BONDS BROKEN AT ATOMICALLY FLAT CRYSTAL SURFACES—II

CRYSTALS CONTAINING MANY ATOMS IN A PRIMITIVE UNIT CELL

J. K. MACKENZIE and J. F. NICHOLAS

Division of Tribophysics, C.S.I.R.O., University of Melbourne, Australia

Abstract—For an arbitrary crystal with an atomically flat surface, a calculation is made of the number of atoms in a unit cell of surface which have exactly 1, 2, 3, ... broken bonds. Detailed calculations are given for the sodium chloride, caesium chloride, diamond, and close-packed hexagonal structures.

1. INTRODUCTION

A BOND associated with a given atom in a crystal can be defined by a vector u drawn from the atom and such a bond will be called the u-bond associated with the given atom. Given a set of bonds $u_i (i = 1, ..., m)$ and a plane with normal h, the problem to be considered is that of calculating the number (per unit area) of these bonds which are intersected (broken) by the plane and also the number of atoms per unit area which have exactly j broken bonds ($0 < j \leqslant m$). If all the atoms on one side of the plane are removed from the crystal, the surface so formed can be described as atomically flat and the calculations described will give the surface densities of broken bonds and of atoms with specified bonds broken.

In Part I[1] a method for making these calculations was described for crystals containing one atom in a primitive unit cell and the calculations were made in detail for nearest and second nearest neighbour bonds in body-centred and face-centred cubic crystals. In this paper the theory is extended to an arbitrary crystal structure containing many atoms in a unit cell and specific calculations are made for sodium chloride, diamond, caesium chloride, and close-packed hexagonal structures, attention being restricted to what might be called the relevant nearest neighbour bonds.

2. GENERAL THEORY

Consider an infinite crystal structure with atoms at the points

$$x_l = l_1 a_1 + l_2 a_2 + l_3 a_3 + d_r, \quad (r = 0, 1, ..., s-1) \tag{1}$$

where l_1, l_2, l_3 are integers and each d_r has, in general, fractional components when referred to the base vectors a_1, a_2, a_3, i.e. a structure containing s atoms per unit cell. This unit cell is not necessarily primitive. Then the crystal with an atomically flat surface with outward normal h consists of all those atoms at points x_l for which

$$h \cdot x_l \leqslant \delta, \quad 0 \leqslant \delta < 1, \tag{2}$$

where δ is a constant restricted to the stated range by a suitable choice of origin.

Now consider the atoms on the rth sub-lattice, i.e. all atoms with a given d_r, and associate with each atom a set of vectors u_i ($i = 1, ..., m$). These vectors will be referred to as bonds though, for the purposes of this section, they need not end on atoms. The same set is associated with each atom on a given sub-lattice but the set may vary

from one sub-lattice to another; thus both the u_i and m may depend on r. It is easily seen that the u_i-bond associated with the atom at x_l satisfying relation (2) is broken (intersects the surface $h \cdot x = \delta$) only if the projection of u_i onto h is greater than the perpendicular distance of x_l from the surface. Thus, atoms which have broken u_i-bonds satisfy the inequalities

$$0 \leqslant \delta - h \cdot x_l < h \cdot u_i. \quad (3)$$

Further progress depends essentially on restricting the surface to be parallel to a lattice plane so that the components of h when referred to the base vectors reciprocal to a_1, a_2, a_3 can be taken to be integers without a common factor, i.e. Miller indices of the plane. Now on the rth sub-lattice there is one atom per unit cell defined by a_1, a_2, a_3, and it is well known that the atoms on such a sub-lattice may all be thought of as lying on the set of planes

$$h \cdot x = h \cdot d_r - P, \quad (-\infty < P < \infty), \quad (4)$$

where P is the integer $-h \cdot [l_1 l_2 l_3]$. Further, to every integer P there is exactly one atom within a unit cell of surface of area $V|h|$, where $V = a_1 \cdot a_2 \times a_3$ is the volume of the unit cell, and $|h|$ the magnitude of h. Hence, it follows from equation (3) that the number $N_r(h, u_i)$ of atoms in a unit cell of surface which have broken u_i-bonds is given by the number of integer values of P for which

$$h \cdot d_r - \delta \leqslant P < h \cdot u_i + h \cdot d_r - \delta. \quad (5)$$

On defining the symbol $[y]^+$ to mean the integer greater than or equal to y (thus modifying a well known number theoretic symbol) a little consideration shows that

$$N_r(h, u_i) = \begin{cases} [h \cdot u_i + h \cdot d_r - \delta]^+ - [h \cdot d_r - \delta]^+, \\ \qquad\qquad \text{if } h \cdot u_i \geqslant 0, \\ 0, \qquad\quad \text{if } h \cdot u_i \leqslant 0. \end{cases} \quad (6)$$

If $h \cdot u_i$ is an integer, the first line of equation (6) reduces to $h \cdot u_i$. Further, in the general case, the relations (3) show that if $h \cdot u_j \geqslant h \cdot u_i$ any atom with a broken u_i-bond must also have a broken u_j-bond. Thus, the essential results of Part I have been reproduced.

Therefore, on selecting from the set u_i ($i = 1$, ..., m) the largest ordered subset v_j ($j = 1$, ..., p) such that

$$h \cdot v_1 \geqslant h \cdot v_2 \geqslant ... \geqslant h \cdot v_p \geqslant 0,$$

or, since $h \cdot u_j \geqslant h \cdot u_i$ implies

$$N_r(h, u_j) \geqslant N_r(h, u_i),$$

such that

$$N_r(h, v_1) \geqslant N_r(h, v_2) \geqslant ... \geqslant N_r(h, v_p) \geqslant 0, \quad (7)$$

it follows that any atom with a broken v_j-bond has at least all the bonds v_1, v_2, ..., v_j broken. Hence, if $B_j = B(v_1 v_2 ... v_j)$ denotes an atom with only the bonds v_1, ..., v_j broken, then the number $N_r(B_j)$ of such atoms in a unit cell of surface is given by

$$N_r(B_j) = \begin{cases} N_r(h, v_j) - N_r(h, v_{j+1}), \\ \qquad\qquad \text{for } 1 \leqslant j \leqslant p-1, \\ N_r(h, v_p), \quad \text{for } j = p. \end{cases} \quad (8)$$

The above results apply to a specific lattice plane with normal h. If h is now allowed to vary from one lattice plane to another, account must be taken of the variation of the sub-set v_j and/or p with h. This sub-set can vary in two ways: (a) bond vectors will enter or leave the sub-set when h crosses one of the zones $h \cdot u_i = 0$ and (b) the ordering of the bond vectors within the sub-set will change when h crosses any of the zones $h \cdot u_i = h \cdot u_j > 0$. Thus, if h is plotted on a stereographic projection the traces of these zones divide the projection into regions, and both the sub-set v_j and their order remains fixed within a region but varies from one region to another. Within any region, the appropriate sequence of vectors $v_1 v_2 ... v_p$ will be referred to as the bond order.

The above calculations must be carried through for each of the r sub-lattices each with its own associated set u_i.

In detailed consideration of the results, two approaches may be used: (a) consider particular values of δ, or (b) allow δ to vary from 0 to 1 and consider the average values of $N_r(h, u_i)$ and $N_r(B_j)$.

The first approach is useful when considering such problems as the possibility of charged surfaces

in ionic crystals. In this case specific values of δ must be chosen and formulae (6) and (8) applied. However, it should be remembered that $N_r(h, u_i)$ and $N_r(B_j)$ are, in general, discontinuous as h varies even when these quantities are normalized to refer to unit area of surface by division by $V|h|$.

The second approach is, in general, likely to be closer to reality in that if a crystal is cut, it is impossible to cut to a specific value of δ and the measurable quantities are the averaged values of N_r with δ uniformly distributed over the range 0–1. It is readily shown that

$$\langle N_r(h, u_i)\rangle_{\mathrm{AV}:\delta} = \begin{cases} h \cdot u_i, & \text{if } h \cdot u_i \geqslant 0, \\ 0, & \text{if } h \cdot u_i \leqslant 0, \end{cases} \quad (9)$$

and the corresponding value of $\langle N_r(B_j)\rangle_{\mathrm{AV}:\delta}$ is easily found on averaging equation (8). When normalized to refer to unit area by division by $V|h|$, these averaged values of $N_r/V|h|$ vary continuously as h varies continuously and so will give correct values for the density of atoms with broken bonds averaged over the whole of an irrational dividing plane. It is only for these averaged values that the restriction of h to a lattice plane can be removed.

If the bond u_i is associated with q of the sub-lattices, the total number of atoms per unit area with broken u_i-bonds is, for $h \cdot u_i$ positive,

$$\sum_{r=1}^{q} \langle N_r(h, u_i)\rangle_{\mathrm{AV}:\delta}/V|h| = h \cdot u_i/\Omega|h|, \quad (10)$$

where $\Omega = V/q$ is the volume per atom with a u_i-bond; this generalizes a formula derived in Part I.

If the crystal structure is such that a primitive unit cell contains only one atom, but, as for a face-centred cubic crystal, it is more convenient to use a non-primitive unit cell containing many atoms, it is physically obvious that the results obtained by adding the numbers N_r for all sub-lattices associated with the non-primitive unit cell must be the same as would be obtained by calculating the total number in one step using a primitive unit cell; the two sets of results must, of course, both be referred to the same area of surface. The formal proof which will not be given here depends on elementary number theoretic

considerations and the result

$$\sum_{i=0}^{n-1} [y+i/n]^+ = [ny]^+ + n - 1, \quad (11)$$

for any integer n and arbitrary y.

A characteristic feature of the foregoing results is that the numbers N_r depend only on the scalar products $h \cdot u_i$, $h \cdot d_r$ (and also on δ). Once the bond vectors u_i and the d_r are given in terms of their components relative to the basis a_1, a_2, a_3 and h is determined by its Miller indices, these scalar products are invariant to any change of basis. Thus the results are independent of any homogeneous distortion of the structure. For example, for the set of bonds [100], [$\bar{1}$00], [010], [0$\bar{1}$0], [001], [00$\bar{1}$] considered in connection with a simple cubic lattice in Part I, the results obtained for N (but not n) hold *for this set of bonds* in an arbitrary triclinic lattice. The symmetries of the problem (e.g. the sufficiency of considering only planes for which $h \geqslant k \geqslant l \geqslant 0$) are a function of the bond set and not of the crystal symmetry. However in physical problems the crystal symmetry usually dictates the set of bonds chosen in the first place.

3. CONSIDERATION OF SPECIAL CASES

(3.1) *Face-centred cubic structure*

In this paper, the face-centred cubic lattice will be treated as a combination of four simple cubic sub-lattices with $d_0 = [000]$, $d_1 = \frac{1}{2}[011]$, $d_2 = \frac{1}{2}[101]$ and $d_3 = \frac{1}{2}[110]$. Since all the atoms are equivalent, the set u_i will be the same for all sub-lattices and the total number of broken u_i-bonds in a unit cell of area $a^3|h|$ is given by

$$\sum_{r=0}^{3} N_r(h, u_i).$$

Let h have Miller indices (hkl) relative to the cubic cell. Then, if h, k, l are all odd, the *primitive* unit cell of surface has an area of

$$\tfrac{1}{4}a^3|h| = \tfrac{1}{4}a^2(h^2 + k^2 + l^2)^{1/2}$$

and the number of broken u_i-bonds in such a cell can be shown to be

$$N(h, u_i) = [h \cdot u_i - \delta]^+ - [-\delta]^+, \quad (12)$$

where the last term is zero for $0 \leqslant \delta < 1$. If h,

k, l are of mixed parity, the *primitive* unit cell of surface has an area of $\frac{1}{2}a^3|h|$ and, by using equation (11), the number of broken u_i-bonds in this cell is found to be

$$N(h, u_i) = [2h \cdot u_i - 2\delta]^+ - [-2\delta]^+. \quad (13)$$

Equations (12) and (13) hold for all bonds, whether interatomic or not. However, if the bonds are interatomic bonds, as in Part I, the results can be simplified to those given in Part I, viz.

$$N(h, u_i) = \begin{cases} h \cdot u_i, & \text{for } h, k, l \text{ all odd,} \\ 2h \cdot u_i, & \text{for } h, k, l \text{ of mixed parity.} \end{cases}$$

(3.2) *Sodium chloride structure*

This structure consists of ions on two interpenetrating face-centred cubic lattices: an A-lattice occupied by sodium ions with $d_A \equiv d_0 = [000]$ and a B-lattice occupied by chlorine ions with $d_B \equiv d_1 = \frac{1}{2}[111]$. The primitive unit cell of surface is the same as that for one face-centred cubic lattice but may contain either one ion or else one sodium and one chlorine ion.

The bonds to be considered are the A–B and B–A bonds in the set $\frac{1}{2}\langle 100 \rangle$ and the A–A and B–B bonds in the set $\frac{1}{2}\langle 110 \rangle$, the bond vectors being the same for each sub-lattice. Since the sets of bonds have full cubic symmetry, it is sufficient to restrict h to the unit stereographic triangle for which $h \geqslant k \geqslant l \geqslant 0$. Within this triangle, the bonds to be considered are

$$a = \tfrac{1}{2}[100],$$

$$b = \tfrac{1}{2}[010],$$

$$c = \tfrac{1}{2}[001],$$

$A = \tfrac{1}{2}[110],$	$D = \tfrac{1}{2}[1\bar{1}0],$
$B = \tfrac{1}{2}[101],$	$E = \tfrac{1}{2}[011],$
$C = \tfrac{1}{2}[10\bar{1}],$	$F = \tfrac{1}{2}[01\bar{1}],$

since these bonds and no others have positive values of $h \cdot u_i$ within the triangle.

If h, k, l are all odd, the A- and B-ions lie on alternate (hkl) planes. Then, equation (12) and its extension to include $h \cdot d_B$ in accordance with equation (6) give

and
$$\left. \begin{array}{l} N_A(h, a) = h \cdot a \pm \tfrac{1}{2}, \\ N_B(h, a) = h \cdot a \mp \tfrac{1}{2}, \end{array} \right\} \quad (14)$$

where the upper signs apply if $0 \leqslant \delta < \frac{1}{2}$ and the lower if $\frac{1}{2} \leqslant \delta < 1$. Similar relations hold for the bonds b and c. However, for the bonds A, ..., F, the corresponding results are of the form

$$N_A(h, A) = N_B(h, A) = h \cdot A. \quad (15)$$

Since broken nearest neighbour bonds determine the polarity of the surface, all surfaces of this type are charged and

$$\sum_{a,b,c} \{N_A(h, a) - N_B(h, a)\} = \pm 3.$$

If h, k, l are of mixed parity, each (hkl) plane contains both sodium and chlorine ions and such surfaces are electrically neutral. Further, from equation (13) and its extension to include $h \cdot d_B$,

$$N_A(h, u_i) = N_B(h, u_i) = 2h \cdot u_i \quad (16)$$

for all the bonds a, ..., F.

If only nearest neighbour bonds are considered and the distinction between A–B and B–A bonds is dropped, equations (14) and (16) show that the total number of broken nearest neighbour bonds in a surface cell of area $\frac{1}{2}a^3|h|$ is always

$$N_{A+B}(h, u_i) = 4h \cdot u_i, \quad (17)$$

for $u_i = a$, b, or c. Use of equation (11) gives this result directly. Note that

$$N_{A+B} = 2\langle N_A \rangle_{AV:\delta} = 2\langle N_B \rangle_{AV:\delta}.$$

Since $h \cdot a \geqslant h \cdot b \geqslant h \cdot c$ for all points within the unit triangle the bond order is always abc and there are, in each surface cell of area $\frac{1}{2}a^3|h|$, $2(h+k+l)$ broken bonds distributed over $2h$ ions in accordance with Table 1. Contour plots of the number of ions of a given type are shown in Fig. 1. The last column of Table 1 gives for each type

Table 1. *Types of surface ion and frequency of occurrence for a sodium chloride structure; only nearest neighbour bonds considered*

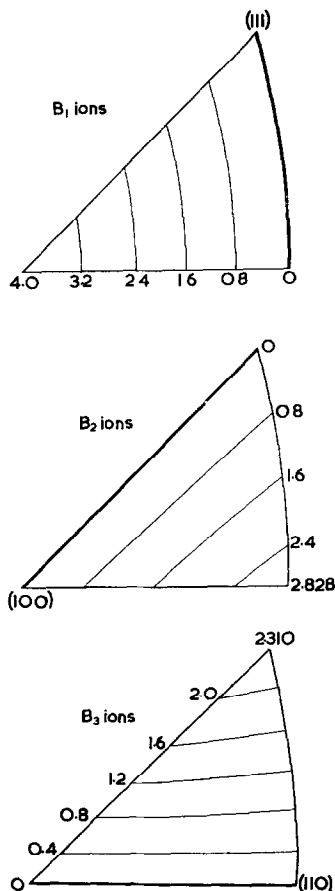| Type of ion	Number $N_{A+B}(B_j)$ in area $\frac{1}{2}a^3\|h\|$	Average density per area a^2 for a random polycrystal
$B_1 = B(a)$	$2(h-k)$	1·4890
$B_2 = B(ab)$	$2(k-l)$	0·9963
$B_3 = B(abc)$	$2l$	0·8395

FIG. 1. Contour plots for the sodium chloride structure of the total density of ions which have 1, 2, or 3 broken nearest neighbour bonds. The density is referred to area a^2 of surface and no distinction is made between sodium and chlorine ions. Zero contours are plotted as thick lines.

of ion the average number per area a^2 in the surface of a polycrystalline specimen with its grains oriented at random. These correspond to the $a^2 \langle n(B_j) \rangle_{\mathrm{AV}}$ defined in Part I where, all results were independent of δ.

When the complete set of bonds a, ..., F is considered, the stereographic triangle is split into the fifteen regions shown in Fig. 2. Within any region the bond order is specified in Table 2 and the number of ions of any type is easily deduced by use of equation (8).
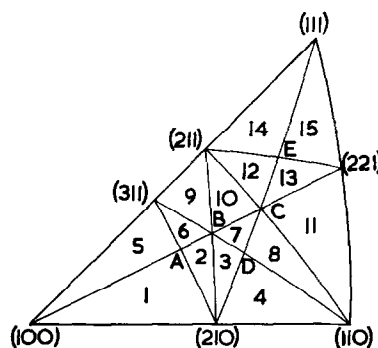

FIG. 2. Regions into which the unit stereographic triangle $(h \geqslant k \geqslant l \geqslant 0)$ is divided when nearest and second nearest neighbour bonds in a sodium chloride structure are considered. The point A is (521), B is (421), C is (321), D is (531) and E is (432).

(3.3) *Diamond structure*

This structure consists of atoms on two inter-penetrating face-centred cubic lattices: an A-lattice with $d_A = [000]$ and a B-lattice with $d_B = \frac{1}{4}[111]$. The primitive unit cell of surface is the same as that for one face-centred cubic lattice but may contain either one or two atoms.

Table 2. *Bond order in the various regions when nearest and second nearest neighbour bonds in a sodium chloride structure are considered*

Region	Bond order	Region	Bond order	Region	Bond order
1	*ABaCDEbFc*	6	*ABaCE DbcF*	11	*ABE abCF cD*
2	*ABaCE DbFc*	7	*ABaE CbDFc*	12	*ABE abC cDF*
3	*ABaCEbDFc*	8	*ABaE CbFDc*	13	*ABE abC cFD*
4	*ABaCEbFDc*	9	*ABaE CDbcF*	14	*ABE abc CDF*
5	*ABaCDEbcF*	10	*ABaE CbDcF*	15	*ABE abc CFD*

o

The only physically significant bonds are the nearest neighbour bonds:

for A-atoms

$a = \frac{1}{4}[111]$,

$b = \frac{1}{4}[1\bar{1}\bar{1}]$,

$c = \frac{1}{4}[\bar{1}1\bar{1}]$,

$d = \frac{1}{4}[\bar{1}\bar{1}1]$;

for B-atoms

$a' = \frac{1}{4}[\bar{1}\bar{1}\bar{1}]$,

$b' = \frac{1}{4}[\bar{1}11]$,

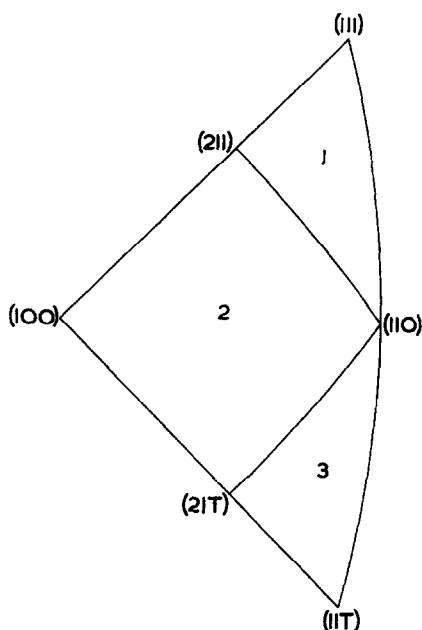$c' = \frac{1}{4}[1\bar{1}1]$,

$d' = \frac{1}{4}[11\bar{1}]$.

FIG. 3. Regions into which the doubled stereographic triangle ($h \geqslant k \geqslant |l|$) is divided when nearest neighbour bonds in the diamond structure are considered.

The symmetry of the bonds allows h to be restricted to the region in which $h \geqslant k \geqslant |l|$. This double stereographic triangle is split into three regions as shown in Fig. 3 and the bond order within each region is specified in Table 3. The number of atoms of any type is easily deduced by use of equation (8) and the results in Section (3·1). Fig. 4 shows contour plots for the average (over δ) number of A-atoms of type B_1, B_2, B_3. The corresponding results for B-atoms are found by reflecting the contour plots about the (100)–(110) line. It may be noted that this is the first structure considered in which the maximum number of

Table 3. *Bond order for various regions for a diamond structure*

Region	1	2	3
Bond order for A-atoms	a	ab	abc
Bond order for B-atoms	$a'c'b'$	$a'c'$	d'

bonds which can be broken from a particular atom varies with the orientation of h.

(3.4) *Caesium chloride structure*

This structure consists of ions on two interpenetrating simple cubic lattices: the first, with $d_0 = [000]$, occupied by caesium ions and the second, with $d_1 = \frac{1}{2}[111]$, occupied by chlorine ions. The primitive unit cell of surface has an area $a^3|h|$ and may contain either one ion or else one caesium and one chlorine ion.

The bonds to be considered are the nearest neighbour bonds in the set $\frac{1}{2}\langle 111 \rangle$ and the second nearest neighbour bonds in the set $\langle 100 \rangle$. The same set applies to all ions.

If $h+k+l$ is even, for all u_t considered.

$$N_r(h, u_t) = h \cdot u_t \qquad (18)$$

independently of r and δ.

If $h+k+l$ is odd, then for u_t a second nearest neighbour bond

$$N_r(h, u_t) = h \cdot u_t \qquad (19)$$

for each r and all δ. However, for u_t a nearest neighbour bond

and

$$\left.\begin{array}{l} N_0(h, u_t) = h \cdot u_t \pm \frac{1}{2}, \\ N_1(h, u_t) = h \cdot u_t \mp \frac{1}{2}, \end{array}\right\} \qquad (20)$$

where the upper signs apply if $0 \leqslant \delta < \frac{1}{2}$ and the lower if $\frac{1}{2} \leqslant \delta < 1$.

When the distinction between Cs–Cl and Cl–Cs bonds and that between Cs–Cs and Cl–Cl bonds is dropped, there follows the general result

$$N(h, u_t) = 2h \cdot u_t \qquad (21)$$

for the total number of broken u_t-bonds in an area $a^3|h|$. This is, or course, the result found in Part I for body-centred cubic crystals. Therefore,
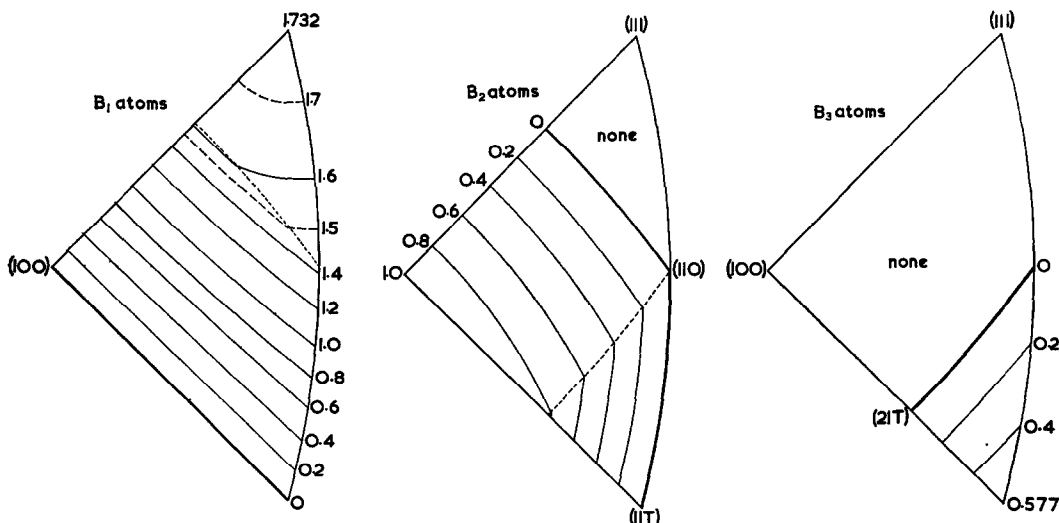
FIG. 4. Contour plots for the diamond structure of the average density (over δ) of A-atoms which have 1, 2, or 3 broken nearest neighbour bonds. The density is referred to area a^2 of surface. Zero contours are plotted as thick lines. Dotted lines show where corners occur in the contours. The average densities (over all h) are 0·8830 for atoms of type B_1, 0·3723 for type B_2, and 0·0348 for type B_3.

all the results previously given for the body-centred cubic structure can be applied to the caesium chloride structure provided only that the values of $N(h, u_i)$ are divided into two parts as nearly equal as possible, one part being allocated to each type of ion in accordance with equations (18), (19), or (20).

(3.5) Close-packed hexagonal structure

This structure consists of atoms on two interpenetrating simple hexagonal lattices. These lattices will be referred to base vectors in the monoclinic system with the two vectors in the basal plane inclined at 120° and the origin of these vectors placed so that

$$d_0 = [000] \text{ and } d_1 = \tfrac{1}{6}[243].$$

Atoms on these two lattices will be described as A- and B-atoms respectively.

Two types of bond about each atom will be considered, namely the nearest neighbour bonds in the basal plane and the nearest neighbour non-basal bonds. In the ideal close-packed structure these bonds will be of equal length but in most real crystals they are unequal. In all cases, the non-basal bonds for an A-atom will differ

from those for a B-atom. Restricting attention to that portion of the stereographic plot in which h, k, and l are all positive, the bonds which may be broken are

$$a = [110] = a',$$
$$b = [100] = c',$$
$$c = [010] = b',$$

$$
\begin{aligned}
A &= \tfrac{1}{6}[243], & A' &= \tfrac{1}{6}[423], \\
B &= \tfrac{1}{6}[2\bar{2}3], & B' &= \tfrac{1}{6}[\bar{2}23], \\
C &= \tfrac{1}{6}[\bar{4}\bar{2}3], & C' &= \tfrac{1}{6}[\bar{2}\bar{4}3], \\
D &= \tfrac{1}{6}[24\bar{3}], & D' &= \tfrac{1}{6}[42\bar{3}], \\
E &= \tfrac{1}{6}[2\bar{2}\bar{3}], & E' &= \tfrac{1}{6}[\bar{2}2\bar{3}],
\end{aligned}
$$

where lower case letters refer to basal vectors, upper case to non-basal vectors, unprimed letters to bonds from A-atoms and primed letters to bonds from B-atoms.

A detailed consideration of the zones defined by $h \cdot u_i = 0$ and $h \cdot u_i = h \cdot u_j > 0$ for the unprimed bonds only leads to a subdivision of the triangle $(h \geqslant 0, \ k \geqslant 0, \ l \geqslant 0)$ into 35 regions as shown in Fig. 5. For the primed bonds, the subdivision is found by reflecting this division

Table 4. Bond order in the various regions for a close-packed hexagonal structure

Region	Bond order for A-atoms	B-atoms	Region	Bond order for A-atoms	B-atoms
1	ABCabc	A'B'C'abc	17	aAbBc	A'abB'cD'C'
2	ABaCbc	A'B'C'abc	18	abABc	A'abB'D'cC'
3	ABabCc	A'B'C'abc	19	abABc	A'abD'B'cC'
4	ABaCbc	A'B'aC'bc	20	aAbBcD	aA'bcB'D'
5	ABabCc	A'B'aC'bc	21	aAbcBD	aA'bcB'D'
6	ABabCc	A'aB'bC'c	22	aAbBcD	aA'bcD'B'
7	ABabCc	A'abB'C'c	23	aAbcBD	aA'bcD'B'
8	AaBbcC	A'aB'bC'c	24	aAbcDB	aA'bcD'B'
9	AaBbcC	A'aB'bcC'	25	abAbcD	aA'bD'cB'
10	AaBbcC	A'abB'C'c	26	abAcBD	aA'bD'cB'
11	AaBbcC	A'abB'cC'	27	abAcDB	aA'bD'cB'
12	aAbBc	A'abB'C'cD	28	abABDcE	abA'D'c
13	abABc	A'abB'C'D'c	29	abABDEc	abA'D'c
14	aAbBc	A'abB'cC'D'	30	abADBcE	abA'D'c
15	abABc	A'abB'D'C'c	31	abADBEc	abA'D'c
16	abABc	A'abD'B'C'c	32	abADcBE	abA'D'c

FIG. 5. Regions into which the stereographic triangle, $h \geqslant 0$, $k \geqslant 0$, $l \geqslant 0$, is divided when nearest neighbour bonds from A-atoms in a close-packed hexagonal structure are considered. The figure is drawn for the ideal structure of axial ratio $\sqrt{(8/3)}$ but the topology and labelling of planes is independent of this ratio.
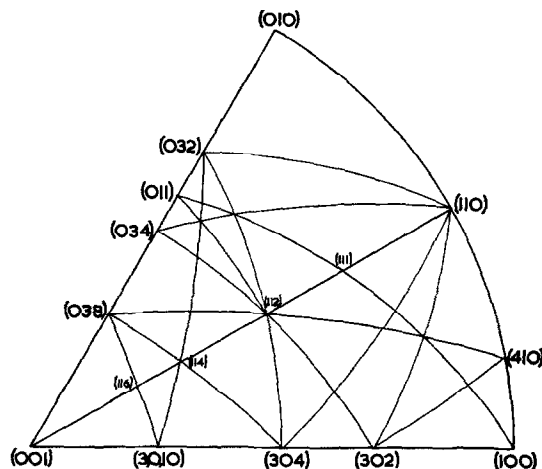

FIG. 6. Regions into which the stereographic triangle, $h \geqslant k \geqslant 0$, $l \geqslant 0$ is divided when nearest neighbour bonds from A- and B-atoms in a close-packed hexagonal structure are considered. The point A is (4 1 14), B is (5 2 12), C is (6 3 14), D is (416), E is (718), F is (10 1 10), G is (414), H is (858), J is (634), K is (744), L is (522) and M is (11 2 2). As for Fig. 5, the figure is drawn for the ideal axial ratio of $\sqrt{(8/3)}$.

about the (001)–(110) zone, i.e. interchanging h and k. Therefore, distinct regions correspond to the superposition of these two subdivisions. As shown in Fig. 6, this leads to 32 regions with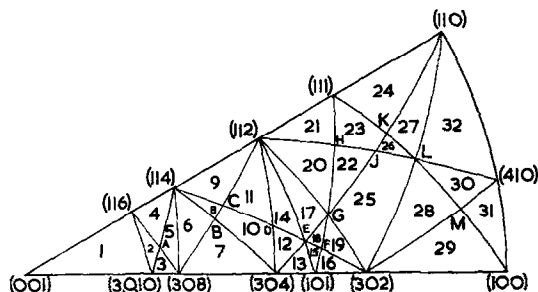in the smaller triangle $h \geqslant k \geqslant 0$, $l \geqslant 0$. The bond order in each region is given in Table 4. For the triangle $k \geqslant h \geqslant 0$, $l \geqslant 0$ the primed and unprimed vectors must be interchanged so that the second set of vectors becomes the bond order for A-atoms and the first set, that for B-atoms. Note that $b' = c$ and $c' = b$.

With so many regions to consider, it becomes pointless to tabulate the values of $N(B_j)$. It is, however, worth recording the number of distinct

Table 5. Average number of surface atoms and the average number of broken bonds in unit cell of surface for a close-packed hexagonal structure

Regions	Average number of surface atoms		Average number of bonds broken	
	A-atoms	B-atoms	Basal bonds	Non-basal bonds
1–11	$\frac{1}{6}(2h+4k+3l)$	$\frac{1}{6}(4h+2k+3l)$	$4(h+k)$	$3l$
12–19	$h+k$	$\frac{1}{6}(4h+2k+3l)$	$4(h+k)$	$\frac{1}{3}(4h+2k)+2l$
20–27	$h+k$	$h+k$	$4(h+k)$	$2(h+k)+l$
28–32	$h+k$	$h+k$	$4(h+k)$	$\frac{1}{3}(8h+4k)$

types of atoms. Among the A-atoms (or the B-atoms) there are two types of B_1 atom, three types of B_2, four of B_3, six of B_4 and B_5, four of B_6, and two of B_7, making twenty-seven types in all, whereas the face-centred cubic structure exhibits only nine types of atom. Table 5 lists the average numbers of surface atoms and of broken bonds in a unit cell of surface of area $V|h|$, the average being over all values of δ.

REFERENCE

1. MACKENZIE J. K., MOORE A. J. W. and NICHOLAS J. F., *J. Phys. Chem. Solids* **23**, 185 (1962) (preceding paper).