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Rational Dependence and the Renormalization of Structure Factors for Phase Determination

By H. Hauptman and J. Karle

U.S. Naval Research Laboratory, Washington 25, D.C., U.S.A.

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The effect of rationally dependent atoms on phase determining formulas is described. This leads to a procedure for reinterpreting and modifying these formulas which is based upon the examination of subsets of the experimental data and a subsequent renormalization of structure factors. Although the nature of the renormalization is structure dependent, no previous structural knowledge is required for carrying out the procedure or computing phases. An example illustrating the features of rational dependence and renormalization is included.

1. Introduction

Since the appearance of our Monograph I (1953), we have endeavored to develop more general and effective phase determining procedures. This has culminated in a current series of papers under the title, 'A Unified Program for Phase Determination' (1959). In these papers exact formulas, valid for all the space groups, are presented which are applicable to structures containing dissimilar atoms as well as those consisting only of similar atoms. The single requirement for exact validity of the formulas is one which concerns a special kind of rational independence modulo 1 of atomic coordinates. Rational dependence occurs when the coordinates of atoms are rational or when they are rationally related to each other in a manner to be defined in § 2.

An integral part of the phase determining procedures previously developed was the introduction of the normalized structure factor $E_{\mathbf{h}}$ with the property that $\langle|E_{\mathbf{h}}|^2\rangle_{\mathbf{h}}=1$, where the average is taken over the set H consisting of all vectors $\mathbf{h}$ in reciprocal space. The characteristic effect of the existence of rational dependence is that $\langle|E_{\mathbf{h}}|^2\rangle_{\mathbf{h}}$ differs significantly from unity when the average is taken over certain subsets of H. Our first attempt to cope with the problem of rational dependence in phase determining relationships appeared in Chapter 5 of Monograph I (1953). In this chapter the nature of the subsets of H and the averages of the corresponding $|E_{\mathbf{h}}|^2$ were employed to infer the structural basis of the rational dependence. From this inference a type of renormalization of structure factors (equation (5·07), Monograph I) was carried out and employed in the phase determining relations (e.g. equation (5·13), Monograph I).

In this paper the renormalization is carried out without first inferring the structural origin of the rational dependence. This leads to a general procedure for renormalization, independent of the nature of the rational dependence, which has the advantage of not requiring a knowledge of the rationally dependent sets of atoms. It is of interest that the phase determining formulas of Monograph I (1953) and of the current series (1959) maintain their validity provided that the renormalization has first been carried out.

In this paper the nature and effect of rational dependence will be discussed by means of illustrative examples and the general treatment of experimental data will be described. It is important to consider this treatment of the data when the averages $\langle|E_{\mathbf{h}}|^2\rangle_{\mathbf{h}}$ taken over various subsets of H differ significantly from unity. Future experience will tell how frequently this occurs in structure determination. In view of the experimental restrictions on collecting scattering data and the tendency of the averages over low order reflections to exaggerate the effects of approximate rational dependence, the need for renormalization may be quite frequent.

2. Rational dependence modulo 1

A set of numbers $r_j, j=1, \ldots, \nu$ is said to be rationally dependent modulo 1 if there exist ν integers m_j, not all zero, such that

$$\sum_{j=1}^{\nu} m_j r_j = u \,, \qquad (2\cdot1)$$

where u is an integer and r_j will be identified later with x_j, y_j, or z_j. The only type of rational dependence which requires special treatment consists of the particular cases of (2·1) in which either $\nu=1$ or $\nu=2$ and $m_1=-m_2$. Atoms are said to be rationally dependent if their x or y or z coordinates satisfy (2·1) in the restricted sense just described. The simplest rationally dependent set, modulo 1, is given by a single atom whose coordinates are all rational, including therefore not only the case of an atom in a fixed special position, e.g. $\frac{1}{2}, \frac{1}{2}, 0$, but also the case of an atom having more general rational coordinates, e.g. $\frac{1}{2}, \frac{1}{3}, \frac{3}{4}$. An example of a rationally dependent pair is given by two atoms in general positions, having as the difference of any of their corresponding coordinates a rational number, e.g. $\mathbf{r}_1=(x, y, z)$ and $\mathbf{r}_2=$

$(x+\frac{1}{2}, y', z')$, since we may take $m_1=-m_2=2$ in (2·1) with $r_1=x$ and $r_2=x+\frac{1}{2}$; or e.g. $\mathbf{r}_1=(x, y, z)$ and $\mathbf{r}_2=(x+\frac{1}{2}, y-\frac{3}{4}, z+\frac{1}{3})$. In the first of these examples $\langle|E_{g00}|^2\rangle>1$, while $\langle|E_{u00}|^2\rangle<1$ (g means even and u means odd). In the case that $\mathbf{r}_1=(x, y, z)$ and $\mathbf{r}_2=(x, y', z')$, $\langle|E_{h00}|^2\rangle>1$.

3. Analysis

The effect of rational dependence is illustrated here for Σ_1 (Monograph I, 1953) of space group $P2/m$ by means of examples of increasing complexity, culminating in the most general case. At the same time the process of renormalization will be seen to be contained in the results of these calculations.

The final section 3·6 will be devoted to summarizing the nature of various phase determining formulas for all the space groups.

3·1. *No rational dependence*

For space group $P2/m$ the quasi-normalized structure factor $\mathscr{E}_{\mathbf{h}}(\mathbf{h}=(hkl))$ (Karle & Hauptman, 1959), is defined by

$$\mathscr{E}_{\mathbf{h}}=\frac{4}{\sigma_2^{1/2}}\sum_{j=1}^{N/4}Z_j\cos 2\pi(hx_j+lz_j)\cos 2\pi ky_j\,, \quad (3\cdot1\cdot1)$$

where

$$\sigma_n=4\sum_{j=1}^{N/4}Z_j^n; \quad (3\cdot1\cdot2)$$

N is the number of atoms per cell in non-rational positions and Z_j is the atomic number of the jth atom. From (3·1·1) it follows that

$$\langle\mathscr{E}_{\mathbf{h}}^2\rangle_k=\frac{4}{\sigma_2}\sum_{j=1}^{N/4}Z_j^2(1+\cos 4\pi(hx_j+lz_j)) \quad (3\cdot1\cdot3)$$

$$=1+\frac{\sigma_4^{1/2}}{\sigma_2}\cdot\frac{4}{\sigma_4^{1/2}}\sum_{j=1}^{N/4}Z_j^2\cos 4\pi(hx_j+lz_j)\,. \quad (3\cdot1\cdot4)$$

Therefore

$$\mathscr{E}'_{2h02l}=\frac{\sigma_2}{\sigma_4^{1/2}}\langle\mathscr{E}_{hkl}^2-1\rangle_k \quad (3\cdot1\cdot5)$$

where $\mathscr{E}'_{2h02l}$ is the quasi-normalized structure factor for the squared structure, i.e. the structure isomorphous to the given one in which Z_j is replaced by Z_j^2. It should be noted that (3·1·4) implies $\langle\mathscr{E}_{\mathbf{h}}^2\rangle_{\mathbf{h}}=1$.

3·2. *An additional atom at* 0, 0, 0

The quasi-normalized structure factor is now

$$\mathscr{E}_{\mathbf{h}}=\frac{1}{\sigma_2^{1/2}}\left(Z+4\sum_{j=1}^{N/4}Z_j\cos 2\pi(hx_j+lz_j)\cos 2\pi ky_j\right), \quad (3\cdot2\cdot1)$$

where

$$\sigma_n=Z^n+\sigma_n^*,\quad \sigma_n^*=4\sum_{j=1}^{N/4}Z_j^n\,. \quad (3\cdot2\cdot2)$$

From (3·2·1) it follows that

$$\langle\mathscr{E}_{\mathbf{h}}^2\rangle_k=\frac{1}{\sigma_2}\left\{Z^2+4\sum_{j=1}^{N/4}Z_j^2(1+\cos 4\pi(hx_j+lz_j))\right\}, \quad (3\cdot2\cdot3)$$

$$=1+\frac{\sigma_4^{*1/2}}{\sigma_2}\cdot\frac{4}{\sigma_4^{*1/2}}\sum_{j=1}^{N/4}Z_j^2\cos 4\pi(hx_j+lz_j)\,. \quad (3\cdot2\cdot4)$$

Therefore

$$\mathscr{E}_{2h02l}^*=\frac{\sigma_2}{\sigma_4^{*1/2}}\langle\mathscr{E}_{hkl}^2-1\rangle_k\,, \quad (3\cdot2\cdot5)$$

where $\mathscr{E}_{2h02l}^*$ is the quasi-normalized structure factor for the squared structure with the atom at the origin deleted. We note that (3·2·4) implies $\langle\mathscr{E}_{\mathbf{h}}^2\rangle_{\mathbf{h}}=1$.

3·3. *Additional atoms at* 0, 0, 0 *and* $\frac{1}{2}$, 0, 0

The quasi-normalized structure factor is now

$$\mathscr{E}_{\mathbf{h}}=\frac{1}{\sigma_2^{1/2}}\left\{Z+(-1)^hZ'+4\sum_{j=1}^{N/4}Z_j\times\cos 2\pi(hx_j+lz_j)\cos 2\pi ky_j\right\} \quad (3\cdot3\cdot1)$$

where

$$\sigma_n=Z^n+Z'^n+\sigma_n^*,\quad \sigma_n^*=4\sum_{j=1}^{N/4}Z_j^n\,. \quad (3\cdot3\cdot2)$$

From (3·3·1) it follows that

$$\langle\mathscr{E}_{\mathbf{h}}^2\rangle_k=\frac{1}{\sigma_2}\left\{(Z+(-1)^hZ')^2+4\sum_{j=1}^{N/4}Z_j^2\times(1+\cos 4\pi(hx_j+lz_j))\right\}, \quad (3\cdot3\cdot3)$$

$$=1+\frac{2}{\sigma_2}ZZ'(-1)^h+\frac{\sigma_4^{*1/2}}{\sigma_2}\cdot\frac{4}{\sigma_4^{*1/2}}\sum_{j=1}^{N/4}Z_j^2\cos 4\pi(hx_j+lz_j)\,. \quad (3\cdot3\cdot4)$$

Therefore

$$\mathscr{E}_{2h02l}^*=\frac{\sigma_2}{\sigma_4^{*1/2}}\left\langle\mathscr{E}_{hkl}^2-\left(1+\frac{2}{\sigma_2}ZZ'(-1)^h\right)\right\rangle_k, \quad (3\cdot3\cdot5)$$

where $\mathscr{E}_{2h02l}^*$ is the quasi-normalized structure factor for the squared structure with the atoms at 0, 0, 0 and $\frac{1}{2}$, 0, 0 deleted. Now we find that (3·3·4) implies that

$$\langle\mathscr{E}_{\mathbf{h}}^2\rangle_{gkl}=1+\frac{2}{\sigma_2}ZZ'\,, \quad (3\cdot3\cdot6)$$

$$\langle\mathscr{E}_{\mathbf{h}}^2\rangle_{ukl}=1-\frac{2}{\sigma_2}ZZ'\,, \quad (3\cdot3\cdot7)$$

while

$$\langle\mathscr{E}_{\mathbf{h}}^2\rangle_{\mathbf{h}}=1\,. \quad (3\cdot3\cdot8)$$

Equations (3·3·6) and (3·3·7) illustrate the characteristic effect of rationally dependent atoms, namely the deviation from unity of averages of $|\mathscr{E}_{\mathbf{h}}|^2$ over certain of the subsets of the indices. In view of (3·3·6) and (3·3·7), (3·3·5) may be written

$$\mathscr{E}_{2h02l}^*=\frac{\sigma_2}{\sigma_4^{*1/2}}\langle\mathscr{E}_{hkl}^2-\overline{\mathscr{E}^2}\rangle_k\,, \quad (3\cdot3\cdot9)$$

where

$$\overline{\mathscr{E}^2}=\langle\mathscr{E}^2\rangle_{gkl},\quad \text{if } h \text{ is even}, \quad (3\cdot3\cdot10)$$

and

$$\overline{\mathscr{E}^2}=\langle\mathscr{E}^2\rangle_{ukl},\quad \text{if } h \text{ is odd}. \quad (3\cdot3\cdot11)$$

Equation (3·3·9) may be rewritten

$$\mathscr{E}^*_{2h\,0\,2l} = \frac{\sigma_2\overline{\mathscr{E}^2}}{\sigma_4^{*1/2}}\left\langle \frac{\mathscr{E}^2_{hkl}}{\overline{\mathscr{E}^2}} - 1 \right\rangle_k \qquad (3\cdot3\cdot12)$$

and is of the same form as (3·1·5) and (3·2·5) with $\mathscr{E}_{hkl}$ replaced by the 'renormalized structure factor' $\mathscr{E}_{hkl}/(\overline{\mathscr{E}^2})^{1/2}$. The renormalized structure factor is obtained from $\mathscr{E}_{hkl}$ by dividing $\mathscr{E}_{hkl}$ by the root mean square of all the $\mathscr{E}$ over the subset to which $\mathscr{E}_{hkl}$ belongs, i.e., in this case, over the *gkl* if h is even and over the *ukl* if h is odd. In equations (3·1·5) and (3·2·5), $\overline{\mathscr{E}^2}$ is equal to unity when the average is taken over any subset defined in terms of the indices alone. In this sense the $\mathscr{E}_{hkl}$ in (3·1·5) and (3·2·5) may be regarded as special cases of renormalization. Although (3·3·12) illustrates the origin of the term 'renormalization', it will be convenient in what follows to use the equivalent form (3·3·9).

3·4. *Additional atoms at* 0, 0, 0; $\frac{1}{2}$, 0, 0 and 0, 0, $\frac{1}{2}$

The quasi-normalized structure factor is now

$$\mathscr{E}_{\mathbf{h}} = \frac{1}{\sigma_2^{1/2}}\left\{Z+(-1)^hZ'+(-1)^lZ'' + 4\sum_{j=1}^{N/4} Z_j \cos 2\pi(hx_j+lz_j)\cos 2\pi k y_j\right\}, \qquad (3\cdot4\cdot1)$$

where

$$\sigma_n = Z^n+Z'^n+Z''^n+\sigma_n^*,\quad \sigma_n^* = 4\sum_{j=1}^{N/4} Z_j^n\,. \qquad (3\cdot4\cdot2)$$

From (3·4·1) it follows that

$$\langle\mathscr{E}^2_{hkl}\rangle_k = \frac{1}{\sigma_2}\left\{[Z+(-1)^hZ'+(-1)^lZ'']^2 + 4\sum_{j=1}^{N/4} Z_j^2[1+\cos 4\pi(hx_j+lz_j)]\right\}, \qquad (3\cdot4\cdot3)$$

$$= 1+\frac{2}{\sigma_2}ZZ'(-1)^h+\frac{2}{\sigma_2}ZZ''(-1)^l+\frac{2}{\sigma_2}Z'Z''(-1)^{h+l} + \frac{\sigma_4^{*1/2}}{\sigma_2}\cdot\frac{4}{\sigma_4^{*1/2}}\sum_{j=1}^{N/4} Z_j^2\cos 4\pi(hx_j+lz_j)\,. \qquad (3\cdot4\cdot4)$$

Therefore,

$$\mathscr{E}^*_{2h\,0\,2l} = \frac{\sigma_2}{\sigma_4^{*1/2}}\langle\mathscr{E}^2_{hkl}-\overline{\mathscr{E}^2}\rangle_k\,, \qquad (3\cdot4\cdot5)$$

where $\mathscr{E}^*_{2h\,0\,2l}$ is the quasi-normalized structure factor for the squared structure with atoms at 0, 0, 0; $\frac{1}{2}$, 0, 0 and 0, 0, $\frac{1}{2}$ deleted. The $\overline{\mathscr{E}^2}$ is the appropriate one of

$$\langle\mathscr{E}^2\rangle_{gkg} = 1+\frac{2}{\sigma_2}(ZZ'+ZZ''+Z'Z'')\,, \qquad (3\cdot4\cdot6)$$

$$\langle\mathscr{E}^2\rangle_{gku} = 1+\frac{2}{\sigma_2}(ZZ'-ZZ''-Z'Z'')\,, \qquad (3\cdot4\cdot7)$$

$$\langle\mathscr{E}^2\rangle_{ukg} = 1+\frac{2}{\sigma_2}(-ZZ'+ZZ''-Z'Z'')\,, \qquad (3\cdot4\cdot8)$$

$$\langle\mathscr{E}^2\rangle_{uku} = 1+\frac{2}{\sigma_2}(-ZZ'-ZZ''+Z'Z'')\,, \qquad (3\cdot4\cdot9)$$

i.e. in (3·4·5) $\overline{\mathscr{E}^2}=\langle\mathscr{E}^2\rangle_{gkg}$ if h and l are both even, $\overline{\mathscr{E}^2}=\langle\mathscr{E}^2\rangle_{gku}$ if h is even and l is odd, etc. We note again that although the averages in equations (3·4·6)–(3·4·9) differ from unity, we still have $\langle\mathscr{E}^2_{\mathbf{h}}\rangle_{\mathbf{h}}=1$ where $\mathbf{h}$ ranges over all vectors in reciprocal space.

3·5. *General case*

The quasi-normalized structure factor, including additional atoms Z_{1j} in rational positions, is

$$\mathscr{E}_{\mathbf{h}} = \frac{1}{\sigma_2^{1/2}}\left\{\sum_{j=1}^{N_1} Z_{1j}\cos 2\pi(hx_{1j}+ky_{1j}+lz_{1j}) + 4\sum_{j=1}^{N/4} Z_j\cos 2\pi(hx_j+lz_j)\cos 2\pi k y_j\right\}, \qquad (3\cdot5\cdot1)$$

where

$$\sigma_n = \sum_{j=1}^{N_1} Z_{1j}^2+\sigma_n^*,\quad \sigma_n^* = 4\sum_{j=1}^{N/4} Z_j^n\,, \qquad (3\cdot5\cdot2)$$

and the N_1 atoms Z_{1j} constitute a rationally dependent set which causes significant deviations from unity in the averages of $\mathscr{E}^2_{\mathbf{h}}$ over certain subsets.

It follows from (3·5·1) that

$$\mathscr{E}^2_{hkl} = A_{hkl}+4\sum_{j=1}^{N/4} Z_j^2\cos 4\pi(hx_j+lz_j)(1+\cos 4\pi k y_j)+R\,, \qquad (3\cdot5\cdot3)$$

where

$$A_{hkl} = \frac{1}{\sigma_2}\left\{\left[\sum_{j=1}^{N_1} Z_{1j}\cos 2\pi(hx_{1j}+ky_{1j}+lz_{1j})\right]^2+\sigma_2^*\right\}, \qquad (3\cdot5\cdot4)$$

and R is a double summation which satisfies

$$\langle R\rangle_k = 0\,. \qquad (3\cdot5\cdot5)$$

Let $\mathbf{h}=(h,k,l)$ be equal to the fixed vector $\mathbf{h}_1=(h_1,k_1,l_1)$. We average both sides of (3·5·3) over all integers k such that $A_{h_1kl_1}=A_{h_1k_1l_1}$, obtaining

$$\langle\mathscr{E}^2_{h_1kl_1}\rangle_k = A_{h_1k_1l_1}+\frac{\sigma_4^{*1/2}}{\sigma_2}\mathscr{E}^*_{2h_1\,0\,2l_1} \qquad (3\cdot5\cdot6)$$

where $\mathscr{E}^*_{2h_1\,0\,2l_1}$ is the quasi-normalized structure factor for the squared structure with the N_1 atoms Z_{1j} deleted.

Consider all values of h, k and l such that

$$A_{hkl} = A_{h_1k_1l_1}\,. \qquad (3\cdot5\cdot7)$$

We now average both sides of (3·5·3) over this set of h, k and l, obtaining

$$\langle\mathscr{E}^2_{hkl}\rangle_{hkl} = A_{h_1k_1l_1}\,. \qquad (3\cdot5\cdot8)$$

Equation (3·5·6) may be rewritten in the form

$$\mathscr{E}^*_{2h_1\,0\,2l_1} = \frac{\sigma_2}{\sigma_4^{*1/2}}\langle\mathscr{E}^2_{h_1kl_1}-A_{h_1kl_1}\rangle_k\,, \qquad (3\cdot5\cdot9)$$

where it is clear from (3·5·8) that $A_{h_1k_1l_1}$ is an average of $\mathscr{E}^2_{hkl}$ over an appropriate set of indices. We replace k_1 in the above argument by k_2, k_3, ... in turn, and average over k_1, k_2, k_3, ..., obtaining finally

$$\mathscr{E}^*_{2h_1 0 2l_1}=\frac{\sigma_2}{\sigma_4^{*1/2}}\langle \mathscr{E}^2_{h_1 k l_1}-A_{h_1 k l_1}\rangle_k\,, \qquad (3\cdot5\cdot10)$$

where the average in (3·5·10) is now taken over all k, and for each fixed k_i,

$$A_{h_1 k_i l_1}=\langle \mathscr{E}^2_{hkl}\rangle_{hkl}\,, \qquad (3\cdot5\cdot11)$$

where the average in (3·5·11) is over all h, k, and l such that $A_{hkl}=A_{h_1 k_i l_1}$. Equation (3·5·10) represents the general case of renormalization for Σ_1 in space group $P2/m$.

3·6. Σ_2, Σ_3, *basic and integrated formulas*

The same methods for obtaining the formulas for Σ_1 in $P2/m$ in sections 3·1–3·5 may be employed to obtain similar formulas in the other space groups, including non-centrosymmetric space groups having centrosymmetric projections. The Sayre (1952) formula Σ_2 represented in algebraically exact form by

$$\mathscr{E}'_{\mathbf{h}}=\frac{\sigma_2}{\sigma_4^{1/2}}\langle \mathscr{E}_{\mathbf{k}}\mathscr{E}_{\mathbf{h}-\mathbf{k}}\rangle_{\mathbf{k}} \qquad (3\cdot6\cdot1)$$

is unaffected by rational dependence. Here $\mathscr{E}'_{\mathbf{h}}$ is the quasi-normalized structure factor for the entire squared structure.

On carrying through the derivation of Σ_3 by algebraic means in space group $P\bar{1}$, for example, the result is

$$\mathscr{E}^{**}_{\mathbf{h}}=\frac{\sigma_2^{3/2}}{\sigma_6^{*1/2}}\langle \mathscr{E}_{\mathbf{k}}(\mathscr{E}^2_{(\mathbf{h}+\mathbf{k})/2}-\overline{\mathscr{E}^2})\rangle_{\mathbf{k}}\,, \qquad (3\cdot6\cdot2)$$

where $\mathscr{E}^{**}_{\mathbf{h}}$ is the quasi-normalized structure factor for the cubed structure with the rationally dependent atoms deleted. As before, $\overline{\mathscr{E}^2}$ is the average value of $\mathscr{E}^2$ over the subset to which $\mathscr{E}^2_{(\mathbf{h}+\mathbf{k})/2}$ belongs.

The basic and integrated formulas for phase determination, derived by means of the probability methods employing averages over the indices (Hauptman & Karle, 1958; Karle & Hauptman, 1958; also the series on a unified program for phase determination, 1959 ff.), have exact validity if there is no rational dependence. In the case of rational dependence, we have found that these formulas require the same type of renormalization as that already described in sections 3·1–3·5. For example in the first of the papers concerned with a unified program for phase determination (Karle & Hauptman, 1959), the types of functions which appear in the averages over all indices are

$$\lambda_{p\mathbf{h}}=|\mathscr{E}_{\mathbf{h}}|^p-\mu_p\,, \qquad (3\cdot6\cdot3)$$

and

$$\Lambda_{t\mathbf{h}}=\frac{|\mathscr{E}_{\mathbf{h}}|^t-1}{\log|\mathscr{E}_{\mathbf{h}}|}-M_t\,, \qquad (3\cdot6\cdot4)$$

where

$$\mu_p=\langle|\mathscr{E}_{\mathbf{k}}|^p\rangle_{\mathbf{k}} \qquad (3\cdot6\cdot5)$$

and

$$M_t=\left\langle\frac{|\mathscr{E}_{\mathbf{k}}|^t-1}{\log|\mathscr{E}_{\mathbf{k}}|}\right\rangle_{\mathbf{k}}. \qquad (3\cdot6\cdot6)$$

In order to include the effect of rational dependence in these formulas to a first approximation, it is merely necessary to reinterpret the averages in (3·6·5) and (3·6·6) to mean that they are taken only over that subset $\mathbf{k}$ to which the corresponding $|E_{\mathbf{h}}|$ of (3·6·3) and (3·6·4) belongs. It should be noted that this is the only change introduced into the phase determining formulas, e.g. (3·1·1), (3·1·2), (3·2·1) and (3·2·2) of our paper (1959), since the $\mathscr{E}'$ in these formulas still refer to the quasi-normalized structure factors for the entire squared structure.

4. Procedure

It is assumed that in accordance with well-known procedures a list of the magnitudes of the normalized structure factors is available. In searching for subsets for which $\overline{|E|^2}$ differs significantly from unity it is convenient to have a listing in decreasing order of $|E|^2$. Each subset must be describable by means of one or more congruences of the following form

$$ah+bk+cl\equiv n\ (\mathrm{mod}\ m)\,, \qquad (4\cdot1)$$

where a, b, c and the prime factors of m are small integers (ordinarily <11). Whether a set of means $\overline{|E_i^2|}$ is to be considered a significant one requiring renormalization depends upon the magnitudes of the deviations from unity, the number of contributors, and the number of means in the set. In forming this evaluation, it is necessary to know that the standard deviation of $|E_{\mathbf{h}}|^2$ is $\sqrt{2}$ or 1 depending upon whether the distribution of $|E_{\mathbf{h}}|$ is centric or acentric. Then the respective standard deviations of the means are $(2/n)^{1/2}$ or $(1/n)^{1/2}$, where n is the number of contributors to the corresponding mean. Once significant subsets have been obtained, the averages, $\overline{|\mathscr{E}|^p}$ or $\overline{(|\mathscr{E}|^t-1)/\log|\mathscr{E}|}$, over these subsets, rather than over all reciprocal space, are employed in the phase determining formulas.

Table 1. *Averages over subsets for the mineral spurrite, space group $P2_1/a$, showing the need for renormalization*

Subsets	$\langle\mathscr{E}^2\rangle$	$\overline{\frac{(\lvert\mathscr{E}\rvert^3-1)}{\log\lvert\mathscr{E}\rvert}}$	n	$\sqrt{(2/n)}$
$g\,0\,l$, $h+l\equiv 0$ (mod 3)	3·344	8·955	42	0·22
$g\,0\,l$, $h+l\not\equiv 0$ (mod 3)	1·365	3·743	85	0·15
$g\,g\,l$, $h+l\equiv 0$ (mod 3)	2·462	6·557	81	0·16
$g\,g\,l$, $h+l\not\equiv 0$ (mod 3)	1·216	3·373	160	0·11
$u\,u\,l$, $h+l\equiv 0$ (mod 3)	1·531	4·173	97	0·14
$u\,u\,l$, $h+l\not\equiv 0$ (mod 3)	0·758	2·222	192	0·10
$h\not\equiv k$ (mod 2)	0·580	1·725	633	0·06
All data	1·017	2·859	1290	0·04

In this space group the normal value for $\langle\mathscr{E}^2\rangle_{g0l}$ is 2 while that for $\langle\mathscr{E}^2\rangle_{hkl}$ is 1. The third column contains averages suitable for use in the integrated formulas. The fourth column shows the number of elements in each subset

As an example, Table 1 illustrates our experience with the mineral spurrite. Reference to column 5 indicates that the various averages show significant deviations from their expected values. The subsets of

Table 1 were obtained by inspection of the experimental data previous to the structure determination. The employment of the averages of Table 1 facilitated the solution of the problem to be published at a future date. It is of interest that, in this case, the structural origin for the renormalization depends upon the presence of six rationally dependent atoms. Their position vectors, $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_6$ satisfy the following relations approximately

$$\mathbf{r}_2-\mathbf{r}_1 \approx \mathbf{r}_4-\mathbf{r}_3 \approx \mathbf{r}_6-\mathbf{r}_5 \approx (\tfrac{1}{3}, 0, \tfrac{1}{3}) , \quad (4\cdot2)$$

$$\mathbf{r}_1-\mathbf{r}_3 \approx (0, \tfrac{1}{2}, 0) , \quad (4\cdot3)$$

and

$$\mathbf{r}_1-\mathbf{r}_5 \approx (0, \tfrac{1}{4}, \tfrac{1}{4}) . \quad (4\cdot4)$$

5. Concluding remarks

As may be seen from the foregoing sections the treatment of the problem of rational dependence does not require a previous knowledge of structure. The renormalization procedure is based merely upon inspection of the averages of subsets. This process should be readily amenable to programming on automatic computing facilities.*

More general effects of rational dependence, which are included in (2·1) when $\nu=2$ and $m_1 \neq -m_2$ or $\nu>2$, change only the higher order terms in the phase determining formulas and therefore do not usually have a significant effect.

In general the average $\overline{E_{\mathbf{h}}^2}$ over all vectors in reciprocal space is unity, even for the case of rationally dependent atoms. However, when atomic coordinates overlap in projection, $\mathbf{E}_{\mathbf{h}}^2>1$ in that projection. With the finite number of data available from experiment this may cause a deviation from unity of the over-all average.

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* Since this paper was written, a program for renormalization has been developed by Dr Stanley Block of the National Bureau of Standards for the IBM 704.

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The Crystal Structure of Iron(II) Chloride Tetrahydrate

BY BRUCE R. PENFOLD* AND J. A. GRIGOR

Chemistry Department, University of Canterbury, Christchurch, New Zealand and School of Chemistry, University of Minnesota, Minneapolis 14, *Minnesota, U.S.A.*

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The crystal structure of iron(II) chloride tetrahydrate has been determined by means of electron-density projections down the three crystallographic axes. Atomic coordinates have been refined by three-dimensional least-squares treatment of the diffraction data of the three equatorial zones. The crystals are monoclinic, space group $P2_1/c$ with $a=5\cdot91$, $b=7\cdot17$, $c=8\cdot44$ Å, $\beta=112°\ 10'$. The structure consists of discrete $Fe(H_2O)_4Cl_2$ groups, two per unit cell. They are distorted octahedra and it is suggested that they are held together by O–H · · · Cl hydrogen bonds. Bond distances within a group are Fe–Cl, 2·38; Fe–O(1), 2·09; Fe–O(2), 2.59 Å.

1. Introduction

The available crystal structural data on hydrated metallic halides are extremely limited (e.g. see Wells, 1954). There are only about ten detailed structure determinations reported in the literature and of these, only three, namely cobalt(II) chloride dihydrate ($Co(H_2O)_2Cl_2$) (Vajnštejn, 1949), copper(II) chloride dihydrate ($Cu(H_2O)_2Cl_2$) (Harker, 1936 and Petersen & Levy, 1957), and copper(II) fluoride dihydrate ($Cu(H_2O)_2F_2$) (Geller & Bond, 1958) refer to simple salts of transition metals. Of general interest in such crystals are (*a*) the nature of the metal–halogen bonds, (*b*) the stereochemical requirements of the water molecule, and (*c*) the nature of the hydrogen bonding. We propose to undertake a study of the crystal structures of a series of hydrated iron(II) halides as a contribution to the crystal chemistry of hydrated halides generally. The tetrahydrates of the chloride and fluoride of iron(II) are both readily available and, as such

* Present address: Department of Chemistry, Harvard University, Cambridge 38, Massachusetts, U.S.A.