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A necessary and sufficient region to express a crystal-structure type uniquely as a point in a high-dimensional space

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Abstract. When a crystal-structure type is represented in a high-dimensional parameter space, a restricted region is shown to be necessary and sufficient to express all the possible types just as a first Brillouin zone can do this in the lattice-vibration theory. A systematic method is presented to find the region with the aid of a computer. As an example, the method is applied to the Bravais lattice types and the eight inequalities are obtained which bound the region.

1. Introduction

In order to investigate various crystal structures theoretically, it is best to project them as the points in a high-dimensional parameter space. This idea can be realised easily, but has not been used very often. The projection is usually in one-to-many correspondence so that no crystal structure is specified uniquely in the space. The main purpose of the present paper is to remove this fault. For example, let us consider a crystal of the Bravais lattice type which consists of one atom per primitive cell. The three edge vectors $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ of a primitive cell determine the structure uniquely. They are represented most conveniently by their lengths (a, b, c) and the angles between them (α, β, γ). However the choice of a primitive cell is not unique, so that there can be many other sets of parameters $(a, b, c; \alpha, \beta, \gamma)$ corresponding to the same crystal. This arbitrariness often makes it difficult to determine whether any two given crystals are equivalent or not when they are represented differently by the parameters. Obviously there must be some restrictive conditions on the choice of a primitive cell to specify the crystal uniquely. These conditions limit the parameter space within the necessary and sufficient region to represent all the possible types. The situation is very similar to the representation of lattice vibrations in reciprocal space where the first Brillouin zone is necessary and sufficient to express all the possible modes of vibration. However in the present case such conditions cannot be found so easily because we must deal with at least six-dimensional space which exceeds our usual ability of visualisation. (The parameter space of the two-dimensional Bravais lattice type is three dimensional, and so the restricted region is obtained rather easily (Hosoya 1979).) In the present paper we obtain the region using a group-theoretical treatment.

2. Representation matrices

First it is necessary to choose the most convenient set of parameters. As will be seen later, the conventional set $(a, b, c; \alpha, \beta, \gamma)$ does not suit our group-theoretical treatment,

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since it cannot be a basis of any representation matrices. (This can easily be seen from the difference between the former three parameters and the others in their dimensions.) The set of $(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c})$ itself is often useful and will be used below in some cases, but has the disadvantage of redundance. Its explicit description contains nine components, but the three degrees of freedom are assigned to the rotation of the primitive cell as a whole, which has no meaning in the present consideration. Thus we should use a set of six components. We find the following inner products best:

$$A = \pm \boldsymbol{a} \cdot \boldsymbol{a} \qquad B = \pm \boldsymbol{b} \cdot \boldsymbol{b} \qquad C = \pm \boldsymbol{c} \cdot \boldsymbol{c}$$
$$D = \pm \boldsymbol{b} \cdot \boldsymbol{c} \qquad E = \pm \boldsymbol{c} \cdot \boldsymbol{a} \qquad F = \pm \boldsymbol{a} \cdot \boldsymbol{b}. \tag{1}$$

Here the sign is chosen according to whether the coordinate system of (a, b, c) is right- or left-handed. In other words, the sign is equivalent to the coefficient $\boldsymbol{a} \cdot \boldsymbol{b} \times \boldsymbol{c} / |\boldsymbol{a} \cdot \boldsymbol{b} \times \boldsymbol{c}|$. Physically, the parameters must fulfil the following conditions in order to construct a primitive cell:

$$\beta + \gamma \geqslant \alpha \tag{2}$$
$$\gamma + \alpha \geqslant \beta \tag{3}$$
$$\alpha + \beta \geqslant \gamma. \tag{4}$$

These are derived from the following relations:

$$\cos^{-1}[E/(CA)^{1/2}] + \cos^{-1}[F/(AB)^{1/2}] \geqslant \cos^{-1}[D/(BC)^{1/2}] \tag{5}$$
$$\cos^{-1}[F/(AB)^{1/2}] + \cos^{-1}[D/(BC)^{1/2}] \geqslant \cos^{-1}[E/(CA)^{1/2}] \tag{6}$$
$$\cos^{-1}[D/(BC)^{1/2}] + \cos^{-1}[E/(CA)^{1/2}] \geqslant \cos^{-1}[F/(AB)^{1/2}]. \tag{7}$$

We must recognise that the above six-dimensional space is a representation space of a certain group and the region to be found is a fundamental region of the group. The group was denoted the group of primitive transformations in the previous paper of the author (Hosoya 1979). It is essentially a transformation group of primitive cells or some other equivalent objects (Hosoya 1979, 1980). In the present case, the operations are the affine mapping of the Bravais lattice onto itself, which creates an infinite group. The group is most simply represented by the following 3×3 matrices t operating on (a, b, c) whose components t_{ij} are all indices:

$$\begin{pmatrix} \boldsymbol{a}' \\ \boldsymbol{b}' \\ \boldsymbol{c}' \end{pmatrix} = \begin{pmatrix} t_{11} & t_{12} & t_{13} \\ t_{21} & t_{22} & t_{23} \\ t_{31} & t_{32} & t_{33} \end{pmatrix} \begin{pmatrix} \boldsymbol{a} \\ \boldsymbol{b} \\ \boldsymbol{c} \end{pmatrix}. \tag{8}$$

They are easily translated to 6×6 matrices T operating on the above six-dimensional position vectors as follows:

$$\begin{pmatrix} A' \\ B' \\ C' \\ D' \\ E' \\ F' \end{pmatrix} = \begin{pmatrix} T_{11} & T_{12} & T_{13} & T_{14} & T_{15} & T_{16} \\ T_{21} & T_{22} & T_{23} & T_{24} & T_{25} & T_{26} \\ T_{31} & T_{32} & T_{33} & T_{34} & T_{35} & T_{36} \\ T_{41} & T_{42} & T_{43} & T_{44} & T_{45} & T_{46} \\ T_{51} & T_{52} & T_{53} & T_{54} & T_{55} & T_{56} \\ T_{61} & T_{62} & T_{63} & T_{64} & T_{65} & T_{66} \end{pmatrix} \begin{pmatrix} A \\ B \\ C \\ D \\ E \\ F \end{pmatrix}$$
$$= \begin{pmatrix} t_{11}^2 & t_{12}^2 & t_{13}^2 & 2t_{12}t_{13} & 2t_{13}t_{11} & 2t_{11}t_{12} \\ t_{21}^2 & t_{22}^2 & t_{23}^2 & 2t_{22}t_{23} & 2t_{23}t_{21} & 2t_{21}t_{22} \\ t_{31}^2 & t_{32}^2 & t_{33}^2 & 2t_{32}t_{33} & 2t_{33}t_{31} & 2t_{31}t_{32} \\ t_{21}t_{31} & t_{22}t_{32} & t_{23}t_{33} & t_{22}t_{33}+t_{23}t_{32} & t_{23}t_{31}+t_{21}t_{33} & t_{21}t_{32}+t_{22}t_{31} \\ t_{31}t_{11} & t_{32}t_{12} & t_{33}t_{13} & t_{32}t_{13}+t_{33}t_{12} & t_{33}t_{11}+t_{31}t_{13} & t_{31}t_{12}+t_{32}t_{11} \\ t_{11}t_{21} & t_{12}t_{22} & t_{13}t_{23} & t_{12}t_{23}+t_{13}t_{22} & t_{13}t_{21}+t_{11}t_{23} & t_{11}t_{22}+t_{12}t_{21} \end{pmatrix} \begin{pmatrix} A \\ B \\ C \\ D \\ E \\ F \end{pmatrix}. \tag{9}$$

The matrices t and T are in two-to-one correspondence, for t and $-t$ give the same T. However this disadvantage is easily removed as will be shown below.

Some element T keeps a point in the six-dimensional space. Thus we can assign such an element to a particular geometrical object (point, line, plane, etc) which is invariant under its operation, just as an inversion centre, a rotational axis or a mirror plane (Hahn 1983). We shall hereafter call such a geometrical alternative an element. On the special positions several elements are located simultaneously. We can find the generating elements of the whole group among the elements on a few special positions.

Such a special position can be found with the knowledge of the hierarchy of the Bravais lattices (Hosoya 1979). Among the 14 Bravais lattice types, simple cubic (SC), face-centred cubic (FCC), body-centred cubic (BCC) and hexagonal (HEX) are the most symmetrical; the others can be derived as subgroups of these four types. Their primitive-cell vectors can be chosen as in figure 1. (The choice is fit for the present purpose.) Their cartesian coordinates are as follows, where the parameters a_1, a_2, a_3, a_4 and c are arbitrary positive values:

simple cubic $\quad \boldsymbol{a} = (a_1, 0, 0)$

$\boldsymbol{b} = (0, a_1, 0)$

$\boldsymbol{c} = (0, 0, a_1)$

face-centred cubic $\quad \boldsymbol{a} = (0, a_2, a_2)$

$\boldsymbol{b} = (a_2, 0, a_2)$

$\boldsymbol{c} = (a_2, a_2, 0)$

body-centred cubic $\quad \boldsymbol{a} = (a_3, a_3, a_3)$

$\boldsymbol{b} = (-a_3, a_3, a_3)$

$\boldsymbol{c} = (0, 0, 2a_3)$

hexagonal $\quad \boldsymbol{a} = (0, 0, c)$

$\boldsymbol{b} = (2a_4, 0, 0)$

$\boldsymbol{c} = (a_4, \sqrt{3}a_4, 0).$

They are represented in our new space as follows:

simble cubic $\quad (x_1, x_1, x_1, 0, 0, 0).$ (10)

face-centred cubic $\quad (2x_2, 2x_2, 2x_2, x_2, x_2, x_2).$ (11)

body-centred cubic $\quad (3x_3, 3x_3, 4x_3, 2x_3, 2x_3, x_3).$ (12)

hexagonal $\quad (x_4, 2y, 2y, y, 0, 0).$ (13)

Here x_1, x_2, x_3, x_4 and y are arbitrary positive values which are related to a_1, a_2, a_3, a_4 and c. These six-component vectors can be regarded as defining the position

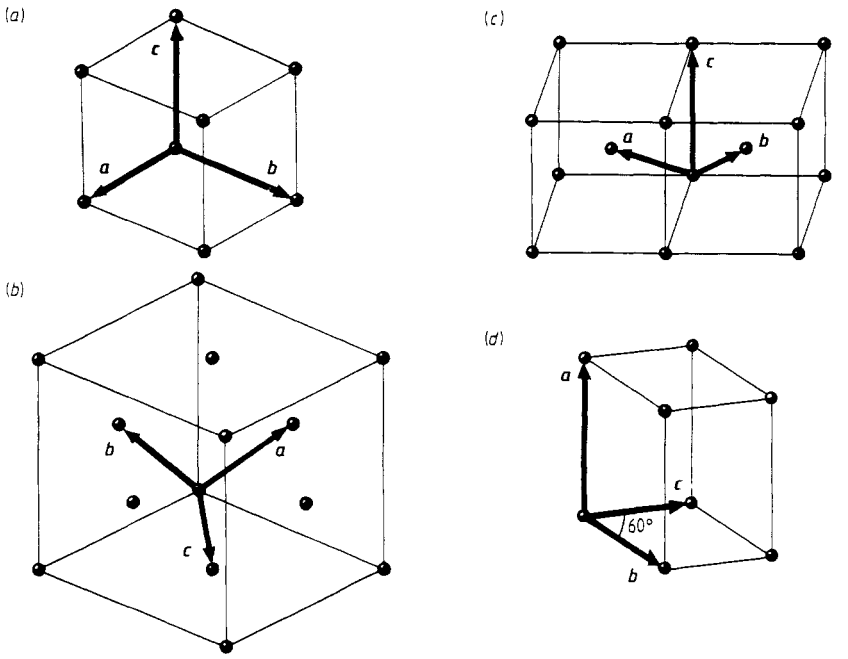


Figure 1. The edge vectors of the primitive cells for the most symmetrical crystals of the Bravais lattice types, (*a*) simple cubic, (*b*) face-centred cubic, (*c*) body-centred cubic and (*d*) hexagonal.

of a point in six-dimensional space. The positions of this kind corresponding to SC, FCC, BCC and HEX are called the highest symmetrical positions (HSP) below.

The group of elements which leave the HSP unchanged are easily obtained by the corresponding point-group operations. The group for the simple cubic crystal consists of 24 elements which are generated from the following two elements:

$$C_3 = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix} \tag{14}$$

$$C_4 = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix}. \tag{15}$$

It should be noticed that our distinctive definition between right- and left-handed systems eliminates every improper rotation which brings a system to an enantiomor-

phous one. (This restriction also determines the sign of t uniquely for the given T, because the determinant of t must be $+1$ for the proper rotations.) Thus the point group of a simple cubic lattice is regarded as 432 instead of $m3m$. The names of the operations are adopted so that they suggest the corresponding point-group operations.

The groups corresponding to the other three HSP are given more conveniently in other spaces than those of (A, B, C, D, E, F). Thus the coordinate is transformed by the following matrices, each corresponding to FCC, BCC and HEX:

$$TR_{\mathrm{F}} = \begin{pmatrix} 1 & 1 & 1 & 2 & -2 & -2 \\ 1 & 1 & 1 & -2 & 2 & -2 \\ 1 & 1 & 1 & -2 & -2 & 2 \\ 1 & -1 & -1 & 2 & 0 & 0 \\ -1 & 1 & -1 & 0 & 2 & 0 \\ -1 & -1 & 1 & 0 & 0 & 2 \end{pmatrix} \tag{16}$$

$$TR_{\mathrm{B}} = \begin{pmatrix} 1 & 1 & 0 & 0 & 0 & -2 \\ 1 & 1 & 1 & -2 & -2 & 2 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 1 & 1 & 0 \\ 0 & 0 & 0 & -1 & 1 & 0 \\ 1 & -1 & 0 & 1 & -1 & 0 \end{pmatrix} \tag{17}$$

$$TR_{\mathrm{H}} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{3} & \frac{4}{3} & -\frac{4}{3} & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2/\sqrt{3} & -1/\sqrt{3} \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & -1/\sqrt{3} & 0 & 2/\sqrt{3} & 0 & 0 \end{pmatrix}. \tag{18}$$

The transformations mean the use of new basis vectors which become perpendicular to each other when the corresponding type of the highest symmetry is realised. For each of SC, FCC and BCC, in its own space, the representation matrices are the same. For the hexagonal type the group consists of 12 elements made up from the following two generators:

$$C_6 = \begin{pmatrix} \frac{1}{4} & \frac{3}{4} & 0 & 0 & 0 & -\sqrt{3}/4 \\ \frac{3}{4} & \frac{1}{4} & 0 & 0 & 0 & \sqrt{3}/4 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & \sqrt{3}/2 & 0 \\ 0 & 0 & 0 & -\sqrt{3}/2 & \frac{1}{2} & 0 \\ \sqrt{3}/4 & -\sqrt{3}/4 & 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix} \tag{19}$$

$$C_2' = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & -1 & 0 \end{pmatrix}. \tag{20}$$

Due to elimination of the improper rotations, the point group is 622 instead of $6/mmm$.

3. Construction of a fundamental region

The method used below is essentially the same as that of determining the Wigner-Seitz cell in the reciprocal space. The boundary of a region is constructed by the set of planes which bisect perpendicularly the lines connecting the equivalent points. A pivotal point is chosen arbitrarily in the space, and the equivalent points are obtained by operating the elements of the group of primitive transformations on the pivotal point. We need to operate only the elements which transfer the point into the adjacent fundamental regions. Such elements are those of the HSP on the boundaries (figure 2). This consideration drastically reduces the number of operations to be tried. However it is somewhat difficult to find which HSP are located on the boundary. We do not even know how many HSP there are on the boundaries. Only a trial and error method is applicable. Thus starting from an arbitrarily chosen set of HSP, we determine the smallest volume enclosed by the boundaries, in the method stated in detail below. Since the result is given by a set of inequalities, we can ascertain if other HSP are located within it, by substituting their coordinates into the inequalities. If any other HSP is found in the region, we include it into the initial set and try again to get the smaller volume. In the present case, after several trials, the set (10)-(13) was found to be on the boundary of a certain fundamental region. Other nearby HSP are confirmed to be outside the region. Such a procedure is almost impossible without the aid of a computer, since we must start from at least four HSP corresponding to SC, FCC, BCC and HEX, each of which contains 24, 24, 24 and 12 elements respectively, so that we must operate at least 84 matrices at every trial. Thus a simple BASIC program was written and used on a personal computer.

We can obtain the perpendicular bisecting planes rather easily. Once a pivotal point is chosen, then its equivalent points are obtained by operating the transformation matrices of the HSP on the coordinate vector of the pivot. If a pivotal point $(A_0, B_0, C_0, D_0, E_0, F_0)$ is transformed into a point $(A_1, B_1, C_1, D_1, E_1, F_1)$, the equation of the perpendicular bisecting plane is as follows:

$$(A_0-A_1)A+(B_0-B_1)B+(C_0-C_1)C+(D_0-D_1)D+(E_0-E_1)E+(F_0-F_1)F=0. \tag{21}$$

For the HSP other than simple cubic, the equation should be obtained in the transferred space where the operation is orthogonal, and then translated into the original space.

The boundaries are not unique but changeable according to the position of the pivotal point (figure 2). We should find the most convenient boundaries by setting the pivotal point at an appropriate position. When the pivotal point is at a general position, a lot of boundary planes appear and their equations are generally formed by non-integer coefficients. However if the pivotal point is at an HSP, the perpendicular bisect plane to be constructed by an element of the HSP cannot be defined. Hence we first locate the pivotal point at a general position and then make it draw to some HSP. At the end of this process, many boundaries coincide with each other and the final equations have rather simple coefficients (figure 2). In the present case, the pivotal point is taken at $(1, 1, 1, 0.5, 0.5-d, 0.5-2d)$ and the boundaries are determined at the limit of $d=0$. The natural boundaries in (5)-(7) should be also taken into account.

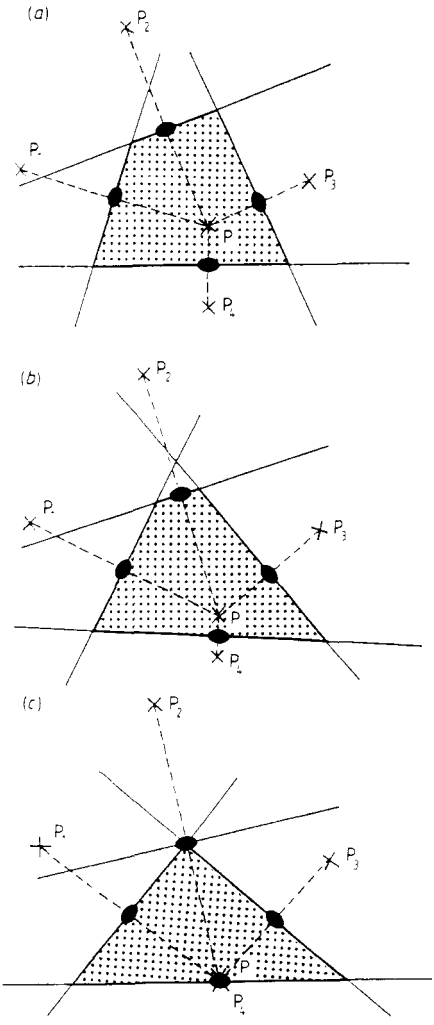


Figure 2. Schematic drawing for the construction of a fundamental region. The perpendicular bisect planes between an arbitrarily chosen pivotal point P and all its equivalent points (P_1, P_2, P_3, P_4) bound the region. Though the highest-symmetrical positions (HSP) (represented by black ovals) are definite, the shape of the region depends on the pivotal point. The simplest shape (*c*) where P coincides with P_4 is most desirable, but is obtained only as a limiting case in the series (*a*)-(*b*)-(*c*).

Even after the above reduction of the boundaries, there still remain a lot of them, most of which are outside the region. Mathematically we have a set of inequalities which contains many unnecessary ones, for they can be deduced from the others. In order to obtain the true boundaries, we use a Monte Carlo method. A test point is located at a position which satisfies all the inequalities, and it is driven step by step along a certain line until it encounters a boundary (violates its inequality). Then it is reflected into a randomly chosen direction and moved again until it meets with another boundary and so on (figure 3). If we continue this procedure for a sufficiently long time, we can obtain a set of true boundaries which have been encountered at least

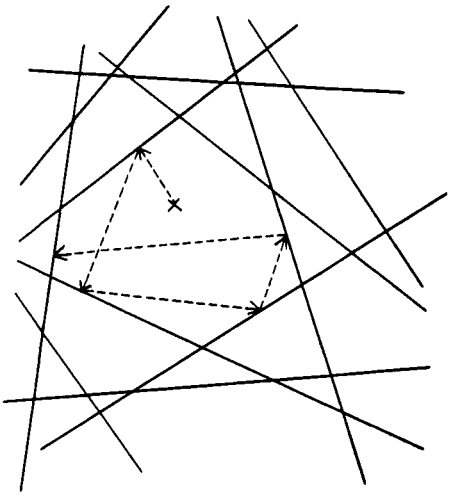


Figure 3. Schematic view of the Monte Carlo method used to determine the most inner boundaries of the region.

once. To avoid overlooking the other true boundaries, we inquire whether all of the other inequalities are deduced from the present set.

Finally the following eight inequalities are obtained which bound a fundamental region of the Bravais lattice type:

$$D - E \geqslant 0 \tag{22}$$

$$E - F \geqslant 0 \tag{23}$$

$$B - C + 5E - 5F \geqslant 0 \tag{24}$$

$$C - 2D - 2E + 4F \geqslant 0 \tag{25}$$

$$A - B + 2D - 2E \geqslant 0 \tag{26}$$

$$C - 2E \geqslant 0 \tag{27}$$

$$-E + 2F \geqslant 0 \tag{28}$$

$$\cos^{-1}[E/(CA)^{1/2}] + \cos^{-1}[F/(AB)^{1/2}] > \cos^{-1}[D/(BC)^{1/2}]. \tag{29}$$

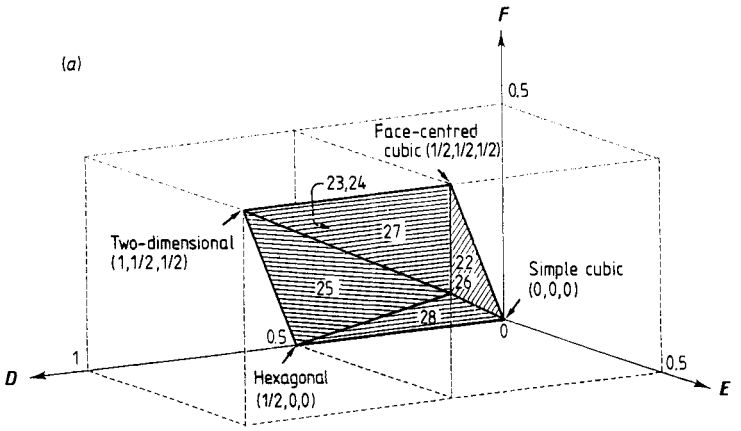
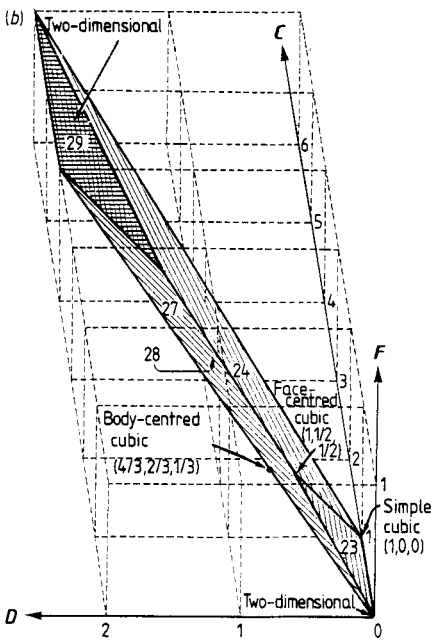


Figure 4.



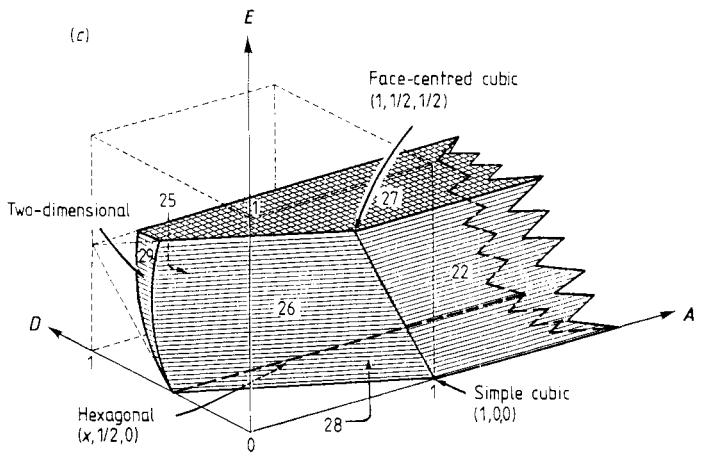


Figure 4. The three-dimensional cross sections of the fundamental region obtained here. All the hatched lines are parallel to the horizontal plane in each figure. The figures (*a*), (*b*) and (*c*) correspond to the condition ($A = B = C = 1$), ($A = B = 1$ and $D = E$) and ($B = C = 1$ and $E = F$) respectively. The numbers of the boundary equations (22)-(29) are written on the corresponding planes. Special positions are also indicated, most of which are the highest-symmetrical positions (HSP) or correspond to the two-dimensional (flattened) structures. As is seen in 4(*c*), the region extends infinitely along the A axis, which is caused by the distinction between a and b or c in the hexagonal type (figure 1) where a can be infinitely elongated keeping b and c finite.

The three-dimensional cross sections of this region may help the readers' comprehension and its future applications (figure 4(*a*)-(*c*)).

4. Discussion

The expansion of the present method to more complex crystals than the Bravais lattice type can be done easily by adding atoms into the primitive cell. The inner products between the edge vectors ***a***, ***b***, ***c*** and the newly added atomic coordinates are adopted as the increased components of the parameter space. The elements of the primitive transformations are similarly obtained from those of the HSP. The remaining procedures are also analogous.

Such fundamental regions may have a variety of uses in condensed matter physics, especially in the theoretical investigation of phase transitions. Many structural phase transitions are regarded to occur by freezing of a soft mode of lattice vibration. Such a mode is usually assigned to a particular position in the first Brillouin zone of the higher-symmetry phase. However this treatment is impossible in the transitions which accompany the complete change of its crystal structure. For example the well known transition from face-centred cubic iron to body-centred cubic cannot be treated in this way. In such a case the present fundamental region provides a useful alternative tool, since it contains both structures simultaneously. Moreover our parameter space can be expanded to any dimension, and therefore any transitions may be considered in the single parameter space.

It is an important object in solid state physics to determine the most stable crystal-structure type for any given component atoms. Of course much work has been done on this subject, which has given some rather useful results. However, almost all of the work picks up only several types as possibilities and compares them to each other. Thus we have no guarantee against the existence of another type which is more stable. For example, only NaCl, CsCl and zincblende types are usually considered to obtain the most stability in AB compounds. Such a treatment is obviously insufficient, since it does not exhaust even the types of HSP, because there are five more HSP in the fundamental region in this case, two of which are tetragonal, while the others are hexagonal (Hosoya 1980). Ideally the possible energy of any crystal should be calculated as a continual function in its parameter space stated above, and the minimal point should be found in it as determining the realised crystal-structure type. Such consideration is inevitable in order to obtain a stable structure under pressure, especially under uniaxial pressure. However, as far as the author knows, even the Madelung constant for ionic AB-type crystals has not been calculated in the whole area of its fundamental region. Thus intensive effort should be made in this direction, where the exact knowledge of each fundamental region must be given first.

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