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A Method for Indexing Powder Photographs, Using Linear Diophantine Equations, and some Tests for Crystal Classes

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An extension in scope and directness of the Hesse method for indexing powder photographs can be made by direct solution of linear Diophantine equations. For most cases of tetragonal and hexagonal crystals the extended method demands much less ingenuity than the original procedure. In addition, some tests are devised to determine the crystal class by using Diophantine relations, and by tests for linear dependence of vectors in a linear vector space. The latter method is more general than the former and gives much more information concerning the crystal class.

Introduction

In a recent publication Hesse (1948) proposed a novel method for indexing powder photographs. The most important contribution by Hesse is the recognition that the value of $\sin^2\theta_i = q_i$ can be regarded as a kind of hyper-number, similar to a complex number. In particular, for the tetragonal and hexagonal classes, he sets

$$q_i = M_i A + N_i C,$$

where the symbols have the following significance:

	Tetragonal	Hexagonal
M	h^2+k^2	h^2+hk+k^2
N	l^2	l^2
A	$\frac{1}{4}\lambda^2/a_1^2$	$\frac{1}{3}\lambda^2/a_1^2$
C	$\frac{1}{4}\lambda^2/a_3^2$	$\frac{1}{4}\lambda^2/a_3^2$

Further, he notes that A and C can be regarded as analogues of 1 and $\sqrt{(-1)}$ of complex numbers so that q_i can be represented by the quantities M_i and N_i, i.e.

$$q_i = [M_i, N_i].$$

Then, provided A and C are incommensurate, an equation relating several of the q's, with m_i integers,

$$m_1 q_1 + m_2 q_2 + m_3 q_3 + \ldots = 0, \quad (1)$$

requires that

$$m_1 M_1 + m_2 M_2 + m_3 M_3 + \ldots = 0, \quad (2a)$$

$$m_1 N_1 + m_2 N_2 + m_3 N_3 + \ldots = 0. \quad (2b)$$

In addition he shows that an equation

$$m_1 q_1 = m_2 q_2, \quad (3)$$

which implies

$$m_1 M_1 = m_2 M_2, \quad (3a)$$

$$m_1 N_1 = m_2 N_2 \quad (N_1 = l_1^2,\ N_2 = l_2^2), \quad (3b)$$

requires that $l_1 = l_2 = 0$ if m_1 and m_2 are relatively prime and not both squares.

From these relations a relatively systematic procedure for indexing hexagonal and tetragonal powder photographs follows. It is the purpose of this paper to extend the method somewhat in scope and in directness for these classes, so that the solution can be obtained with little exercise of ingenuity once relations of the form (1) and (3) have been found. A criterion is also developed for assigning a crystal to one of three types: (*a*) cubic; (*b*) tetragonal, hexagonal; (*c*) orthorhombic, monoclinic, triclinic. A more direct method for indexing tetragonal and hexagonal patterns also follows. Finally, an even more powerful test for crystal class is developed, based on linear dependence of vectors in a linear vector space.

General theory

It will be assumed that relations of the form (1) have been found and fall within the possible limits of error for the q values as noted by Hesse. Quite generally we have

$$q_i = \tfrac{1}{4}\lambda^2 |\,h\,|^2$$
$$= \tfrac{1}{4}\lambda^2(h_i^2 b_1^2 + k_i^2 b_2^2 + l_i^2 b_3^2 + h_i k_i 2b_1 b_2 \cos\beta_3 + h_i l_i 2b_1 b_3 \cos\beta_2 + k_i l_i 2b_2 b_3 \cos\beta_1), \quad (4)$$

in which the b's are reciprocal-axis lengths and the β's are reciprocal-lattice axial angles. The quadratic form in parentheses in the right-hand member of (4) represents a vector in the six-space with elements e_1, e_2, e_3, e_4, e_5 and e_6,

$$q_i = \tfrac{1}{4}\lambda^2(h_i^2 e_1 + k_i^2 e_2 + l_i^2 e_3 + h_i k_i e_4 + h_i l_i e_5 + k_i l_i e_6). \quad (5)$$

The basis elements e_i are

$$\left.\begin{aligned} e_1 &= b_1^2, & e_4 &= 2b_1 b_2 \cos\beta_3, \\ e_2 &= b_2^2, & e_5 &= 2b_1 b_3 \cos\beta_2, \\ e_3 &= b_3^2, & e_6 &= 2b_2 b_3 \cos\beta_1. \end{aligned}\right\} \quad (6)$$

We assume that the e_j forms a linearly independent set, i.e. no relation of the form

$$m_1 e_1 + m_2 e_2 + m_3 e_3 + m_4 e_4 + m_5 e_5 + m_6 e_6 = 0 \quad (7)$$

exists with the m's integers and not all equal to zero. This requirement is met except for cases such as a tetragonal crystal having $a_1 = a_3$, or an orthorhombic crystal having $a_1 = a_2$, or $a_1 = \sqrt{3}\, a_2$ (pseudo-hexagonal). If these exceptions occur, the crystal will be assigned a higher symmetry, but this is inevitable if powder methods only are used.

If two of the bases, such as e_1 and e_2, become equal, they are to be considered as identical. With this in mind we can list the form for the e's for the various crystal classes as shown in Table 1.

In the preceding argument we assumed that a relation of form (3) could be found for triclinic, monoclinic and orthorhombic crystals with non-degenerate e values. This leads to the contradiction that both q numbers must vanish. Accordingly we conclude that a relation of form (3) is impossible for these three crystal classes if the e bases are non-degenerate. On the other hand, equations of the following forms:

Table 1. *Form of e's for the various crystal classes*

	e_1	e_2	e_3	e_4	e_5	e_6
Cubic	b_1^2	b_1^2	b_1^2	0	0	0
Tetragonal	b_1^2	b_1^2	b_3^2	0	0	0
Hexagonal	b_1^2	b_1^2	b_3^2	b_1^2	0	0
Orthorhombic	b_1^2	b_2^2	b_3^2	0	0	0
Monoclinic	b_1^2	b_2^2	b_3^2	0	$2b_1b_3\cos\beta_2$	0
Triclinic	b_1^2	b_2^2	b_3^2	$2b_1b_2\cos\beta_3$	$2b_1b_3\cos\beta_2$	$2b_2b_3\cos\beta_1$

Following this convention, the q values for a cubic crystal would be $q = \frac{1}{4}\lambda^2(h^2+k^2+l^2)\,e_1$, and similarly for the other cases.

We can now devise a test for crystal classes. Suppose we find relations of the form (3) with m_1 and m_2 containing no common factor and not both squares. It follows that the crystals cannot be orthorhombic, monoclinic, or triclinic. An equation of type (3), $m_1q_1 = m_2q_2$, requires

$$m_1h_1^2 = m_2h_2^2, \tag{8-1}$$

$$m_1k_1^2 = m_2k_2^2, \tag{8-2}$$

$$m_1l_1^2 = m_2l_2^2, \tag{8-3}$$

$$m_1h_1k_1 = m_2h_2k_2, \tag{8-4}$$

$$m_1h_1l_1 = m_2h_2l_2, \tag{8-5}$$

$$m_1k_1l_1 = m_2k_2l_2. \tag{8-6}$$

Assuming that there are no accidental coincidences in e values, there will be six equations, (8-1) to (8-6) inclusive, for a triclinic crystal. For a monoclinic crystal e_4 and e_6 vanish and only (8-1), (8-2), (8-3), and (8-5) enter consideration. An orthorhombic crystal has $e_4 = e_5 = e_6 = 0$ and only (8-1) to (8-3) inclusive need be considered.

The equations (8-1) to (8-3) have no solution in integers other than the trivial one

$$h_1 = h_2 = k_1 = k_2 = l_1 = l_2 = 0.$$

This in turn requires

$$h_1k_1 = h_2k_2 = h_1l_1 = h_2l_2 = k_1l_1 = k_2l_2 = 0$$

and $$q_1 = q_2 = 0.$$

Thus

$$q_1 = \tfrac{1}{4}\lambda^2(h_1^2e_1+k_1^2e_2+l_1^2e_3+h_1k_1e_4+h_1l_1e_5+k_1l_1e_6) = 0,$$

and similarly for q_2. This contradicts the fact that q_1 and q_2 are not zero. This general proof for the triclinic case includes the monoclinic and orthorhombic classes as special cases. For the latter two we merely omit from consideration (8-4) and (8-6), or (8-4) to (8-6) inclusive. This is equivalent to setting the corresponding e numbers equal to zero.

$$m_1(h_1^2+k_1^2) = m_2(h_2^2+k_2^2), \tag{9-1}$$

$$m_1(h_1^2+k_1^2+l_1^2) = m_2(h_2^2+k_2^2+l_2^2), \tag{9-2}$$

and $$m_1(h_1^2+h_1k_1+k_1^2) = m_2(h_2^2+h_2k_2+k_2^2), \tag{9-3}$$

with m_1 and m_2 containing no common factor, and not both squares, do have non-trivial solutions. The cubic case corresponding to (9-2) is readily distinguished by its simplicity of form and needs no further discussion. Hence we see that if the e values are independent, the presence of equations of type (3) permits the crystals to be assigned to one of three types: (*a*) cubic; (*b*) tetragonal or hexagonal; (*c*) orthorhombic, monoclinic, or triclinic. If no such relations are found after exhaustive search, it is likely, but not certain, that the crystals are of type (*c*).

Some discussion of the effect of accidental coincidences of the e values is desirable. Suppose we consider the triclinic case and let $e_4 = e_5 = e_6$. The test still succeeds since these coincidences leave equations (8-1) to (8-3) unchanged; these have only the trivial solution, and we are led to the contradiction $q_1 = q_2 \equiv 0$ as before.

Suppose $e_4 = e_1$, $e_6 = e_2$, and that e_1, e_2, e_3, e_4 are independent. Then a relation (3) requires

$$m_1(h_1^2+h_1k_1) = m_2(h_2^2+h_2k_2),$$
$$m_1(k_1^2+k_1l_1) = m_2(k_2^2+k_2l_2),$$
$$m_1l_1^2 = m_2l_2^2,$$
$$m_1h_1l_1 = m_2h_2l_2.$$

The third of these relations requires that $l_1 = l_2 \equiv 0$. This reduces the second relation to

$$m_1k_1^2 = m_2k_2^2,$$

which requires $k_1 = k_2 \equiv 0$. Finally this reduces the first relation to $$m_1h_1^2 = m_2h_2^2,$$

which also has only the trivial solution $h_1 = h_2 \equiv 0$. In this case the test still succeeds. Another set of coincidences which can be resolved in the same manner and for which the test succeeds is the following: e_1 independent, $e_2 = e_4 = e_5 \mp e_1$, $e_3 = e_6 \mp e_1$ or e_2.

A particular coincidence of e values for which the present test fails is the following: $e_1 = e_4$, $e_2 = e_6$, and

$e_3 = e_5$. Non-trivial solutions for the resulting Diophantine equations can be found.

Enhancement of symmetry

Some accidental coincidences of the e values can lead to an apparent increase of symmetry, not in its true sense, but with respect to the metrical properties of the unit cell. The powder method, if unaided by other observations, provides measurements only of the metrical properties of unit cells, and it might be desirable to introduce the idea of powder symmetry classes.

Suppose that we had a rhombohedral cell with reciprocal-axis angles equal to 60°. The crystal cell then has tetrahedral angles and corresponds to the primitive cell of a body-centered cubic cell. We might inquire whether or not these cases could be distinguished by powder methods. The general rhombohedral cell is expressible in terms of two bases e_1 and e_4, whereas the cubic cell requires only one base e_1. Clearly, if $b_1 = b_2 = b_3$, $\beta_1 = \beta_2 = \beta_3 = 60°$, the general quadratic form requires only one e base. However, a complete proof that this is representable by a cubic cell is desirable.

For the special case of the rhombohedral cell above $e_1 = e_2 = e_3 = e_4 = e_5 = e_6$, and the quadratic form becomes $(h^2+k^2+l^2+hk+kl+lh)\,e_1$. We may wonder whether or not this quadratic form can ever assume a value corresponding to one of the 'forbidden lines' of a cubic pattern. It is well known that integers of the form $(8r+7)\,4^s$ cannot be represented as a sum of the squares of three integers. The three square terms in the quadratic form above cannot represent such numbers, but we may wonder whether the cross product terms would make this possible for a rhombohedral cell so that it could be distinguished from a cubic cell. This cannot occur.

The quadratic form $(h^2+k^2+l^2+hk+kl+lh)$ is positive definite, i.e. it is always positive, and can be zero only when $h = k = l = 0$. It is always possible to transform such a form into a sum of squares with each square having the same multiplier, g. Thus the form is reducible to $g(H^2+K^2+L^2)$. In addition, this particular form is one such that (H, K, L) will also be integers, and g has a value $\frac{1}{2}$. The multiplier g is combined with e_1 (rhombohedral) giving $\frac{1}{2}e_1$ the basis element for the cubic representation:

$$\begin{aligned}(h^2+k^2+l^2+hk+kl+lh)\,e_1 &= \tfrac{1}{2}(H^2+K^2+L^2)\,e_1\\ &= (H^2+K^2+L^2)\,e_1'.\end{aligned}$$

Thus we see that the rhombohedral cell is metrically equivalent to a cubic cell and is indistinguishable by powder methods alone (at a fixed temperature, etc.). If other data—such as optical data—were available, the ambiguity might be resolved.

A similar case is provided by a rhombohedral cell with the crystal cell angle 60°, which has tetrahedral reciprocal-cell angles. This is equivalent to a face-centered cubic cell and would be indexed as such using only powder data. The rhombohedral quadratic form for this case is

$$(h^2+k^2+l^2-\tfrac{2}{3}hk-\tfrac{2}{3}kl-\tfrac{2}{3}lh)\,e_1,$$

which can be reduced to $\frac{1}{3}(H^2+K^2+L^2)\,e_1$ in cubic form. A recent report shows that precisely this case has occurred for NiO. This has long been called cubic with the NaCl structure, but the recent investigation by Rooksby (1948) shows that line splitting occurs as the temperature is lowered and that the lattice is really rhombohedral. At higher temperatures degeneracy occurs with an apparent increase in powder symmetry.

Solution of linear Diophantine systems

There is a well-known theorem concerning equations of the forms

$$m_1x+m_2y = m_3z \tag{10-1}$$

and

$$m_1x^*+m_2y^* = 1, \tag{10-2}$$

when we require the values of m_1, m_2, m_3, x, y, z to be integers. The second equation (10-2), which might be called a reduced equation, is obtained by setting $m_3z = 1$ in equation (10-1). The corresponding integral solutions x, y of the reduced equation, if such exist, are denoted by x^*, y^*. The theorem states that if m_1 and m_2 (integers) contain no common factor, and if m_3z is not zero, then there are an infinite number of integral solutions x, y, z for such equations. The solutions for the general equation (10-1) can be constructed from the general solutions of the reduced equation (10-2). Particular solutions of (10-2) can be found by inspection or by the Euclidean division algorithm (Fine, 1904, pp. 212, 342; Wright, 1939, pp. 3–6).

Let x^0, y^0 be a particular solution of (10-2), i.e. some pair of integers satisfying (10-2) with m_1, m_2 relatively prime. Then the general solution of the reduced equation (10-2) is

$$x^* = x^0-m_2t, \tag{11-1}$$

$$y^* = y^0+m_1t, \tag{11-2}$$

where t is any integer. It follows that the general solution of (10-1) is

$$x = m_3zx^* = m_3z(x^0-m_2t), \tag{12-1}$$

$$y = m_3zy^* = m_3z(y^0+m_1t). \tag{12-2}$$

Since x^0, y^0, m_1, m_2, m_3, t, z are integers, the values of x, y will also be integral.

This method can be used to solve equations of the form (2), expressing all of the remaining M's and N's in terms of some M_i and N_j which are known to be different from zero. In the example to follow, only three-term equations like (10-1) were used, but methods for four- and higher-term equations are equally simple. When solving equations of the form (10-1) it must be remembered that m_1 and m_2 must have no common factor if the previous methods are to apply. In the event that m_1 and m_2 have a common factor, then either (*a*) the factor common to m_1, m_2 must also be a factor of m_3z, or (*b*) no integral solution other than $x = y = z = 0$ exists. These facts are of use in solving equations of the form $m_1M_1+m_2M_2 = m_3M_3$. This case may arise for a tetragonal or hexagonal crystal with few powder lines so that no equations of form (3) are found, or if the q values related by an equation of form (3) appear in no other equations.

Tetragonal and hexagonal crystals

To demonstrate the method, we will use the data and relations presented by Hesse (1948) for the substance W_2B. These data and relations are:

$$q_1 = 0{\cdot}0847,\quad q_4 = 0{\cdot}2698,\quad q_7 = 0{\cdot}4025,$$
$$q_2 = 0{\cdot}1694,\quad q_5 = 0{\cdot}3179,\quad q_8 = 0{\cdot}4229,$$
$$q_3 = 0{\cdot}2334,\quad q_6 = 0{\cdot}3384,\quad q_9 = 0{\cdot}5724,$$

for which Hesse found the independent relations

$$(a)\ 2q_1 = q_2,\qquad (d)\ q_1+q_5 = q_7,$$
$$(b)\ q_1+q_3 = q_5,\qquad (e)\ q_1+q_6 = q_8.$$
$$(c)\ 2q_2 = q_6,\qquad (f)\ q_2+q_7 = q_9,$$

and the dependent relations

$$(g)\ q_6 = 4q_1,\qquad (i)\ q_8 = 5q_1,$$
$$(h)\ q_7 = q_3+2q_1,\qquad (j)\ q_9 = q_3+4q_1.$$

We note that no relation including q_4 was discovered.

First we note that relations (a), (c), (g) and (i) are of form (3), and hence we conclude that the crystals are cubic, tetragonal, or hexagonal. The cubic case is ruled out since the q's are not of the form $\frac{1}{4}\lambda^2 b_1^2(h^2+k^2+l^2)$. Accordingly only the tetragonal and hexagonal classes remain for consideration, but no assumption need be made as to whether it is one or the other.

On the basis of (a), (c), (g) and (i) we find

$$q_1 = [M_1, 0],\ q_2 = [M_2, 0],\ q_6 = [M_6, 0],\ q_8 = [M_8, 0],$$

exactly as Hesse did. We now solve for the other M's in terms of M_1, the smallest non-zero M. Clearly M_1, M_2, M_6 and M_8 cannot be zero, since the contrary assumption requires $q_1 = q_2 = q_6 = q_8 = 0$.

Relations (b), (d) and (f) require

$$N_3 = N_5 = N_7 = N_9,$$

since $N_1 = 0$, and we have

$$q_3 = [M_3, N_3],\quad q_7 = [M_7, N_3],$$
$$q_5 = [M_5, N_3],\quad q_9 = [M_9, N_3].$$

Next we solve equation (b): $q_1+q_3 = q_5$.

$$-M_3+M_5 = M_1, \tag{13-1}$$
$$-M_3^*+M_5^* = 1. \tag{13-2}$$

A particular solution of (13-2), found by inspection, is $M_3^0 = 0$, $M_5^0 = 1$. Then

$$M_3^* = M_3^0+t = t,$$
$$M_5^* = M_5^0+t = 1+t,$$

and $$M_3 = M_1 t,\qquad q_3 = [M_1 t, N_3],$$
$$M_5 = M_1(1+t),\quad q_5 = [M_1(1+t), N_3].$$

Similarly we solve equation (d): $q_1+q_5 = q_7$; finding $M_5 = M_1 t'$ and $M_7 = M_1(1+t')$. By the previous step $M_5 = M_1(1+t)$ and we find $t' = 1+t$. Then

$$M_7 = M_1(2+t)\quad\text{and}\quad q_7 = [M_1(2+t), N_3].$$

Equation (f) leads to

$$M_2 = M_7 t'\quad\text{and}\quad M_9 = M_7(1+t')$$

and hence to

$$M_2 = M_1 t'(2+t),\quad M_9 = M_1(1+t')(2+t).$$

We further see that t' must be unity or greater; t' cannot be zero since M_2 cannot be zero ($N_2 = 0$). The forms of q_2 and q_9 are

$$q_2 = [M_1 t'(2+t), 0]\quad\text{and}\quad q_9 = [M_1(1+t')(2+t), N_3].$$

Solving equation (e) we find

$$q_6 = [M_1 t'', 0]\quad\text{and}\quad q_8 = [M_1(1+t''), 0],$$

and we note that t'' must be unity or greater. Finally equation (j) leads to

$$M_3 = M_1 4t'''\quad\text{and}\quad M_9 = M_1 4(1+t''').$$

In previous steps we found

$$M_3 = M_1 t\quad\text{and}\quad M_9 = M_1(1+t')(2+t).$$

Equating these separate results we have relations between the various t's:

$$4t''' = t\quad\text{and}\quad 4(1+t''') = (1+t')(2+t).$$

Replacing t by $4t'''$ in the second and rearranging, we have

$$t' = \frac{2}{2+4t'''}.$$

The only value of t''' which permits t' to be an integer is $t''' = 0$. Hence $t''' = 0$, $t = 0$, $t' = 1$. Solving equation (g) (or by inspection) we find $M_6 = 4M_1 = t''M_1$, so that $t'' = 4$. Hence $M_8 = M_1(1+t'') = 5M_1$.

The form of all q's except q_4 is now determined:

$$q_1 = [M_1, 0],\qquad q_6 = [4M_1, 0],$$
$$q_2 = [2M_1, 0],\qquad q_7 = [2M_1, N_3],$$
$$q_3 = [0, N_3],\qquad q_8 = [5M_1, 0],$$
$$q_5 = [M_1, N_3],\qquad q_9 = [4M_1, N_3].$$

The sequence of M values corresponds to a tetragonal crystal with $M_1 = 1, 2, 4, 5, 8, 9, \ldots$

$$M_1 = 1\quad (h,k) = (1,0),$$
$$M_1 = 2\quad (h,k) = (1,1),$$
$$M_1 = 4\quad (h,k) = (2,0),$$
etc.,

and with $N_3 = l^2 = 1, 4, 9, \ldots$. Clearly N_3 cannot be zero since $M_3 = 0$. The sequence of M values does not match any sequence for a hexagonal crystal.

To determine which choice of M_1 and N_3 is the simplest permissible, it is necessary to introduce q_4 into the scheme. Diligent search would lead to the equation $10q_1+q_3 = 4q_4$. If this relation had not been found, we could proceed by a trial-and-error procedure.

First we note that

$$q_4 = 0{\cdot}2698\quad\text{and}\quad q_3 = [0, N_3] = 0{\cdot}2334,$$

and conclude that q_4 is not of the form $[0, mN_3]$ nor of the form $[0, l_4^2]$ for any small values of l_3 and l_4. We also note that q_4 is not of the form $[M_4, 0]$ if M_4 and M_1 are any of the small integers of the form a^2+b^2. Accordingly we conclude that q_4 must be of the form $[M_4, N_4]$. If we let M_1 and N_3 assume possible low-order values, we find that the pair (M_1, N_3) equal to $(2,4)$ permits q_4 to be fitted to the form $\left[5\frac{M_1}{2}, \frac{N_3}{4}\right]$ and the problem is solved.

$$\begin{array}{llll} q_1 = [2,0] & (110) & q_6 = [8,0] & (220) \\ q_2 = [4,0] & (200) & q_7 = [4,4] & (202) \\ q_3 = [0,4] & (002) & q_8 = [10,0] & (310) \\ q_4 = [5,1] & (211) & q_9 = [8,4] & (222) \\ q_5 = [2,4] & (112) & & \end{array}$$

Additional useful relations

If we find a pair of relations of the form

$$q_1+q_2 = q_3, \quad q_2+q_3 = q_4, \tag{14}$$

then the crystals cannot be orthorhombic, monoclinic, or triclinic, but can be cubic, tetragonal, or hexagonal. This follows from a well-known theorem (Carmichael, 1915, p. 14) concerning simultaneous Diophantine forms. The theorem states that the equations

$$x^2+y^2 = z^2, \quad y^2+z^2 = t^2 \tag{15}$$

have no solution in integers unless at least one is zero. The only integral solutions are $y = 0$, $x = z = t$, and $x = y = z = t = 0$. The remainder of the proof follows that given for equations of type (3). That cubic, tetragonal and hexagonal crystals can satisfy the equations (14) is easily verified. The proof that cubic and tetragonal crystals can satisfy the simultaneous equations (14) follows from the theorem that any integer is expressible as a sum of four squares.

When hexagonal crystals satisfy the simultaneous equations (14), they also simultaneously satisfy a more severe set of conditions. It can easily be verified by inspection that if the first pair of the following equations are satisfied then the second pair can also be satisfied for some set of integers which satisfy the first pair:

$$\left.\begin{aligned} (h_1^2+h_1k_1+k_1^2)+(h_2^2+h_2k_2+k_2^2) &= (h_3^2+h_3k_3+k_3^2), \\ (h_2^2+h_2k_2+k_2^2)+(h_3^2+h_3k_3+k_3^2) &= (h_4^2+h_4k_4+k_4^2), \\ h_1+h_2 &= h_3+k_3, \\ h_2+h_3 &= h_4+k_4. \end{aligned}\right\} \tag{16}$$

An example of a solution to the above equations is

$$(h_1, k_1) = (0,1), \quad (h_2, k_2) = (4, -2),$$
$$(h_3, k_3) = (1,3) \quad \text{and} \quad (h_4, k_4) = (5,0).$$

Linear dependence relations

In the first section of this paper it was shown that the numbers q can be regarded as vectors in a linear vector space of one, two, three, four, or six dimensions corresponding to the cubic, tetragonal or hexagonal, orthorhombic, monoclinic, and triclinic classes of crystals. This implies that the maximum number of linearly independent vectors (q numbers) is equal to the dimensionality of the vector space. Thus, if the crystal is cubic, all of the q numbers can be expressed as a rational multiple of any one of the q numbers. For a tetragonal (or hexagonal) crystal, rational linear combinations of two q numbers will generate all the remaining q numbers. Corresponding combinations of three, four, or six q numbers will generate all the q numbers for the orthorhombic, monoclinic, or triclinic classes if the e numbers are non-degenerate. These considerations make possible a direct test for crystal classes which is distinct from the previous tests based on Diophantine forms and is more powerful than the previous tests since any relations of form (1) will serve; special relations of form (3) are not needed.

To perform the test we obtain all of the q numbers as before and obtain *all independent* relations of form (1). For the present purpose we include more relations than are used for the analysis using Diophantine forms. In particular we include relations among four or more of the q numbers (which satisfy the predetermined limits of error), so that the maximum possible number of relations is at hand. If the number of q numbers exceeds the number of relations by six, then the test fails. However, this case will not arise if all relations have been found.

Suppose that we have α q numbers and that we have found β relations of form (1). We write the coefficients m_i of the relations in matrix form

$$\begin{pmatrix} m_{11} & m_{12} & m_{13} & \cdots & m_{1\alpha} \\ \vdots & & & & \vdots \\ \vdots & & & & \vdots \\ m_{\beta 1} & \cdots & \cdots & \cdots & m_{\beta\alpha} \end{pmatrix} \equiv (m)$$

and then determine the rank of the resulting matrix. The rank of the matrix is the order of the largest non-zero determinant contained in the matrix. If the rank of the matrix is r, then r of the q numbers can be expressed as rational linear conbinations of the remaining $(\alpha-r)$ q numbers. Then $(\alpha-r)$ is the number of linearly independent q numbers or the order of the vector space.

When the matrix (m) is being written, we can omit any relations of form (1) which are implied by other relations which we include in it. If, for example, we have relations

$$2q_1-q_2 = 0, \quad 2q_2-q_4 = 0, \quad 4q_1-q_4 = 0,$$

then any two imply a third of these. The rank of matrix (m) is not altered by including or omitting a relation implied by others which are included.

Having found the number $(\alpha-r)$ of linearly independent q numbers, in principle we could then find the e numbers which are the bases of the vector space. Suppose that the vector space turns out to have six dimensions and that q_1, q_2, …, q_6 are a linearly independent set of vectors covering the space by rational linear combinations. Each of these q numbers is of the form

$$q_1 = Q_{11}e_1 + Q_{12}e_2 + \ldots + Q_{16}e_6,$$

or in general in matrix form

$$\begin{pmatrix} q_1 \\ q_2 \\ q_3 \\ q_4 \\ q_5 \\ q_6 \end{pmatrix} = \begin{pmatrix} Q_{11} & \cdots & Q_{16} \\ \cdot & & \\ \cdot & & \\ \cdot & & \\ \cdot & & \\ Q_{61} & \cdots & Q_{66} \end{pmatrix} \begin{pmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{pmatrix}. \tag{17}$$

The rank of matrix (Q) must be six since the six q numbers are linearly independent, and hence the determinant of the matrix (Q) does not vanish. This insures the existence of a matrix (Q^{-1}), the matrix inverse to (Q); i.e.

$$(Q^{-1})(Q) = (E) = \text{diagonal identity matrix.} \tag{18}$$

If we then multiply the matrix equation (17) by (Q^{-1}) by left-multiplication, we will have solved for the e bases of the vector space,

$$(Q^{-1})(q) = (Q^{-1})(Q)(e) = (E)(e) = (e). \tag{19}$$

Actually we cannot perform the calculation implied by (19) until we know the elements of the matrix (Q). This does not affect the argument since we assert only that a non-singular (Q) matrix exists, and that this insures the existence of the set of e bases once a set of linearly independent q numbers is found.

As an example of this method, we can refer to the second tetragonal crystal example presented by Hesse, that for Mo–B. The previous tests based on Diophantine forms fail to determine the class of this powder pattern since no relations of suitable form are found. Hesse found three relations

$$q_1 + q_3 - q_4 = 0, \quad q_1 + 2q_2 - 2q_3 = 0, \quad q_2 - 2q_4 + q_6 = 0,$$

with the matrix

$$\begin{pmatrix} 1 & 0 & 1 & -1 & 0 \\ 1 & 2 & -2 & 0 & 0 \\ 0 & 1 & 0 & -2 & 1 \end{pmatrix} = (m).$$

It is easily verified that no third-order determinant contained in this matrix vanishes, and that there are among the set q_1, q_2, q_3, q_4 and q_6 only two linearly independent q numbers. Hence the crystal is at least tetragonal or hexagonal. To establish the class completely, we need to find more independent relations since there are eleven q numbers listed by Hesse. Six additional independent relations were found (with a maximum deviation from zero of 0·0003). They are

$$\begin{aligned} 7q_1 + q_6 - 2q_7 &= 0 \ (0{\cdot}0003) \\ q_5 + 2q_6 - 2q_8 &= 0 \ (0{\cdot}0000) \\ q_1 + q_2 + q_5 - q_8 &= 0 \ (0{\cdot}0002) \\ q_1 - q_2 + q_4 - q_5 - q_7 + q_9 &= 0 \ (0{\cdot}0002) \\ q_3 - q_4 - q_6 + q_8 + q_9 - q_{10} &= 0 \ (0{\cdot}0000) \\ 2q_2 - 2q_3 + q_8 - 2q_9 + q_{11} &= 0 \ (0{\cdot}0001) \end{aligned}$$

The complete matrix for the system then is readily shown to have rank nine, and hence all relations are independent, and only two of the eleven q numbers are linearly independent. This confirms the class of the crystal as tetragonal or hexagonal. We have definitely excluded the orthorhombic, monoclinic, or triclinic classes if no accidental coincidences among the e numbers occur.

It is not necessary to evaluate all of the sub-determinants contained in the matrix in order to determine its rank. There is a theorem which states that the rank of a matrix is unchanged if the elements of a row (column) are added to the corresponding elements of another row (column) of the matrix (Bôcher, 1907, chs. 3, 4, 5). By use of such elementary transformations the matrix is readily transformed to the equivalent matrix

$$\begin{pmatrix} 1 & 2 & -2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & -2 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 7 & 0 & 0 & 0 & 0 & 1 & -2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 2 & 0 & -2 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 1 & 0 & 0 & -1 & 0 & 0 & 0 \\ 1 & -1 & 0 & 1 & -1 & 0 & -1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & -1 & 0 & 1 & 1 & -1 & 0 \\ 0 & 2 & -2 & 0 & 0 & 0 & 0 & 1 & -2 & 0 & 1 \end{pmatrix}$$

$$\rightarrow \begin{pmatrix} 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

which clearly has rank nine. (This transformation was performed very quickly and was accomplished in nineteen steps. Fewer steps would suffice since we need zeroes only on one side of the non-zero diagonal.)

Another procedure which suggests itself is to examine a subset of equations, such as the first three listed for this example, and to express the dependent q numbers in terms of the linearly independent ones. Thus we can express q_3, q_4 and q_6 as linear combinations of q_1 and q_2. These are then substituted in the remaining equations to see whether or not they are satisfied. If the original set (q_1, q_2 in this case) of q numbers is a complete set, then all the remaining q numbers will be expressible as some linear combination of them. If not, then it will not prove possible by these substitutions to express the remaining q numbers in terms of q_1 and q_2, and the set will have to be augmented.

If this variation is employed, care must be exercised to make sure that the original subset, selected as being linearly independent, does not actually contain more q numbers than are really needed. This case could arise if, for example, we had a tetragonal crystal and a subset of three relations among six q numbers. For this subset we would necessarily find at least three independent q numbers, whereas actually only two are needed. If we solved for three of the q numbers in terms of the remaining three and then substituted these results in the remaining relations, they would necessarily be satisfied. We might then erroneously conclude that the crystal was orthorhombic. In the example worked out above, using this short procedure we found two independent q numbers (confirmed by the full procedure). We might have been in error when we called the crystal tetragonal or hexagonal. It conceivably could be cubic on the basis of the subset of three relations with only one of the q numbers being linearly independent. This would require that a linear dependence relation exist between q_1 and q_2 of the form $m_1q_1 = m_2q_2$. Since no such relation exists, the short procedure was valid in this case.

In seeking the additional relations among the q numbers needed for the linear dependence test, tables were prepared of: (a) multiples of the q's up to $10q$; (b) $q_{k+1}-q_k$; (c) $q_{k+2}-q_k$; (d) $q_{k+3}-q_k$; (e) $q_{k+4}-q_k$; (f) $2q_{k+1}-q_k$, etc. The next step consists in examining these tables for numbers which are equal within the permitted limits of error. For the present purpose this limit was set at 0·0003 in $\sin^2\theta$. If the limit is not made so small, accidental equalities of a spurious nature will be listed and the procedure will fail. As Hesse has stated, the use of focusing cameras is almost a necessity.

The relation $7q_1+q_6-2q_7 = 0$ (0·0003) was found by noting that the quantity $2q_7-q_6$ was equal to $7q_1$. The relation $q_3-q_4-q_6+q_8+q_9-q_{10} = 0$ (0·0000) was found by noting that $(q_{10}-q_9)+(q_4-q_3) = (q_8-q_6)$. Similarly $2(q_8-q_6) = q_5$ becomes $q_5+2q_6-2q_8 = 0$ (0·0000). The equality $(q_{11}-q_9) = 2(q_3-q_2)+(q_9-q_8)$ becomes $2q_2-2q_3+q_8-2q_9+q_{11} = 0$ (0·0001). It is possible to guard against spurious relations by cross checking to see whether they imply relations which are not of the desired precision. Thus the relation (spurious) $q_8-q_6 = q_7-q_5$ (0·0004) was rejected because of the relation $2(q_8-q_6) = q_5$ (0·0000). These relations, if both correct, taken together require $2(q_8-q_6) = 2(q_7-q_5)$, or $2q_7 = 3q_5$. The latter is not correct since $2q_7 = 0·8722$, while $3q_5 = 0·8730$, the difference 0·0008 being far outside the acceptable range. The rejection of $q_8-q_6 = q_7-q_5$ also implies rejection of $q_8-q_7 = q_6-q_5$.

It must be emphasized that the selection of these relations must be done with care, since this is the only point in the procedure at which observational or subjective errors enter. The outcome of the remainder of the procedure is completely dependent on the care used at the start.

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An Extended Table of Atomic Scattering Factors

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A table of atomic scattering factors is given for the elements H to Cu for values of $(4\pi \sin\theta)/\lambda$ up to 30.

In applying the sector method of electron diffraction (Viervoll, 1947) we have for some time made use of new tables of atomic scattering factors, f, which cover a greater range of $(\sin\theta)/\lambda$ than the corresponding tables used by the X-ray crystallographers. Our f values (Table 2) are given as functions of $s = (4\pi \sin\theta)/\lambda$ (A.$^{-1}$), where θ is the Bragg angle.

The calculations of the f values are mainly based on those of James & Brindley (1931), who give the functions for values of s up to about 14. We have extended the s range to 30. For our purpose we did not find it necessary to apply wave functions 'with exchange' which would introduce very small effects for higher s values. These effects would be somewhat greater for smaller s values (Brindley & Ridley, 1938), but may still be assumed to be without significance for ordinary structure determinations.

The atomic scattering factor may be considered as a sum of electronic scattering factors, each of which corresponds to an electron of the atom. James & Brindley found that a suitable linear transformation of the s scales could bring the scattering factors of the same electron group (same n and l) in different atoms to coincide very closely.