

Site-symmetrized expressions of structure amplitudes. BY K. KURKI-SUONIO, *Department of Physics, University of Helsinki, Helsinki 17, Finland.*

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The deficiencies of the conventional structure-factor formalism based on spherical atoms are clearly seen if atomic site symmetry is included in the expressions. Fluorite, cuprite, iron nitride and the h.c.p. structure are given as important examples of the failure of the conventional expressions.

In diffraction studies of simple structures it is often possible to point out that definite components of the structure give rise to a certain class of reflexions because of destructive interference of the scattering by the other components. This seems to make direct conclusions on the state of the atoms without complicated analysis possible, on the basis of a few reflexions. In such connexions the conventional spherical atom expressions of structure amplitudes may lead to misinterpretation of data, because non-sphericities allowed by the atomic-site symmetry may violate the conventional extinction rules.

The site symmetry is emphasized by Dawson (1967*a*, 1969) in his general structure-factor formalism, and it is properly taken into account in the applications (Dawson, 1967*b, c, d*; Dawson, Hurley & Maslen, 1967; Dawson & Willis, 1967). It can, however, be included quite simply also in the conventional formalism, where we see most clearly the deficiencies of the spherical expressions. Generally, atoms of one kind *A* give the contribution

$$F_j^{(A)} = \sum f_n(\mathbf{b}_j) \exp \{2\pi i \mathbf{b}_j \cdot \mathbf{r}_n\} \quad (1)$$

to the structure amplitude F_j . Here $f_n(\mathbf{b})$ and \mathbf{r}_n are the scattering amplitude (temperature factor included) and the nuclear position, respectively, of the *n*th atom of the kind *A* in the unit cell. If all atoms *A* are assumed similar this is simply

$$F_j^{(A)} = f_A(\mathbf{b}_j) \sum \exp \{2\pi i \mathbf{b}_j \cdot \mathbf{r}_n\}, \quad (2)$$

and if they are at special positions, this will yield some extinction rule.

If the surroundings of the atoms are not identical, also the atoms themselves will differ, and a correction must be added in equation (2). If the site symmetries are completely different, this correction can never be assumed to vanish. If the surroundings differ only by orientation of the neighbours, the atoms will be related by simple transformations, and it is possible to reduce equation (1) to a form which includes the atomic factor of just one atom with different directions of \mathbf{b} . Thus, the correction can be understood as caused by certain deformations of the atom *A*. Especially, if the atom is not centrosymmetric the atomic factor will be complex with $f(-\mathbf{b}) = f^*(\mathbf{b})$, and the decomposition $f(\mathbf{b}) = \text{Re}f + i \text{Im}f$ corresponds to that of the atomic density into its symmetric and antisymmetric part. For instance, in the best known case of the diamond the failure of the conventional extinction rules is due to the non-vanishing imaginary part of the atomic factor, *cf.* Dawson (1967*b*).

Fluorite is another example with f.c.c. structure. It has the three atom structural unit: Ca at (0, 0, 0) F_A at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and F_B at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. The fluorine atoms have tetrahedral site symmetry and they are related by inversion. This yields

$$F_{hkl} = (\text{f.c.c.})^\dagger \times \left[f_{\text{Ca}} + 2\text{Re}f_{F_A} \cos \frac{\pi}{2}(h+k+l) + 2\text{Im}f_{F_A} \sin \frac{\pi}{2}(h+k+l) \right].$$

The extinction of the fluorine contribution in the 'odd' or calcium reflexions is, thus, never complete, since $\text{Im}f_{F_A}$ vanishes only when one of the indices is zero (*cf.* Kurki-Suonio & Meisalo, 1966).

Cuprite contains an f.c.c. lattice of copper and b.c.c. lattice of oxygen. The conventional expression is

$$F_{hkl} = (\text{f.c.c.}) \times f_{\text{Cu}} + (\text{b.c.c.}) \times f_{\text{O}} \exp \left\{ -i \frac{\pi}{2}(h+k+l) \right\},$$

while the correct site symmetrized expression can be written

$$F_{hkl} = f_{\text{Cu1}}(hkl) + f_{\text{Cu1}}(\bar{h}\bar{k}\bar{l}) \exp \{i\pi(k+l)\} + f_{\text{Cu1}}(h\bar{k}l) \exp \{i\pi(h+l)\} + f_{\text{Cu1}}(hk\bar{l}) \exp \{i\pi(h+k)\} + 2\text{Re}f_{\text{O}_A} \cos \frac{\pi}{2}(h+k+l) + 2\text{Im}f_{\text{O}_A} \sin \frac{\pi}{2}(h+k+l).$$

Again, the conventional extinction rules fail. The 'all-odd' or copper reflexions always contain a contribution from the asymmetry of oxygen. Similarly, the 'one-even, two-odd' or oxygen reflexions include a component due to deformation of copper atoms. Finally, the rule for complete extinction concerning the 'one-odd, two-even' reflexions is not exactly valid, since the deformation contribution from neither kind of atom will vanish, except when one of the indices is zero (*cf.* Kurki-Suonio, 1969).

For the cubic iron nitride (Fe_4N) we can write the conventional expression

$$F_{hkl} = (\text{f.c.c.}) \times f_{\text{Fe}} + f_{\text{N}} \exp \{i\pi(h+k+l)\}.$$

The three iron atoms at the face centres are related by symmetry, while the one at the origin has a different site symmetry. The general expression is

$$F_{hkl} = f_{\text{Fe1}} + f_{\text{N}} \exp \{i\pi(h+k+l)\} + f_{\text{Fe2}}(hkl) \exp \{i\pi(k+l)\} + f_{\text{Fe2}}(klh) \exp \{i\pi(h+l)\} + f_{\text{Fe2}}(lkh) \exp \{i\pi(h+k)\}.$$

† For brevity we use the notation

$$(\text{f.c.c.}) = \begin{cases} 4 & \text{for } hkl \text{ all even or all odd} \\ 0 & \text{for } hkl \text{ with mixed parity} \end{cases}$$

$$(\text{b.c.c.}) = \begin{cases} 2 & \text{for } (h+k+l) \text{ even} \\ 0 & \text{for } (h+k+l) \text{ odd.} \end{cases}$$

We see that the 'mixed parity' or nitrogen reflexions will always contain a potential contribution due to deformations of the iron atoms.

The unit cell of the h.c.p. structure contains two atoms in the positions $\pm(\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$. They have non-centrosymmetric positions related by inversion. Hence, the structure amplitudes are

$$F_{hkl} = 2\text{Re}f_A \cos \frac{\pi}{2} [\frac{1}{3}(h+2k)+1] \\ + 2\text{Im}f_A \sin \frac{\pi}{2} [\frac{1}{3}(h+2k)+l],$$

where the second term is the correction due to asymmetry of the atoms. The reflexions with $h \geq k \geq 0$ and $l \geq 0$ form a complete list of non-identical reflexions. In the reflexions of this list $\text{Im}f_A$ vanishes by symmetry only if $h=k$. According to the conventional extinction rule all reflexions with odd l and $h=k+3n$ (n is any integer) are forbidden. This is now exact only for $n=0$, all of the other 'forbidden' reflexions being regular though very weak.

No systematic search was made to find all critical cases. These examples are given just to show the rather obvious principle and to remind us about the dangers of the conventional expressions. The correction due to atomic deformations is small, of course, but it must not be assumed zero.

Unfortunately, elaborate collection of accurate data and careful analysis of them can scarcely be avoided if one wants to make sure about its significance.

This subject is treated in more detail in an internal report of the Department of Physics, University of Helsinki.

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