

## Representation Quadrics for Crystal Structures. I. Metallic Elements with No Variable Coordinates

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### Abstract

Summation of the components of interatomic vectors,  $\mathbf{r}_n$ , normal to a crystallographic plane,  $(hkl)$ , divided by the area of the periodic repeat unit over which the vectors operate, provides a quantity,  $\sigma_n(hkl)$ , defined as an interaction factor. If all values of  $\sigma_n$  for a given interatomic vector are plotted in the directions normal to all planes in the structure, the result is a structural quadric, with geometric properties analogous to representation quadrics for single-crystal properties. All the atomic interactions in a crystal can thus be represented by a group of quadrics having common semiaxes. It is proposed that crystal properties are a function or functions of the structural quadrics and calculations incorporating some simplifying assumptions are presented to indicate possible applications of the concept.

### Introduction

The relationships between point-group symmetry and single-crystal properties are well defined. Magnitudes and directions of vectors representing linear compressibility in all crystallographic directions, for example, may be calculated directly from elastic constants and illustrated graphically as representation quadrics. Young's moduli can also be calculated from elastic constants and represented by rather more complex figures. Similarly, variation of thermal expansion and diffusion coefficients may be determined as functions of crystallographic direction after measurement of values in one, two, or three known directions and may be represented as quadrics whose geometric properties – plotting the reciprocals of the square roots of the magnitudes produces ellipsoids or hyperboloids – provide a means of determining and visualizing the relationships between applied and resultant forces. Single-crystal optical properties can also be represented as quadrics if relative dielectric impermeabilities are plotted as functions of crystallographic direction, though it is more useful to consider the reciprocal roots, the indices of refraction, which can be represented by spherical or ellipsoidal optic indicatrices.

The relationships between representation quadrics for single-crystal properties and the crystal structure are not so well understood, however. Aside from theories of covalent bonding, which describe interatomic forces only among nearest neighbors in terms of orbital configurations, and the Brillouin-zone–Fermi-surface treatments resulting from the band theory of metals, there is inadequate basis for quantitative understanding of the relationships between properties and the atomic arrangements of any but the simplest structures. There is a definite need, therefore, for a general geometric formulation to represent atomic interactions in crystals, regardless of structural complexity or bond type. Ideally, such a formulation will be strictly geometric, based on a static model, expressed in terms of structural variables – lattice parameters and atomic coordinates – and define certain geometric conditions which must be satisfied by all crystals under all conditions. Once the geometric conditions are defined, it should then be possible to evaluate interatomic forces more directly and, conversely, to predict how structural variables must change in response to changes in conditions, particularly temperature and pressure. The work described here is only a first step toward such a general geometric formulation and is restricted to simple structures – metallic elements with no variable coordinates. Subsequent work will show, however, that the method is applicable to all structures and that the greatly increased complexity introduced by consideration of more complex chemistry and variable atomic coordinates is tractable and informative.

### General considerations

The Madelung constant was developed as a means of expressing the relative contributions of ions of like and unlike charge on successive coordination spheres about a single ion so that all the attractive and repulsive energies in an ionic crystal could be expressed as a function of the nearest-neighbor distance in the Born–Landé equation for lattice energy. The factors considered were the coordination number in each successive sphere and the distance from the central ion,

expressed as a multiple of the nearest-neighbor distance, so the Madelung summation is strictly a function of the structure. Because of the non-directional nature of ionic forces, however, it makes no reference to crystallographic direction, is applicable only to purely ionic crystals, and is difficult to calculate for complex crystals. The method developed below utilizes the essence of the Madelung summation but differs from it in that the components of all interatomic vectors,  $r_n$ , normal to a crystallographic plane,  $(hkl)$ , are summed over a periodic repeat unit and divided by the area over which those components operate. An interaction factor,  $\sigma_n$ , is thereby derived for each successive interatomic distance for each crystallographic direction. The summation may be carried out over as many successive distances in as many directions as needed. The mathematical form of the numerical values of a single  $\sigma_n$  over all crystallographic directions proves to be that of a representation quadric. The geometric effects of all the interatomic vectors in a crystal can be represented in all crystallographic directions by a group of quadrics with common semiaxes which coincide with the crystallographic axes in the same way as the representation quadrics for properties.

**Interaction factors**

The interaction factor is defined by

$$\sigma_n(hkl) = \frac{\sum r_n(hkl)}{A_{hkl}}, \tag{1}$$

where  $\sum r_n(hkl)$  is the sum of the magnitude of all the components of the interatomic vectors,  $r_n$ , normal to the  $(hkl)$  plane and  $A_{hkl}$  is the area of the crystallographic repeat unit over which the summation is made. As shown below, the value of  $\sigma_n$  is also defined as a multiple,  $M_n$ , of the interplanar spacing,  $d_{hkl}$ ,

divided by  $A_{hkl}$ :

$$\sigma_n(hkl) = M_n \frac{d_{hkl}}{A_{hkl}}. \tag{2}$$

*F.c.c. and f.c.t. metals*

The method of summing interatomic vectors in anisotropic crystals may be illustrated with the structure of tetragonal indium, as shown in Fig. 1. To show the relationship between that structure and c.c.p. metals, the unit cell chosen is f.c. tetragonal rather than

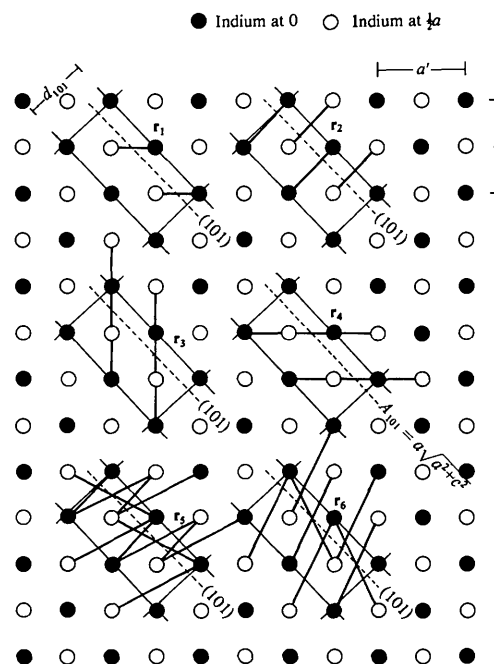


Fig. 1. Method of summation of components of interatomic vectors  $r_1$  through  $r_6$ , normal to the  $(101)$  plane of tetragonal indium. The  $a'$  parameter corresponds to  $\sqrt{2} a$  of the b.c. tetragonal unit cell.

Table 1. *Interatomic vectors for face-centered cubic metals and the tetragonal distortion (M at 000;  $\frac{1}{2}10$ ;  $\frac{1}{2}01$ ,  $0\frac{1}{2}$ )*

$r_n$ , f.c.c.	$hkl$	Coordination	$r_n$ (Å), Pb	$r_n$ f.c.t.	$hkl$	Coordination	$r_n$ (Å), In	$r_n$ (Å), $\delta'$ Pu
$r_1 = \frac{1}{2}\sqrt{2} a$	$\langle 110 \rangle$	12	3.5005	$r_1 = \frac{1}{2}\sqrt{2a^2}$	$\langle 110 \rangle$	4	3.2517	3.339
$r_2 = \frac{1}{2}\sqrt{4} a = a$	$\langle 200 \rangle$	6	4.9505	$r_2 = \frac{1}{2}\sqrt{a^2 + c^2}$	$\langle 101 \rangle$	8	3.3767	3.243
$r_3 = \frac{1}{2}\sqrt{6} a$	$\langle 112 \rangle$	24	6.0631	$r_3 = \frac{1}{2}\sqrt{4a^2} = a$	$\langle 200 \rangle$	4	4.5986	4.722
$r_4 = \frac{1}{2}\sqrt{8} a = \sqrt{2} a$	$\langle 220 \rangle$	12	7.0011	$r_4 = \frac{1}{2}\sqrt{4c^2} = c$	$\langle 002 \rangle$	2	4.9459	4.446
$r_5 = \frac{1}{2}\sqrt{10} a$	$\langle 310 \rangle$	24	7.8274	$r_5 = \frac{1}{2}\sqrt{5a^2 + c^2}$	$\langle 211 \rangle$	12	5.7052	5.728
$r_6 = \frac{1}{2}\sqrt{12} a = \sqrt{3} a$	$\langle 222 \rangle$	8	8.5745	$r_6 = \frac{1}{2}\sqrt{2a^2 + 4c^2}$	$\langle 112 \rangle$	12	5.9191	5.560
$r_n = \frac{1}{2}\sqrt{h^2 + k^2 + l^2} a; h^2 + k^2 + l^2 = 2N$				$r_7 = \frac{1}{2}\sqrt{8a^2}$	$\langle 220 \rangle$	4	6.5034	6.678
				$r_8 = \frac{1}{2}\sqrt{4a^2 + 4c^2}$	$\langle 202 \rangle$	8	6.7535	6.486
				$r_9 = \frac{1}{2}\sqrt{10a^2}$	$\langle 310 \rangle$	8	7.2710	7.466
				$r_{10} = \frac{1}{2}\sqrt{9a^2 + c^2}$	$\langle 301 \rangle$	8	7.3278	7.424
				$r_{11} = \frac{1}{2}\sqrt{a^2 + 9c^2}$	$\langle 103 \rangle$	8	7.7670	7.075
				$r_{12} = \frac{1}{2}\sqrt{8a^2 + 4c^2}$	$\langle 222 \rangle$	8	8.1704	8.023
				$r_n = \frac{1}{2}\sqrt{(h^2 + k^2) a^2 + l^2 c^2}$				

the usual b.c. tetragonal cell, and the Miller indices correspond to the f.c.t. cell.

As shown in Table 1, successive interatomic vectors in face-centered cubic metals can be developed systematically with crystallographic terms. Interatomic distances are shown to be equal to  $\frac{1}{2}(h^2 + k^2 + l^2)^{1/2}a$ , where  $a$  is the unit-cell parameter and  $h^2 + k^2 + l^2$  is the quadratic form of the Miller indices of the directions of the vectors  $\langle hkl \rangle$ . In all cases, the coordination number is equal to the multiplicity of planes with the same indices  $\{hkl\}$ . If the f.c.c. metal structure is distorted by expansion in the [001] direction, as in tetragonal indium, or by compression, as in  $\delta'$ -plutonium, the interatomic vectors are split into two or more vectors whose magnitudes and directions are also listed in Table 1. The directions and coordination numbers are defined in the same way as for f.c.c. except that they are in accordance with multiplicity requirements of tetragonal symmetry.

It is now necessary to define the unit area over which the summation is to be made. In the plane of the projection the linear repeat unit has been chosen as  $(a^2 + c^2)^{1/2}$ , the distance between the two lines drawn normal to the (101) plane in Fig. 1. Normal to the projection, the linear repeat unit has been chosen as  $a$ . The area over which the summation is to be made, therefore, is a rectangle with  $A_{101} = a(a^2 + c^2)^{1/2}$ .

If a (101) plane, which will be normal to the projection, is drawn, as shown by the dashed line, it is seen that there are four  $r_1$  interatomic vectors operating across that plane, each with a component normal to (101) equal to  $\frac{1}{2}d_{101}$ . The sum of those components is thus  $2d_{101}$ , or  $2ac/(a^2 + c^2)^{1/2}$ . The interaction factor is now defined as the sum of the components normal to the plane, divided by the area over which they operate:  $\sigma_1(101) = 2[d/A]_{101} = 2c/(a^2 + c^2)$ . The same result will be obtained by summing across any of the  $\{101\}$  planes. Similarly, the interaction factors  $\sigma_2(101)$  through  $\sigma_6(101)$  can be obtained by summing the components of the  $r_n$  vectors shown in Fig. 1. The same procedure may be used to sum the components of any interatomic vector,  $r_n$ , operating across any plane,  $(hkl)$ , and an interaction factor,  $\sigma_n(hkl)$ , may thus be obtained.

This has been done for the 12 interatomic vectors of the f.c.t. structure, as defined in Table 1, normal to some 50 planes. For clarity of presentation, ease of mathematical manipulation, and to avoid tabulating over 600 terms, it is convenient to develop generalized expressions in a compact form. Proceeding from the logical assumption that the net effect of any interatomic interaction will be some function of the inverse of the interatomic distance,  $r_n$ , an interaction function is defined as

$$S_n = \frac{\sigma_n}{R_n}, \quad (3)$$

where  $R_n = f_n(r_n)$ , that is, some function of the interatomic distance. The total of all interactions across a given plane  $(hkl)$  can now be written as

$$\sum S_n(hkl) = \frac{\sigma_1(hkl)}{R_1} + \frac{\sigma_2(hkl)}{R_2} + \dots + \frac{\sigma_n(hkl)}{R_n}, \quad (4)$$

or more compactly as

$$\sum S_n(hkl) = \sum_{i=1}^n \frac{\sigma_n(hkl)}{R_n}. \quad (5)$$

Because the value of  $\sigma_n(hkl)$  proves to be, in all cases, a multiple,  $M_n$ , of  $d_{hkl}/A_{hkl}$ , (5) may be rewritten as

$$\sum S_n(hkl) = \frac{d_{hkl}}{A_{hkl}} \sum_{i=1}^n \frac{M_n(hkl)}{R_n}. \quad (6)$$

The result of the summations in f.c.t. metals are summarized in Table 2 in accordance with the notation developed above. The results for only four crystallographic directions are tabulated; in these,  $M_n$  values appear as integrals within the brackets and  $d_{hkl}/A_{hkl}$  values appear as common factors outside the brackets. The results have been generalized as  $\sum S_n(hkl)$ , in which it is seen that both  $d_{hkl}/A_{hkl}$  and  $M_n$  are strictly functions of the lattice parameters and the crystallographic directions. It is obvious, therefore, that it is necessary only to determine  $\sigma_n$  values across the (100) and (001) planes in order to write the  $\sum S_n(hkl)$  expression, valid for all directions. Summation over all planes in the [001] zone produces a single expression,  $\sum S_n(hk0)$ , indicating a circular section normal to the [001] axis. For the f.c.c. structure,  $\sum S_n(hkl)$  reduces to a single expression, valid for all crystallographic directions.

A particularly useful property of the interaction functions is that, if any two are equated, a single expression is derived in terms of  $R_n$  and  $(c/a)^2$ , as shown in Table 2. Use of that relationship will be reserved for future work.

#### *B.c.c. and f.c.t. metals*

The systematic development of expressions for body-centered cubic metals and the tetragonal distortion, as exemplified by protactinium and  $\beta$ -mercury, has been accomplished and the data are presented in Tables 3 and 4. The expressions are seen to be comparable in all respects to those developed for face-centered metal structures.

#### *H.c.p. metals*

Expressions for the first six coordination spheres of hexagonal-close-packed metals have been derived, as shown in Table 5. They prove to be similar to those for

Table 2. *Summations of interaction functions for f.c.c. metals and the tetragonal distortion*

Face-centered tetragonal metals

$$\sum S_n(hk0) = \frac{c}{c^2} \left[ \frac{2}{R_1} + \frac{2}{R_2} + \frac{4}{R_3} + \frac{0}{R_4} + \frac{20}{R_5} + \frac{4}{R_6} + \frac{8}{R_7} + \frac{8}{R_8} + \frac{20}{R_9} + \frac{18}{R_{10}} + \frac{2}{R_{11}} + \frac{16}{R_{12}} \right]$$

$$\sum S_n(001) = \frac{c}{a^2} \left[ \frac{0}{R_1} + \frac{4}{R_2} + \frac{0}{R_3} + \frac{4}{R_4} + \frac{8}{R_5} + \frac{16}{R_6} + \frac{0}{R_7} + \frac{16}{R_8} + \frac{0}{R_9} + \frac{4}{R_{10}} + \frac{36}{R_{11}} + \frac{16}{R_{12}} \right]$$

$$\sum S_n(101) = \frac{c}{a^2 + c^2} \left[ \frac{2}{R_1} + \frac{6}{R_2} + \frac{4}{R_3} + \frac{4}{R_4} + \frac{28}{R_5} + \frac{20}{R_6} + \frac{8}{R_7} + \frac{24}{R_8} + \frac{20}{R_9} + \frac{22}{R_{10}} + \frac{38}{R_{11}} + \frac{32}{R_{12}} \right]$$

$$\sum S_n(111) = \frac{c}{a^2 + 2c^2} \left[ \frac{4}{R_1} + \frac{8}{R_2} + \frac{8}{R_3} + \frac{4}{R_4} + \frac{48}{R_5} + \frac{24}{R_6} + \frac{16}{R_7} + \frac{32}{R_8} + \frac{20}{R_9} + \frac{40}{R_{10}} + \frac{40}{R_{11}} + \frac{48}{R_{12}} \right]$$

$$\begin{aligned} \sum S_n(hkl) = \frac{c}{l^2 a^2 + (h^2 + k^2) c^2} & \left[ \frac{2(h^2 + k^2)}{R_1} + \frac{2(h^2 + k^2) + 4l^2}{R_2} + \frac{4(h^2 + k^2)}{R_3} + \frac{4l^2}{R_4} \right. \\ & + \frac{20(h^2 + k^2) + 8l^2}{R_5} + \frac{4(h^2 + k^2) + 16l^2}{R_6} + \frac{8(h^2 + k^2)}{R_7} + \frac{8(h^2 + k^2) + 16l^2}{R_8} + \frac{20(h^2 + k^2)}{R_9} \\ & \left. + \frac{18(h^2 + k^2) + 4l^2}{R_{10}} + \frac{2(h^2 + k^2) + 36l^2}{R_{11}} + \frac{16(h^2 + k^2) + 16l^2}{R_{12}} \right] \end{aligned}$$

For  $\sum S_n(h_1 k_1 l_1) = \sum S_n(h_2 k_2 l_2)$ 

$$\frac{1}{R_1} - \frac{2C-1}{R_2} + \frac{2}{R_3} - \frac{2C}{R_4} + \frac{10-4C}{R_5} + \frac{8C-2}{R_6} + \frac{4}{R_7} - \frac{8C-4}{R_8} + \frac{10}{R_9} + \frac{9-2C}{R_{10}} - \frac{18C-1}{R_{11}} + \frac{8-8C}{R_{12}} = 0$$

$$\text{where } C = \left[ \frac{c}{a} \right]^2$$

Face-centered-cubic metals

$$\sum S_n(hkl) = \frac{1}{a} \left[ \frac{4}{R_1} + \frac{4}{R_2} + \frac{24}{R_3} + \frac{16}{R_4} + \frac{40}{R_5} + \frac{16}{R_6} \right]$$

Table 3. *Interatomic vectors for body-centered-cubic metals and the tetragonal distortion ( $M$  at  $000; \frac{1}{2}\frac{1}{2}\frac{1}{2}$ )*

$r_n$ , b.c.c.	$hkl$	Coordi- nation	$r_n$ (Å), Fe	$r_n$ , b.c.t.	$hkl$	Coordi- nation	$r_n$ (Å), Pa	$r_n$ (Å), $\beta$ -Hg
$r_1 = \frac{1}{2}\sqrt{3} a$	$\langle 111 \rangle$	8	2.4824	$r_1 = \frac{1}{2}\sqrt{2a^2 + c^2}$	$\langle 111 \rangle$	8	3.213	3.158
$r_2 = \frac{1}{2}\sqrt{4} a = a$	$\langle 200 \rangle$	6	2.8664	$r_2 = \frac{1}{2}\sqrt{4c^2} = c$	$\langle 002 \rangle$	2	3.238	2.825
$r_3 = \frac{1}{2}\sqrt{8} a = \sqrt{2} a$	$\langle 220 \rangle$	12	4.0537	$r_3 = \frac{1}{2}\sqrt{4a^2} = a$	$\langle 200 \rangle$	4	3.925	3.995
$r_4 = \frac{1}{2}\sqrt{11} a$	$\langle 113 \rangle$	24	4.7534	$r_4 = \frac{1}{2}\sqrt{4a^2 + 4c^2}$	$\langle 202 \rangle$	8	5.088	4.893
$r_5 = \frac{1}{2}\sqrt{12} a = \sqrt{3} a$	$\langle 222 \rangle$	8	4.9648	$r_5 = \frac{1}{2}\sqrt{8a^2}$	$\langle 220 \rangle$	4	5.551	5.560
$r_6 = \frac{1}{2}\sqrt{16} a = 2a$	$\langle 400 \rangle$	6	5.7328	$r_6 = \frac{1}{2}\sqrt{2a^2 + 9c^2}$	$\langle 113 \rangle$	8	5.594	5.093
				$r_7 = \frac{1}{2}\sqrt{10a^2 + c^2}$	$\langle 311 \rangle$	16	6.414	6.473
				$r_8 = \frac{1}{2}\sqrt{8a^2 + 4c^2}$	$\langle 222 \rangle$	8	6.426	6.317
				$r_9 = \frac{1}{2}\sqrt{16c^2} = 2c$	$\langle 004 \rangle$	2	6.476	5.650
				$r_{10} = \frac{1}{2}\sqrt{16a^2} = 2a$	$\langle 400 \rangle$	4	7.850	7.990
$r_n = \frac{1}{2}\sqrt{h^2 + k^2 + l^2} a; h^2 + k^2 + l^2 = 4N$ and $8N + 3$				$r_n = \frac{1}{2}\sqrt{(h^2 + k^2) a^2 + l^2 c^2}$				

Table 4. *Summations of interaction functions for b.c.c. metals and the tetragonal distortion*

Body-centered-tetragonal metals

$$\begin{aligned}\sum S_n(hk0) &= \frac{c}{c^2} \left[ \frac{2}{R_1} + \frac{0}{R_2} + \frac{2}{R_3} + \frac{4}{R_4} + \frac{4}{R_5} + \frac{2}{R_6} + \frac{20}{R_7} + \frac{8}{R_8} + \frac{0}{R_9} + \frac{8}{R_{10}} \right] \\ \sum S_n(001) &= \frac{c}{a^2} \left[ \frac{2}{R_1} + \frac{2}{R_2} + \frac{0}{R_3} + \frac{8}{R_4} + \frac{0}{R_5} + \frac{18}{R_6} + \frac{4}{R_7} + \frac{8}{R_8} + \frac{8}{R_9} + \frac{0}{R_{10}} \right] \\ \sum S_n(hkl) &= \frac{c}{l^2 a^2 + (h^2 + k^2) c^2} \left[ \frac{2(h^2 + k^2) + 2l^2}{R_1} + \frac{2l^2}{R_2} + \frac{2(h^2 + k^2)}{R_3} \right. \\ &\quad + \frac{4(h^2 + k^2) + 8l^2}{R_4} + \frac{4(h^2 + k^2)}{R_5} + \frac{2(h^2 + k^2) + 18l^2}{R_6} + \frac{20(h^2 + k^2) + 4l^2}{R_7} \\ &\quad \left. + \frac{8(h^2 + k^2) + 8l^2}{R_8} + \frac{8l^2}{R_9} + \frac{8(h^2 + k^2)}{R_{10}} \right]\end{aligned}$$

For  $\sum S_n(h, k_1, l_1) = \sum S_n(h_2, k_2, l_2)$ 

$$\frac{1-C}{R_1} - \frac{C}{R_2} + \frac{1}{R_3} - \frac{4C-2}{R_4} + \frac{2}{R_5} - \frac{9C-1}{R_6} + \frac{10-2C}{R_7} + \frac{4-4C}{R_8} - \frac{4C}{R_9} + \frac{4}{R_{10}} = 0 \quad \text{where } C = \left[ \frac{c}{a} \right]^2$$

Body-centered-cubic metals

$$\sum S_n(hkl) = \frac{1}{a} \left[ \frac{2}{R_1} + \frac{2}{R_2} + \frac{8}{R_3} + \frac{22}{R_4} + \frac{8}{R_5} + \frac{8}{R_6} \right]$$

Table 5. *Summations of interaction functions for hexagonal-close-packed metals (M at 000;  $\frac{1}{3}\frac{1}{3}\frac{1}{3}$ )*

$r_n$	$r_n$ (Å), Be	$r_n$ (Å), Mg	$r_n$ (Å), Cd	$r_n$ (Å), Ideal
$r_1 = \frac{1}{2}\sqrt{12a^2 + 9c^2}$	2.2249	3.19688	3.29354	3.28210
$r_2 = a$	2.2854	3.20927	2.97887	3.28210
$r_3 = \frac{1}{2}\sqrt{48a^2 + 9c^2}$	3.1896	4.52984	4.44084	4.64159
$r_4 = c$	3.5829	5.21033	5.61765	5.35965
$r_5 = \frac{1}{2}\sqrt{84a^2 + 9c^2}$	3.9238	5.55147	5.34740	5.64876
$r_6 = \sqrt{3}a$	3.9584	5.55862	5.15955	5.65876

$$\sum S_n(hk0) = \frac{c}{\sqrt{3}(4c^2)} \left[ \frac{8}{R_1} + \frac{24}{R_2} + \frac{32}{R_3} + \frac{0}{R_4} + \frac{112}{R_5} + \frac{72}{R_6} \right]$$

$$\sum S_n(001) = \frac{c}{\sqrt{3}(3a^2)} \left[ \frac{9}{R_1} + \frac{0}{R_2} + \frac{9}{R_3} + \frac{12}{R_4} + \frac{18}{R_5} + \frac{0}{R_6} \right]$$

$$\sum S_n(101) = \frac{c}{\sqrt{3}(3a^2 + 4c^2)} \left[ \frac{17}{R_1} + \frac{24}{R_2} + \frac{41}{R_3} + \frac{12}{R_4} + \frac{130}{R_5} + \frac{72}{R_6} \right]$$

$$\sum S_n(hkl) = \frac{c}{\sqrt{3}(na^2 + mc^2)} \left[ \frac{2m + 3n}{R_1} + \frac{6m}{R_2} + \frac{8m + 3n}{R_3} + \frac{4n}{R_4} + \frac{28m + 6n}{R_5} + \frac{18m}{R_6} \right]$$

$$m = 4(h^2 + hk + k^2); n = 3l^2$$

For  $\sum S_n(h_1, k_1, l_1) = \sum S_n(h_2, k_2, l_2)$ 

$$\frac{3C-2}{R_1} - \frac{6}{R_2} - \frac{8-3C}{R_3} + \frac{4C}{R_4} - \frac{28-6C}{R_5} - \frac{18}{R_6} = 0 \quad \text{where } C = \left[ \frac{c}{a} \right]^2$$

f.c.t. and b.c.t. metals, though somewhat more cumbersome because of the 120° angles between the  $a$  axes, and they do not reduce to a single isotropic case for ideal h.c.p.

### Other structures

The methods outlined above have been used to determine interaction factors for many other structures, compounds as well as metallic elements, and the relationships described above have been found to hold. The interaction factors for cubic crystals are identical in all directions and those for crystals of lower symmetry are functions of lattice parameters and Miller indices when there are no variable coordinates. Space limitations require, however, that discussion of these be included in future work.

### Geometric properties of interaction factors

If the numerical values of  $\sigma_n$  are plotted for all  $\{hkl\}$  planes — as vectors normal to  $\{hkl\}$  — the figures produced are representation quadrics. The magnitude of a vector  $\sigma'_n(hkl)$ , in a direction normal to  $(hkl)$ , is expressed exactly by the equation

$$\sigma'_n(hkl) = \sigma_n(100) \cos^2 \theta_1 + \sigma_n(010) \cos^2 \theta_2 + \sigma_n(001) \cos^2 \theta_3 \quad (7)$$

where  $\sigma_n(100)$ ,  $\sigma_n(010)$ , and  $\sigma_n(001)$  are the interaction factors across the (100), (010), and (001) planes and  $\theta_1$ ,  $\theta_2$ , and  $\theta_3$  are the angles between the vector  $\sigma_n(hkl)$  and the [100], [010] and [001] axes, respectively.

Fig. 3 illustrates the representation quadrics for the 12 coordination spheres in tetragonal indium. To facilitate plotting, values of  $\sigma_n/r_n$ , here referred to as normalized interaction factors, have been plotted; the units are  $\text{\AA}^{-2}$ , therefore. For the case of the f.c.t.

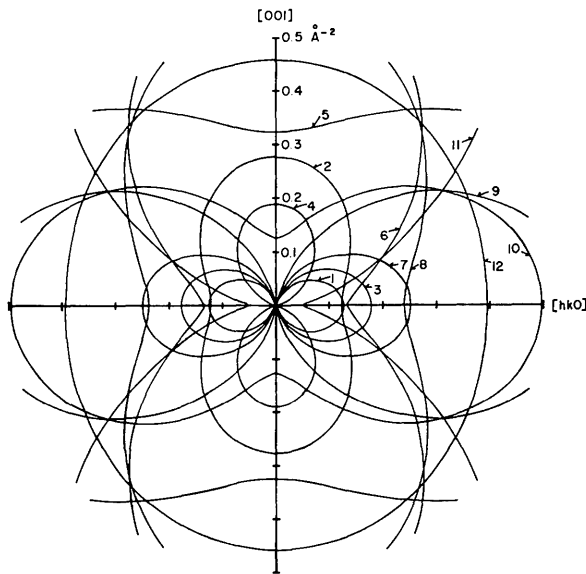


Fig. 2. Normalized interaction factors for tetragonal indium, plotted as functions of crystallographic direction. Each is a representation quadric of revolution with a circular section normal to [001].

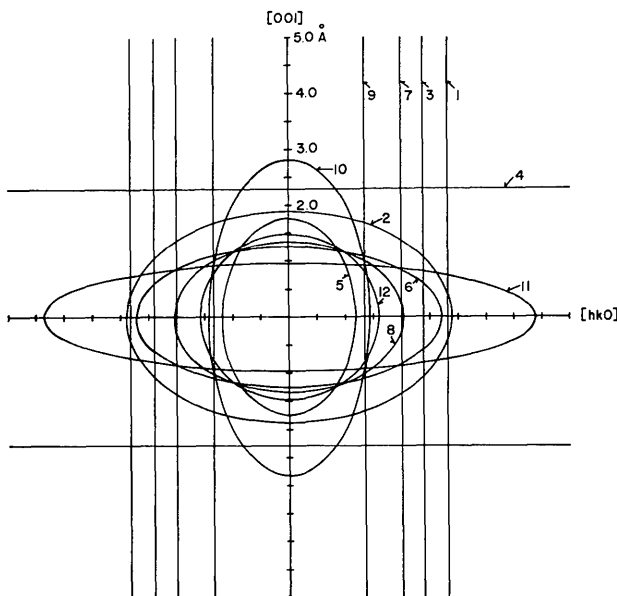


Fig. 3. Root inversions of the representation quadrics for tetragonal indium. The figures are ellipsoids of revolution, cylindrical hyperboloids, and a planar hyperboloid, symmetric about [001].

structure shown in Fig. 2,  $\sigma_n(100) = \sigma_n(010)$ , so the quadrics are figures of revolution, with circular sections normal to [001].

If the root inversions,  $[\sigma'_n(hkl)]^{-1/2}$ , are plotted, the figures produced are ellipsoids of revolution, cylindrical hyperboloids where  $\sigma_n(001) = 0$ , or a planar hyperboloid in the case where  $\sigma_n(100) = 0$ . This is shown in Fig. 3 where the root inversions of  $\sigma_n/r_n$  have been plotted.

For cubic crystals, the quadrics and root inversions are spherical. Though no examples are given here, crystals of lower symmetry produce triaxial quadrics with orientations similar to thermal expansion quadrics.

The quadrics for h.c.p. metals are also figures of revolution. If interaction factors are calculated for a hypothetical h.c.p. metal with the ideal  $c/a = \sqrt{8/3}$ ,  $r_1$  and  $r_2$  are equal and the quadric for  $\sigma_1 + \sigma_2$  is spherical. The quadric for  $\sigma_3$  is also spherical, but those for  $\sigma_4$  and  $\sigma_4 + \sigma_6$  are not, reflecting the fact that beyond the third coordination sphere, the geometric distribution of forces is anisotropic in all cases, providing a qualitative explanation for the fact that the  $c/a$  ratio for h.c.p. metals is never ideal.

### Discussion of possible applications

Although the primary purpose of the present work is to illustrate the method whereby atomic interactions in simple metal structures can be represented by groups of quadrics pertaining to the separate interatomic distances and having common semiaxes, it is obvious that the implications are numerous. It will be shown in subsequent papers that the structural quadrics developed here can be related to property quadrics to provide fundamental information about interatomic forces. It will also be shown that derivation of structural quadrics for crystals having variable coordinates may be used to predict how those coordinates will change with changes in temperature and pressure. In short, it is anticipated that this work will ultimately result in new equations of state for crystalline solids. Though that work is not yet complete and any detailed discussion is beyond the intended scope of this paper, it is possible at this point to present an example of one way structural quadrics may be used.

Fig. 4 shows volume compressibilities, calculated from room-temperature elastic constants selected randomly from the compendium of Simmons & Wang (1971), for metallic elements with the structures already treated. It is obvious that the trends are periodic and, though the compressibilities surely are functions of both the net interatomic forces and the crystal structures, the effect of either on the compressibilities is not at all apparent. A plot of linear compressibilities *versus* atomic numbers shows essentially the same trends.

With the lattice parameters for the metallic elements, tabulated by Wyckoff (1963), and the linear compressibilities, from the elastic constants used to calculate the volume compressibilities shown in Fig. 4, values of the lattice parameters were calculated for the lower and upper limits of a pressure interval, in this case at 0 and  $10^8$  Pa. From these values of the lattice parameters,  $\sigma_1$  through  $\sigma_6$  were calculated for the axial directions for each of the elements for pressures of 0 and  $10^8$  Pa and the differences,  $\Delta\sigma_n$ , were taken. Proceeding on the admittedly oversimplified assumption that the net interatomic forces are a function of  $1/r_n^p$  for all interatomic distances in metal structures, the relationship between the changes in dimensions of the structural quadrics and the change in hydrostatic pressure may be expressed for cubic crystals in all directions as

$$\frac{\Delta\sigma_1}{r_1^p} + \frac{\Delta\sigma_2}{r_2^p} + \frac{\Delta\sigma_3}{r_3^p} + \frac{\Delta\sigma_4}{r_4^p} + \frac{\Delta\sigma_5}{r_5^p} + \frac{\Delta\sigma_6}{r_6^p} = 10^{-12} \text{ N } \text{Å}^{-2},$$

where  $10^{-12} \text{ N } \text{Å}^{-2}$  is the  $\Delta P$ ,  $10^8$  Pa. The  $\Delta P$  value used is immaterial because  $\Delta\sigma_n$  values are functions of the  $\Delta P$ . Similarly, the relationships for hexagonal and tetragonal crystals may be expressed in the same manner except that the numerical values of  $\Delta\sigma_n$  will be different for each crystallographic direction, with the limits in the [100] and [001] directions.

Using the calculated values of  $\sigma_n/r_n$ , with units of  $\text{Å}^{-2}$ , rather than  $\Delta\sigma_n$ , and the values of  $r_n$  at  $10^5$  Pa, values of  $p$ , referred to here as the compressibility exponent, were calculated by iteration for each of the elements. The results of those calculations are shown in Fig. 5, in which it is seen that the values now fall on nearly straight lines with a maximum in each period

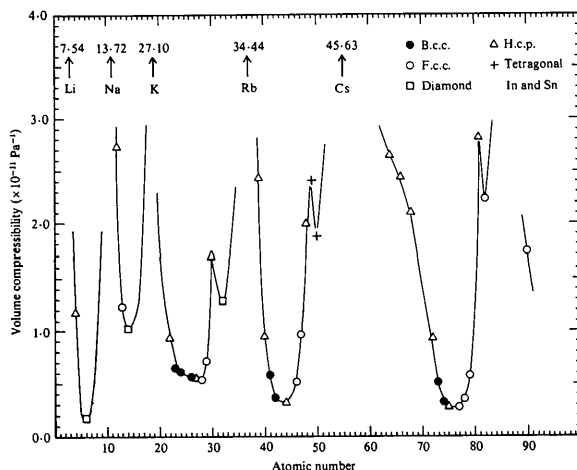


Fig. 4. Volume compressibilities of b.c.c., f.c.c., h.c.p., diamond, and tetragonal In and Sn, calculated from room-temperature elastic constants selected at random from Simmons & Wang (1971).

which coincides with the end of a transition series or, in the case of the second and third periods, with the appearance of molecular structures. The most remarkable feature of the calculated compressibility exponents is that they are independent of structure and, by inference, more directly related to the net interatomic forces. In effect, the influence of structure has been removed from the picture and the results indicate trends of a more fundamental type.

Assignment of one value of the exponent to all interatomic distances is certainly not valid, particularly for h.c.p. metals. For cubic crystals, there is no way to check the validity of the assumption at present. For h.c.p. metals, however, calculation of the exponents provided some interesting insights. If the assumption of one exponent for all distances in h.c.p. were correct, it may be assumed that the same value of  $p$  would be obtained by iteration in all directions. This was not strictly true, though the extreme values, those for the [100] and [001] directions were in nearly all cases within 1% of each other, the notable exceptions being Zn and Cd, which are not shown in Fig. 5. These will be treated in future work. In no case did the calculated exponents tend to converge with inclusion of additional terms, indicating that the differences are a measure of differences in forces operating between nearest neighbors and those between more distant neighbors.

The same calculations could have been carried out using values of  $\Delta\sigma_n$  rather than  $\Delta(\sigma_n/r_n)$ , the difference being merely that the values of the compressibility exponents would have been increased by 1. At this point, the distinction is not important. A quadric may be added to or subtracted from another quadric, multiplied by a constant, divided by a constant, raised to some power, or manipulated in several other ways and still be a quadric. The important fact is that single-crystal properties are some function or functions of the structural quadrics developed in this work and to be developed later and, once those functions are

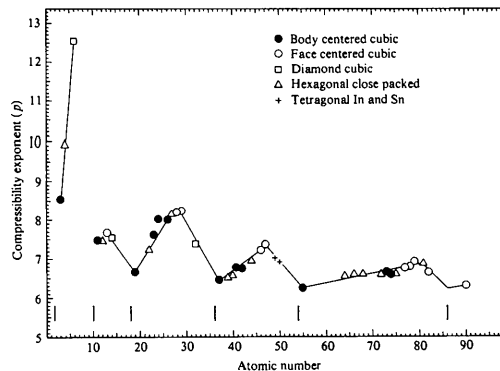


Fig. 5. Compressibility exponents of the elements calculated from the values shown in Fig. 4 and the normalized interaction factors for the appropriate structural type.

discerned, some important fundamental features of bonding and structure will be apparent. Structural quadrics should be a useful concept for future work in crystallography.

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## On the Statistics of Atomic Deviations from the 'Best' Molecular Plane

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### Abstract

An expression for the variance of a deviation of an atom from the best plane of the group to which the atom belongs has been derived and a practical procedure for obtaining the variance, while neglecting correlations between different atoms, is suggested.

One of the results of a structural study, particularly relevant for unsaturated or aromatic organic compounds, is the degree of planarity of a group of atoms. The deviations of the atoms from the best plane of the group are often interpreted in terms of interatomic and/or intermolecular forces, and in order to put such interpretations on a sound basis, it is often of interest to find out how significant these deviations really are. Since the statistics of deviation of atoms from the best plane, and their implementation in practical calculations, have not been, to the author's knowledge, discussed in the crystallographic literature, it was thought desirable to deal with this subject as described in what follows. This can, of course, be presented in a general and rigorous manner, *e.g.* by discussing the transformation of the variance-covariance matrix to the coordinate system of interest (Cramér, 1951). It seems, however, that the evaluation of the variance of an atomic position along a given direction is more appropriate to the level of approximation usually adopted in crystallographic studies.

The usual statistical treatments of the linear transformation of a vector of random variables, and its variance-covariance matrix, assume that all the quantities are referred to a Cartesian system (*e.g.* Linnik, 1961). This is not suitable for our purpose, since the transformations involved include, at least in part, a transition from the triclinic to a Cartesian system and *vice versa*, but can be readily modified as shown below.

We assume here that the frequency distribution of the position of an atom (the outcome of a least-squares refinement) obeys the trivariate normal law (*e.g.* Cruickshank, 1967), with the true position as the mean.

Let

$$\boldsymbol{\xi}^T = (\xi^1 \xi^2 \xi^3), \quad \mathbf{x}^T = (x^1 x^2 x^3) \quad (1)$$

be the possible (random) and mean atomic position vectors, expressed in contravariant components (Patterson, 1967). Then the expectation value

$$\mathbf{B} = E[(\boldsymbol{\xi} - \mathbf{x})(\boldsymbol{\xi} - \mathbf{x})^T] \quad (2)$$

is the variance-covariance matrix of such a position vector. In practice,  $B^{ij}$  is given by  $\lambda^{ij} \sigma(x^i) \sigma(x^j)$ , where  $\lambda^{ij}$  are the correlation coefficients and  $\sigma$  the estimated standard deviation.

Let now

$$\hat{\mathbf{k}}^T = (k_1 k_2 k_3) \quad (3)$$

be a constant unit vector, expressed in *covariant* components (in our case referred to the reciprocal-lattice basis vectors). The scalar product  $\hat{\mathbf{k}}^T(\boldsymbol{\xi} - \mathbf{x})$  is