $q_{latt.}$  to the quadrupole splitting of an  $^{57}\text{Fe}$  or  $^{119}\text{Sn}$  Mössbauer spectrum will be zero, so that in a perfect, completely ordered crystal the observed quadrupole splitting will be a measure of the departure of the electron-density distribution on  $M^*$  from 'spherical' symmetry. This isolation of the  $q_{valence}$  term is always possible in structures in which the sites containing  $M^*$  are surrounded by homogeneous charge configurations embedded in coordination polyhedra of cubic symmetry. It is also always possible in structures in which the coordination polyhedra contain two kinds of charges in SD configurations whose  $\mathbf{M}_s$  symmetry is cubic ( $acfh$  configurations on the cube in Examples 7-9).

It is disappointing that there does not seem to be available, even among likely candidates, a clear-cut example of a real, ordered crystal structure containing  $\text{Fe}^{3+}$  (high-spin) in a cubic environment: in such circumstances the observed quadrupole splitting would yield information concerning departure of the real structure from the point-charge model. In the room-temperature ( $\alpha$ ) form of  $(\text{NH}_4)_3\text{FeF}_6$  the Fe atoms have been stated to occupy the 4(*a*) sites of *Fm*3*m* (on cooling the  $\alpha$  form transforms reversibly into a tetragonal form);  $\text{K}_3\text{FeF}_6$  has been reported to differ from  $\alpha$ - $(\text{NH}_4)_3\text{FeF}_6$  in that the F atoms occupy one-eighth of the 192(*l*) sites of *Fm*3*m* in statistical distribution instead of occupying the 24(*e*) sites (*cf.* Bode & Voss, 1957). Yet Christoe & Drickamer (1970) observed for  $\text{K}_3\text{FeF}_6$  at 295°K and 1 atm a Mössbauer quadrupole splitting of 0.78 mm s<sup>-1</sup> and *only a slightly lower* value for  $(\text{NH}_4)_3\text{FeF}_6$  (presumably  $\alpha$ ). They explain the splitting in  $\text{K}_3\text{FeF}_6$  by a slight trigonal distortion of the  $\text{FeF}_6$  octahedra plus a contribution from covalency. Bode & Voss assume from their results that the distorted  $\text{FeF}_6$  octahedra in  $\text{K}_3\text{FeF}_6$  have identical geometries but different orientations relative to rotation about the threefold axis, the orientations being distributed at random. However, Bode & Voss's evidence could not have distinguished between this arrangement and one in which the F atoms occupy  $\frac{1}{8}$  of the 192(*l*) sites at random *without* the constraint of constant  $\text{FeF}_6$  geometry, quite apart from the uncertain accuracy of the values of the F positional parameters (reported by Bode & Voss) from which the amount of the trigonal distortion was calculated. The possibility thus cannot be ruled out that the line width of the Mössbauer absorption ought to be interpreted as arising from a *distribution* of quadrupole splittings due to  $\text{FeF}_6$  octahedra of slightly different geometries, the visually very good fit of the  $\text{K}_3\text{FeF}_6$  line by a symmetric (Lorentzian) doublet notwithstanding [Fig. 1(*a*) of Christoe & Drickamer's paper]. In any case, it would be difficult to reconcile the splitting in  $\text{K}_3\text{FeF}_6$ , which is explained by the  $\text{FeF}_6$  distortion and covalency, with the comparable splitting in  $\alpha$ - $(\text{NH}_4)_3\text{FeF}_6$  if the  $\text{FeF}_6$  octahedra in the ammonium compound are of symmetry *m*3*m*, as claimed;  $(\text{NH}_4)_3\text{FeF}_6$  can be expected to be no less covalent than  $\text{K}_3\text{FeF}_6$  and in addition is very likely hydrogen-bonded. Distortion of the  $\text{FeF}_6$  octahedra would, of course, be expected in the low-temperature form of  $(\text{NH}_4)_3\text{FeF}_6$ , but unfortunately Christoe & Drickamer are not explicit on the nature and identity of the material they studied.

When the  $M_h$  symmetry of the charge arrangement is not cubic, the structure has ZEF<sub>G</sub> at  $M^*$  only if the charges are located on lattice(s) *metrically indistinguishable* from one of cubic symmetry. This requirement, which can be satisfied by point charges in idealized arrangements, is unlikely to be fulfilled in real structures. Even if the effective sizes of two ions  $A^{a+}$  and  $B^{b+}$  ( $a \neq b$ ) are the same, charges of different magnitude will displace adjacent charges by different

amounts from their idealized positions on a cubic lattice and distortions will result. Normally the effective sizes of  $A^{a+}$  and  $B^{b+}$  are different, which manifests itself by metric distortion of the unit cell of the ordered structure. The success of using a distorted structure as a null matrix and hence as a gauge of the ionicity of  $M^*$  will then depend upon the amount by which the nearest-neighbour atoms surrounding  $M^*$  are displaced from their ideal positions, relative to the interatomic separations in the idealized structure. If the relative displacements are large, estimates of the  $q_{\text{lat}}$  contribution to the quadrupole splitting made from a point-charge model will be uncertain and so will the resolution of the observed quadrupole splitting into the valence and the lattice terms.

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#### References

- AYASSE, C. (1972). Ph.D. thesis. Dalhousie Univ., Halifax, N.S., Canada. August 1972.
- BIRSS, R. R. (1964). *Symmetry and Magnetism*, pp. 91–98. Amsterdam: North-Holland.
- BODE, H. & VOSS, E. (1957). *Z. anorg. allgem. Chem.* **290**, 1–16.
- CHRISTOE, C. W. & DRICKAMER, H. G. (1970). *Phys. Rev.* **B1**, 1813–1822.
- COLLINS, R. L. & TRAVIS, J. C. (1967). *Mössbauer Effect Methodology*, Vol. 3, Edited by I. J. GRUVERMAN, p. 123. New York: Plenum.
- GLADYSHEVSKII, E. I., MARKIV, V. YA., KUZ'MA, YU. B. & CHERKASHIN, E. E. (1963). *Titan i ego splavy (Moscow)*, **10**, 71–73.
- HARARY, F. (1969). *Graph Theory*, Chap. 12. Reading, Mass.: Addison-Wesley.
- HARARY, F. & PALMER, E. M. (1973). *Graphical Enumeration*. New York: Academic Press.
- Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935). Bd. I. *Gruppentheoretische Tafeln*. Berlin: Borntraeger.
- KNOP, O., AYASSE, C., MEADS, R. E., PARKER, W. G. & WOODHAMS, F. W. D. (1975). To be published.
- KNOP, O., BARKER, W. W. & WHITE, P. S. (1975). To be published.
- KOPTSIK, V. A. (1966). *Shubnikovskie gruppy*. Moscow: Izdatel'stvo Moskovskogo Univ.
- KRIP'YAKEVICH, P. I. & MARKIV, V. YA. (1963). *Dopov. Akad. Nauk Ukr. RSR (Kiev)*, **12**, 1606–1608.
- NOWACKI, W. (1933). *Z. Kristallogr.* **86**, 19–31.
- PALMER, E. M. & ROBINSON, R. W. (1975). *On the enumeration of self-dual configurations*. In preparation.
- STEWART, B. M. (1970). *Adventures among the Toroids*. Okemos, Mich.: published by the author.
- WILEY, J. D. & SEMAN, J. A. (1970). *Bell Syst. Tech. J.* **49**, 355–378.
- WYCKOFF, R. W. G. (1963–1965). *Crystal Structures*. 2nd ed, Vols. 1–3. New York: Interscience.