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INTERPRETATION OF SYSTEMATIC EXTRA-EXTINCTIONS

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ABSTRACT

Systematic absences other than space group absences in the reciprocal lattice (=systematic extra-extinctions) can be divided into two categories depending on their origin: (1) structural extinctions and (2) twinning extinctions. To obtain the characteristics of patterns in direct space from the structural extra-extinctions, a new method based on the Fourier transform of convolution has been developed. This approach through the convolution principle is very useful in interpreting not only the extra-extinctions but also the extra-symmetries in reciprocal space.

INTRODUCTION

In the study of crystal structures by x-rays, it is not rare to observe some systematic extinctions or symmetries in reciprocal space which cannot be interpreted simply by the space group criteria. These systematic extinctions or symmetries are called extra-extinctions or extra-symmetries.

In the studies of sulfides or sulfosalts the extra-extinctions and symmetries were found to be extremely common. It was, therefore, strongly desired to establish some systematic way to obtain characteristics of patterns in direct space which cause the extra-extinctions or symmetries in reciprocal space. This problem is expressed in the following way: What is the maximum information we can expect from extra-extinctions or symmetries in reciprocal space without using any information on reflection intensities?

All the extra-extinction and symmetry rules in reciprocal space have been described to belong to the following two groups:

(a) Rules caused by twinning. In this case, each crystallite in twinning is assumed to be large enough so that the diffracted x-rays from one crystallite are incoherent to those from other crystallites. Buerger (1960) explained some possible cases of this kind of extinctions and symmetries.

(b) Rules caused by special arrangements of atoms in crystal structures. Ito (1950) has found in many examples that the extra-extinctions or symmetries in reciprocal space take place by some local symmetries in direct space. The local symmetry is only effective within part of the structure and is different from the space group symmetry, which is effective over the whole structure.

In most cases it is possible to determine whether extra-extinction or symmetry rules are caused by twinning or by single crystals by examining many specimens of the material by x-rays and microscope (Buerger, 1960). Extra-extinction or symmetry rules caused by single crystals are, therefore, discussed in this paper.

GENERAL PRINCIPLE

For simplicity, only the extra-extinction rules will be discussed. When some extra-extinctions are observed in reciprocal space, it is always possible to find a larger reciprocal lattice or a *basic reciprocal lattice*, the extinction rules of which obey the usual space group extinction criteria. We call the reflections belonging to the basic reciprocal lattice *basic reflections*. The reflections which appear inside the basic lattice are called *additional reflections*. The space group derived from the weighted basic reciprocal lattice is generally different from the true space group for the crystal.

Any weighted reciprocal lattice A(s), including the basic and additional reflections, is expressed by a product of two functions—the lattice function, $\Sigma\delta(s-s_{hkl})$, and the function $F_0(s)$, which is the Fourier transform of the electron density in a unit cell of direct space, $\rho_0(r)$—as equation (1) in Fig. 1:

$$A(s) = \sum \delta(s - s_{hkl}) \cdot F_0(s) \qquad (1)$$

The drawings on the right-hand side are schematic representation of the formulas for a one-dimensional case. The electron density $\rho(r)$ in direct space is the

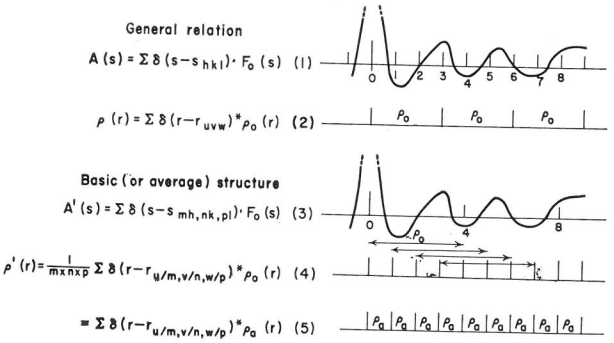

FIG. 1. General relations between A(s) and $\rho(r)$, and their schematic representations for a one-dimensional case.

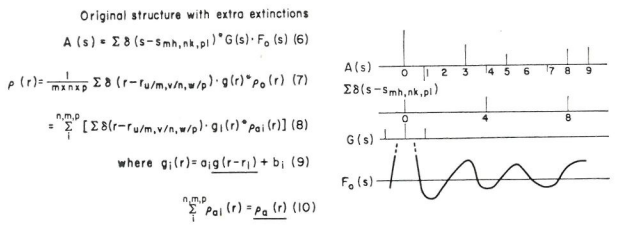

FIG. 2. The relations between A(s) and $\rho(r)$ for structures with extra-extinctions. The function used in formulas are schematically represented for a one-dimensional case.

Fourier transform of A(s), given by equation (2).

$$\rho(r) = \sum \delta(r - r_{u,v,w})^* \rho_0(r) \qquad (2)$$

In this formula $\Sigma\delta(r-r_{u,v,w})$ represents a lattice in direct space, and the asterisk represents convolution of two functions.

Assuming that the basic reflections have indices mh, nk, and pl, we will first consider a structure which only gives the basic reflections. This structure is called *basic structure* or *average structure*, which is different from the original structure with all observed reflections.

The weighted basic reciprocal lattice, A'(s), is expressed as equation (3) by using $F_0(s)$ of the original structure:

$$A'(s) = \sum \delta(s - s_{mh,nk,pl}) \cdot F_0(s) \qquad (3)$$

The electron density $\rho'(r)$ is given as equation (4):

$$\rho'(r) = \frac{1}{m \times n \times p} [\sum \delta(r - r_{u/m,v/p,w/p})]^* \rho_0(r) \qquad (4)$$

The basic lattice in direct space has a sub-cell, the unit translations of which are obtained by dividing those of the original lattice into m, n, and p parts along x, y, and z directions, respectively; ρ_0 represents, however, the electron density in the original cell. The electron density of the basic structure is, therefore, obtained by displacing $\rho_0(r)$ by the unit translation of the sub-cell and superposing all the $\rho_0(r)$'s. Thus the basic structure is a kind of average structure represented by using an average unit cell $\rho_a(r)$ as follows:

$$\rho'(r) = \sum \delta(r - r_{u/m,v/p,w/p})^* \rho_a(r) \qquad (5)$$

In order to find characteristic patterns of the original structure with extra-extinction rules, we can use two sources of information: (a) the average structure and (b) the special extinction rules. This can be done as follows.

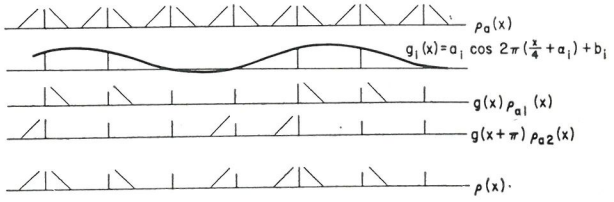

FIG. 3. The derivation of an original structure by means of g(r) and $p_a(r)$ for a simple one-dimensional case.

The weighted reciprocal lattice of the original structure is interpreted to consist of three functions as in equation (6) in Fig. 2. G(s) is a *satellite function* which connects each additional reflection to an appropriate basic reflection. The extra-extinction rules are implicitly expressed by this satellite function. The drawings on the right-hand side in Fig. 2 are schematic representation of the functions for a one-dimensional case. Then the original structure $\rho(r)$ is obtained as equation (7), using a modulation function g(r), the Fourier transform of G(s). If we define $g_i(r)$ and $\rho_{ai}(r)$ as in equations (9) and (10), respectively, by the known g(r) and $\rho_a(r)$, the original structure $\rho(r)$ is expressed as equation (8). The meaning of equation (8) is illustrated for the simple one-dimensional case in Fig. 3.

The average structure $\rho_a(x)$ is obtained by using only the basic reflections. The modulation function g(x) is obtained from G(s). After dividing $\rho_a(x)$ into two parts, $\rho_{a1}(x)$ and $\rho_{a2}(x)$, we apply to them g(x) and $g(x+\pi)$, respectively. The superposition of two patterns makes the final $\rho(r)$, which gives the extra-extinction.

In order to find the final $g_i(r)$ and $\rho_{ai}(r)$ from the known g(r) and $\rho_a(r)$, the intensity data of reflections become necessary. However, the consideration of the space group of the average structure and the original structure can usually limit the possible ways to derive $g_i(r)$ and $\rho_{ai}(r)$ from g(r) and $\rho_a(r)$, without any information on intensity data.

Extra-symmetries, instead of extra-extinctions, are sometimes observed in reciprocal space. The method, explained for the extra-extinctions, is also applicable on extra-symmetries.

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