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A GRAPHICAL METHOD OF EVALUATING CERTAIN CRYSTALLOGRAPHIC STRUCTURE FACTORS

by

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Abstract: A graphical method is described for evaluating structure factors of the form $F(hk) = \sum_{o}^{n} f_r(hk) \cos 2\pi(hx_r + ky_r)$ and electron density expressions of the form $\rho(X, Y) = \sum_H \sum_K F(hk) \cos 2\pi(hX + kY)$. The method depends upon the fact that if, in a [001] projection of a unit cell the normal to the planes (hk0) is graduated with the appropriate cosine function giving the phases of points along the normal; then a circle, with its center at (x/2, y/2), passing through the origin will cut the normal to F(hk0) at the value of $\cos 2\pi(hx + ky)$.

Introduction

The construction discussed below provides a rapid graphical method for evaluating Fourier summations involving trigonometric functions of the form $\cos 2\pi(hX + kY)$, or functions such as $\cos 2\pi hx \cdot \cos 2\pi ky$ which can be reduced to this form.

It is intended to apply to two-dimensional projections of a crystal structure, and the nomenclature used below refers to a [001] projection. It can be used either on the true projection of the unit cell, or with the atomic coordinates referred to a square projection, a procedure which has some advantages to be discussed in Section 3. The real lattice and not the reciprocal lattice is used in these particular applications.

1. Basic Construction for Evaluating Structure Factors

Consider the [001] projection of the unit cell (Fig. 1). AB is the plane (hk0) so that OA = a/h, OB = b/k. OP is the plane through O parallel to AB. The contribution to the structure factor F(hk) from the atom at (x, y) can be obtained from a Bragg-Lipson chart,[1] and the line PQ can be graduated from such a chart. The particular value of this construction lies in the fact that since PQ must be perpendicular to OP, points such as P will lie on the circle OPQ for all planes (hk0). This is the circle with its center at (x/2, y/2) which passes through the origin. In Fig. 2, ON is the normal through the origin to the planes (hk0), and it can be seen that OR is equal and parallel to PQ. Hence, if ON instead of PQ were graduated from the appropriate Bragg-Lipson chart, the value of $f_r(hk) \cos 2\pi(hx_r + ky_r)$ would be the reading at the point where the circle with center $(x_r/2, y_r/2)$ intersects ON; ON will be called the "F(hk) line".

Generalizing the construction, it can be seen that for any (hk0) plane, the structure factor F(hk0) will be the sum of the readings on the corresponding F(hk) line where it is intersected by the n circles corresponding to the n atoms in the projection, i.e., $F(hk) = \sum_{o}^{n} f_r(hk) \cos 2\pi(hx_r + ky_r)$. The method is illustrated in Fig. 3.

2. Basic Construction for Evaluating Electron Density

By analogy with the preceding construction, if a set of normals to the planes (hk0) are graduated as before from a Bragg-Lipson chart, but instead of carrying the values of the atomic scattering factor $f_o(hk0)$, they are given the observed values of F(hk0) (Fig. 4), a circle whose center is at (X/2, Y/2) will cut the $F(h_1k_1)$ line at A, which will give the value of $F(h_1k_1) \cos 2\pi$

1) W.L. Bragg and H. Lipson, Z. Krist. A95, 323 (1936).

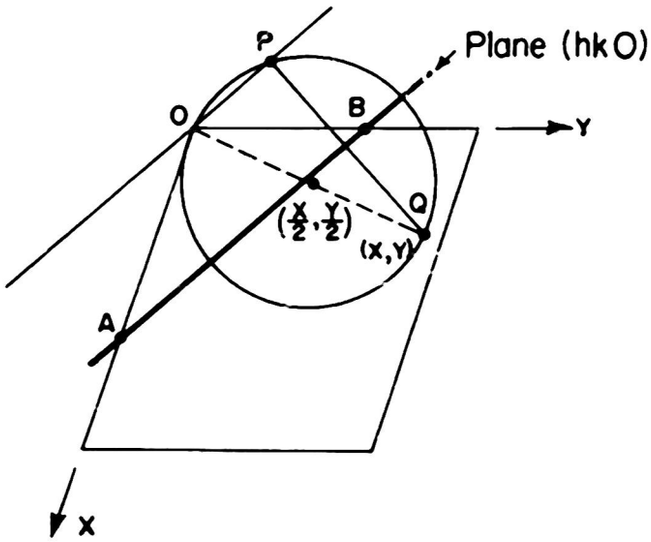

Fig. 1. Basic construction for structure factors of the form $F(hk) = \sum_{o}^{n} f_r(hk) \cos 2\pi(hx_r + ky_r)$.

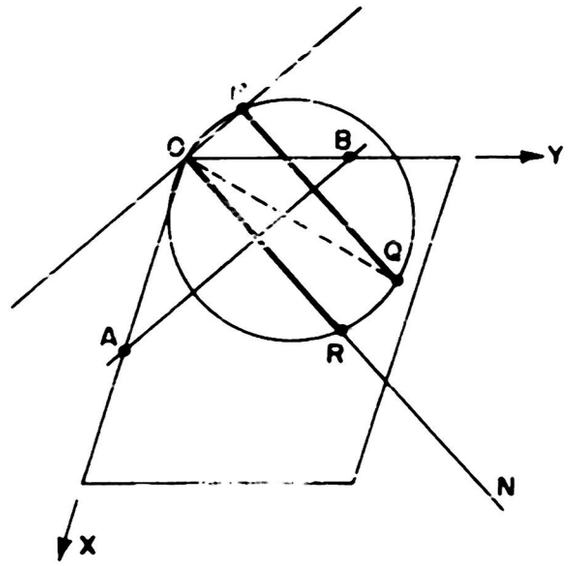

Fig. 2. Use of normal to (hk0) planes to represent F(hk0).

$(h_1X + k_1Y)$ and so on. Hence, the sum of the readings on the circle OABCD, which will be called the "$\rho(X, Y)$ circle," will be $F(h_1k_1) \cos 2\pi(h_1X + k_1Y) + F(h_2k_2) \cos 2\pi(h_2X + k_2Y) + \ldots\ldots\ldots\ldots$ for all the observed values of F(hk0), i.e., the sum will be $\sum_{O}^{H} \sum_{O}^{K} F(hk) \cos 2\pi(hX + kY)$, which is the value of the electron density $\rho(X, Y)$ at the point (X, Y).

3. Use of a Square Projection

There are two main advantages in the use of a square projection: (1) The directions and graduations of the F(hk) lines will then be the same for all crystals, so that a master set can be prepared for all projections instead of a new set being necessary for each one (except in the case of axial projections of cubic crystals or [001] projections of tetragonal crystals, which are already square), and only the numerical values of f(hk) or F(hk) will have to be inserted for each projection. (2) If Bragg-Lipson charts are not available, the F(hk) lines can be graduated with very little labor by making use of the construction shown in Fig. 5 if a square projection is used.

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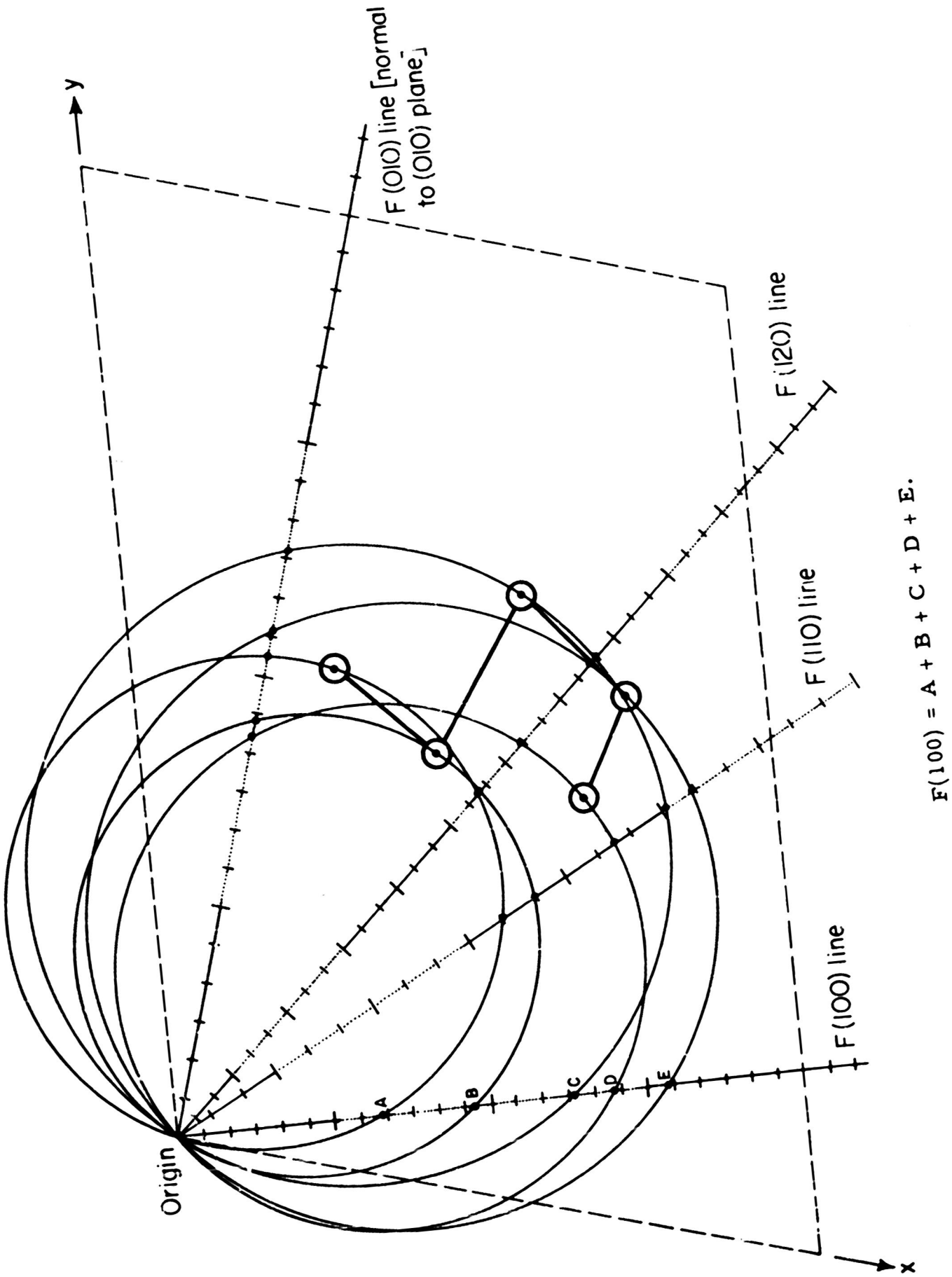

Fig. 3. Example of construction for evaluating structure factors.

If a circle drawn with its center at the point (1/2, 1/2) intersects the F(hk) line at P, OP has to be divided into (h + k) parts; i.e., in Fig. 5, F(4, 2) is divided in 4 + 2 = 6 parts. If the charts are drawn on tracing paper, a piece of graph paper can be conveniently used as a proportional divider to graduate the F(hk) lines. A disadvantage is that the crystal projection is distorted.

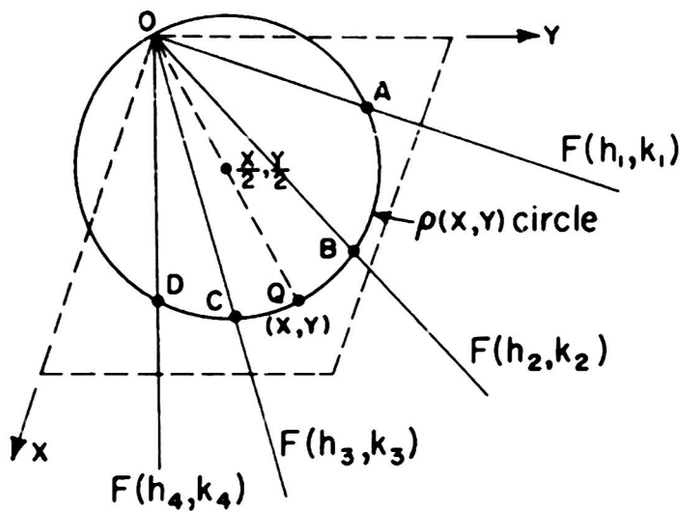

Fig. 4. Basic construction for electron density summations of the form $\rho(X, Y) = \sum_{o}^{H} \sum_{o}^{K} F(hk) \cos 2\pi(hX + kY)$.

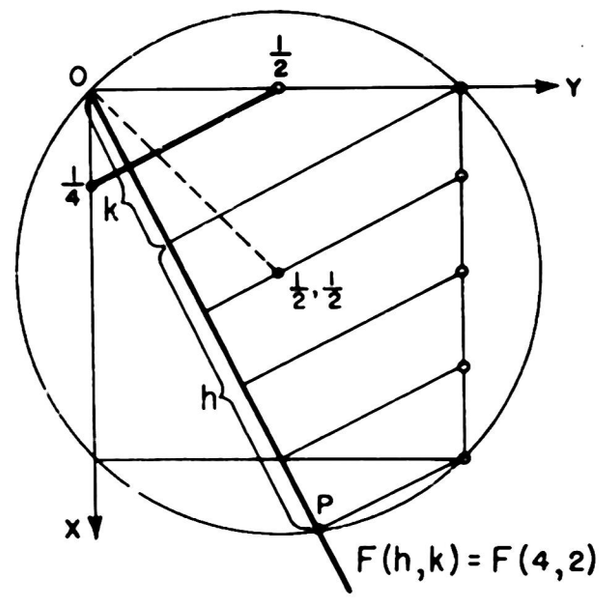

Fig. 5. Graduation of F(hk) lines using a square projection.

4. Extension to Structure Factors of the Form $F(hk) = \sum_{o}^{n} f_r(hk) \cos 2\pi hx_r \cdot \cos 2\pi ky_r$

The expression $f_r(hk) \cos 2\pi hx_r \cdot \cos 2\pi ky_r$ can be rewritten in the form

$$1/2 \left[f_r(hk) \cos 2\pi(hx_r + ky_r) + f_r(hk) \cos 2\pi(hx_r - ky_r) \right] \ldots \quad (1)$$

This is equivalent to placing half an atom at the point (x_r, y_r) and 1/2 an atom at $(x_r, \bar{y}_r)$. Then in Fig. 7 the value of Eq. (1) will be one half the sum of readings

at A and B. Although an atom at $(x_r, \bar{y}_r)$ is actually located at A (Fig.6) so that its contribution to F(hk) occurs at P, it can be seen that if O'Q is drawn parallel to OP, in which case O'Q = OP, the reading at Q will be equivalent to the reading at R, and therefore the atom at $(x_r, \bar{y}_r)$ can be placed at B and the construction confined to one quadrant. Atoms with co-ordinates (x, o) will be unaffected and require one circle, as in Section 1.

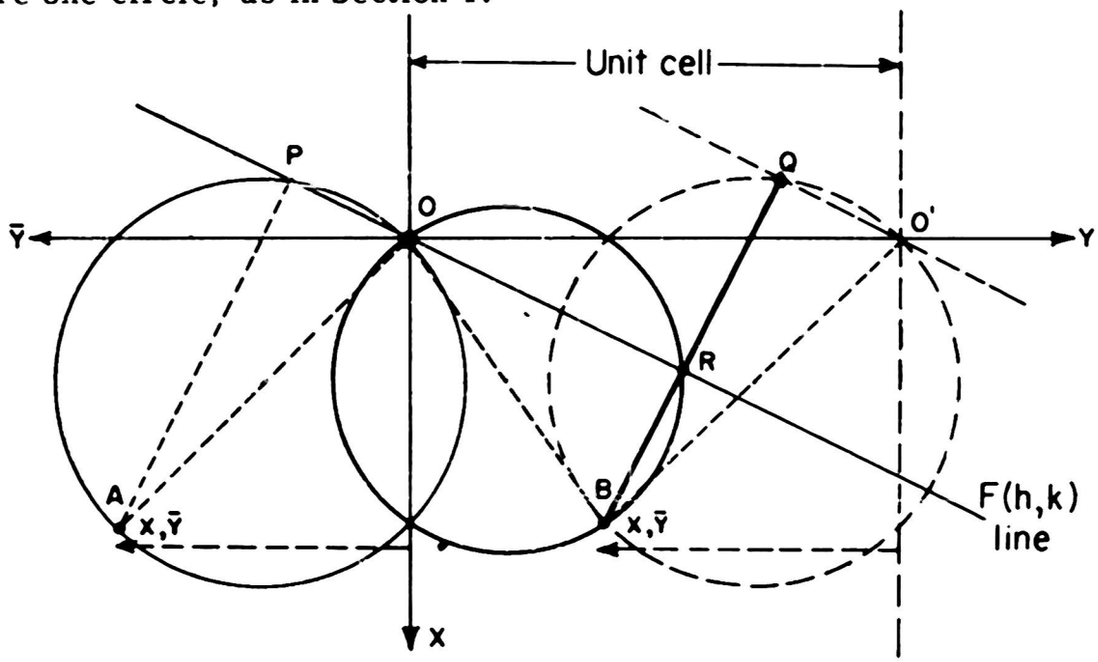

Fig.6. Equivalence of atomic positions $(x, \bar{y})$ and $(x, 1-y)$.

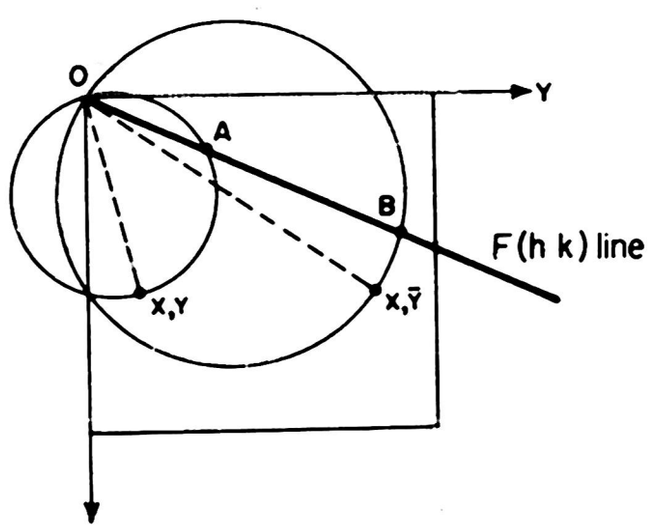

Fig.7. Construction used for structure factors of the form $F(hk) = \sum_{o}^{n} f_r(hk) \cos 2\pi hx_r \cdot \cos 2\pi ky_r$.

5. Cases Where $h\bar{k}0$ Reflections Are Required in Addition to hk0 Reflections

The construction as discussed so far has been confined to a single quadrant, i.e., to F(hk) lines where h and k are both positive. For some projections $F(h\bar{k})$ reflections will not be equivalent to F(hk) reflections, and will have to be included separately in the summations. It can be seen in Fig. 8 that the circles with centers at (0, 1/2), (1/2, 0) and (1/2, 1/2) define a region within which all other (x, y) circles will lie.

This region does not extend into quadrant (3), and hence extension of the F(hk) line will not be necessary; but it does fall partly in quadrants (2) and (4), so that the $F(h\bar{k})$ line will have to extend through the origin into quadrant (4).

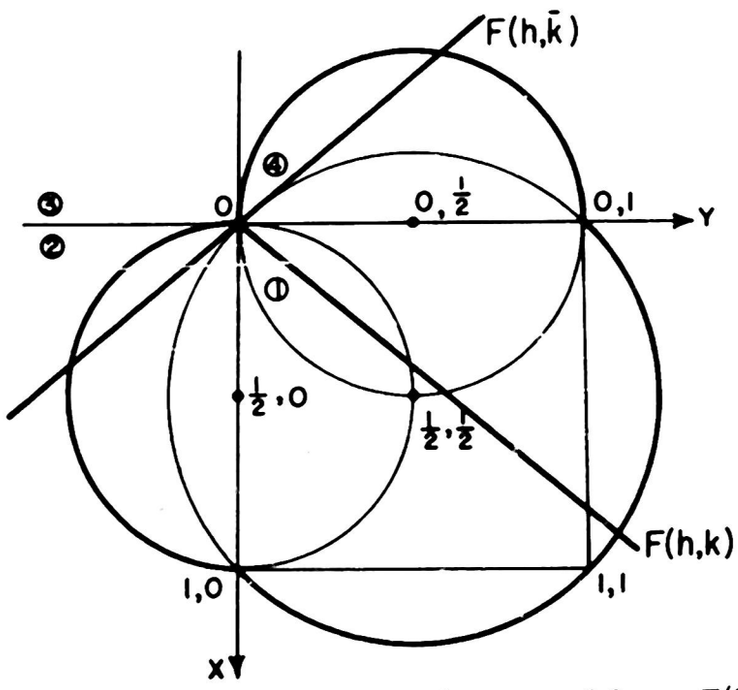

Fig. 8. Extension to structure factors of form $F(h\bar{k}0)$.

6. Circles Tangential to F(hk) Lines

An (x, y) circle will be tangential to an F(hk) line only if (x, y) lies on a line through the origin perpendicular to the F(hk) line, i.e., if (x, y) lies in the (hk) plane. Hence it will make a full $f_I(hk)$ contribution to F(hk).

7. Practical Considerations

There are several limitations on the practical usefulness of the construction.

(a) If the F(hk) lines are graduated with values of the atomic scattering factor f(hk), this becomes confusing when several kinds of atoms are present. For two types of atom two independent sets of numbers can be used (one on each side of the F(hk) line), but more would be impracticable. It would be possible to prepare a separate chart for each species of atom, or, in cases where only F(hk) with h and k positive occurs, i.e., in which only one quadrant is used, to construct a multiple chart (hypothetical example given in Fig. 9) with different f(hk) values in each quadrant. The actual number of graduations used on the F(hk) line will depend largely on the scale chosen for the figure.

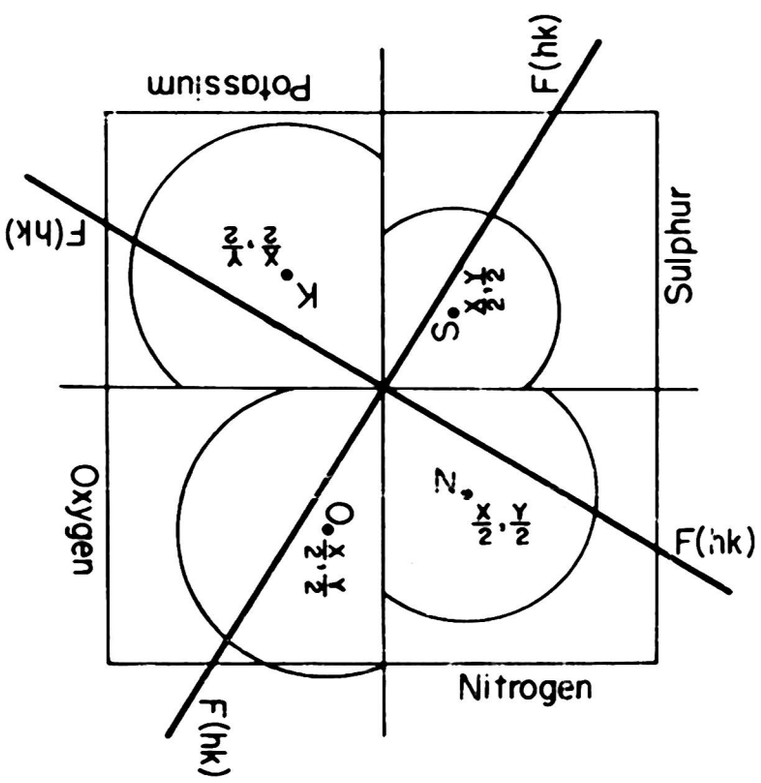

Fig. 9. Composite chart for structure containing several types of atom.

If, for example, the symmetry of the projection is such that only atoms in the section bounded by a/4 and b/4 need be considered, then the use of a 25 cm square would mean that 1mm = 0.001 of the cell edge. In this case the largest interplanar spacing, d_{100} will be 100 cm on the chart, i.e., 360° = 100 cm, and values of f(hk) cos $2\pi(hx + ky)$ could be inserted at 1° intervals. This, however, is an extreme case, and, in the examples so far constructed, values of f(hk) cos $2\pi(hx + ky)$ have been inserted at 15° inter-

vals from Table 1, showing these values for f(hk) = 1, 2 . . . . 99; intermediate values have been interpolated.

(b) If all observed F(hk) lines are inserted in the diagram, it becomes hopelessly crowded. It would be possible to indicate the positive and negative sections of a large number of F(hk) lines, but use of numerical values would be impracticable.

(c) It is very difficult to show several orders of F(hk) on the same line clearly. These are serious handicaps as regards use of the construction for electron density summations, when contributions from all F(hk0) values must be included, but can be circumvented in the case of structure-factor calculations, and even turned to advantage.

8. Introduction of the Temperature Factor

Consider, for example, a crystal in which two kinds of atoms A and B are present, and suppose that the atomic scattering factors of these atoms at rest can be represented by the curves A and B in Fig. 10. Suppose that C and D, respectively, represent the smallest and largest observed values of $(\sin \theta/\lambda)$. The range CD is now divided into sections like CEFG so that $f_o(C)$ and $f_o(G)$ do not differ from $f_o(M)$ by more than 5 percent.

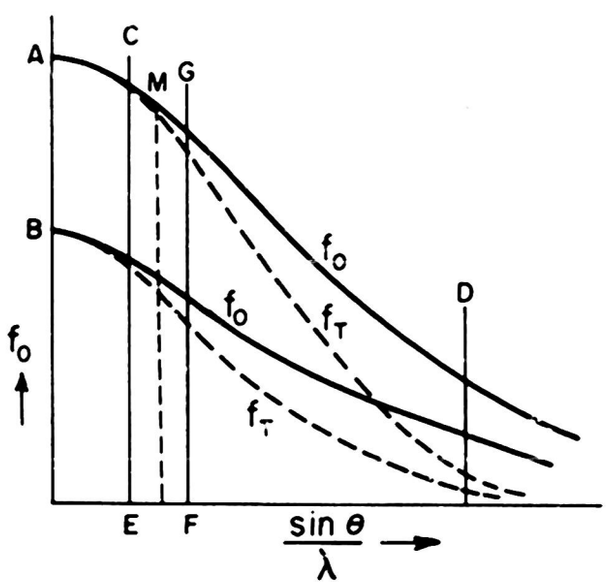

Fig. 10. Atomic scattering factor curves.

A chart such as described in Section 1 can now be constructed with only those F(hk) lines for which 1/2d lies in the range EF, say, 8 F(hk) lines, and this will be quite manageable. The $f_o(A)$ and $f_o(B)$ values are used. Whatever the value of the temperature factor, the ratio

Table 1. Values of A cos 2πR, for A = 1, 2, ... 99; R = 0° x 1/24 → 1/4.

0°	15°	30°	45°	60°	75°	90°	0°	15°	30°	45°	60°	75°	90°
1	1	1	1	0	0	0	51	49	44	36	26	13	0
2	2	2	1	1	1	0	52	50	45	37	26	13	0
3	3	3	2	2	1	0	53	51	46	37	26	14	0
4	4	3	3	2	1	0	54	52	47	38	27	14	0
5	5	4	4	2	1	0	55	53	48	39	28	14	0
6	6	5	4	3	2	0	56	54	48	40	28	14	0
7	7	6	5	4	2	0	57	55	49	40	28	15	0
8	8	7	6	4	2	0	58	56	50	41	29	15	0
9	9	8	6	4	2	0	59	57	51	42	30	15	0
10	10	9	7	5	3	0	60	58	52	42	30	16	0
11	11	10	8	6	3	0	61	59	53	43	30	16	0
12	12	10	8	6	3	0	62	60	54	44	31	16	0
13	13	11	9	6	3	0	63	61	55	45	32	16	0
14	14	12	10	7	4	0	64	62	55	45	32	17	0
15	14	13	11	8	4	0	65	63	56	46	32	17	0
16	15	14	11	8	4	0	66	64	57	47	33	17	0
17	16	15	12	8	4	0	67	65	58	47	34	17	0
18	17	16	13	9	5	0	68	66	59	48	34	18	0
19	18	16	13	10	5	0	69	67	60	49	34	18	0
20	19	17	14	10	5	0	70	68	61	49	35	18	0
21	20	18	15	10	5	0	71	69	61	50	36	18	0
22	21	19	16	11	6	0	72	70	62	51	36	19	0
23	22	20	16	12	6	0	73	71	63	52	36	19	0
24	23	21	17	12	6	0	74	71	64	52	37	19	0
25	24	22	18	12	6	0	75	72	65	53	38	19	0
26	25	23	18	13	7	0	76	73	66	54	38	20	0
27	26	23	19	14	7	0	77	74	67	54	38	20	0
28	27	24	20	14	7	0	78	75	68	55	39	20	0
29	28	25	21	14	8	0	79	76	68	56	40	20	0
30	29	26	21	15	8	0	80	77	69	57	40	21	0
31	30	27	22	16	8	0	81	78	70	57	40	21	0
32	31	28	23	16	8	0	82	79	71	58	41	21	0
33	32	29	23	16	9	0	83	80	72	59	42	21	0
34	33	29	24	17	9	0	84	81	73	59	42	22	0
35	34	30	25	18	9	0	85	82	74	60	42	22	0
36	35	31	25	18	9	0	86	83	74	61	43	22	0
37	36	32	26	18	10	0	87	84	75	62	44	23	0
38	37	33	27	19	10	0	88	85	76	62	44	23	0
39	38	34	28	20	10	0	89	86	77	63	44	23	0
40	39	35	28	20	10	0	90	87	78	64	45	23	0
41	40	36	29	20	11	0	91	88	79	64	46	24	0
42	41	36	30	21	11	0	92	89	80	65	46	24	0
43	42	37	30	22	11	0	93	90	81	66	46	24	0
44	42	38	31	22	11	0	94	91	81	66	47	24	0
45	43	39	32	22	12	0	95	92	82	67	48	25	0
46	44	40	33	23	12	0	96	93	83	68	48	25	0
47	45	41	33	24	12	0	97	94	84	69	48	25	0
48	46	42	34	24	12	0	98	95	85	69	49	25	0
49	47	42	35	24	13	0	99	96	86	70	50	26	0
50	48	43	35	25	13	0	100	97	87	71	50	26	0

of $F(C)_T/F(G)_T$ will not differ appreciably from $F(C)_0/F(G)_0$. Hence, if a scale is assigned to the observed F(hk0) values so that for the trial structure used, the ratio $\sum |F_{obs}| \div \sum |F_{calc}|$ is unity for the group CEFG, this ratio will decrease for each successive group like CEFG, and from the numerical values of the ratios a temperature factor can be calculated (Section 11) by a simple graphical method.

9. Graphical Refinement of a Trial Structure

The structure factors in the group CEFG will be relatively insensitive to the exact location of the atoms, and the sensitivity will increase with each succeeding group. If, therefore, an approximate structure is postulated to give reasonable agreement with the F(hk0) values in the first group, it can be improved by comparison with each group in turn, in the following way: Suppose that for a projection with an atom located so that its (x, y) circle is centered at Q_1, the F(hk) values are calculated and compared with the observed values (Fig. 11). Suppose that agreement would be improved if the values of A_1, B_1, C_1. . . were altered as shown by the arrows to positions A_2, B_2, . . . The best circle that can be drawn through A_2, B_2, C_2. . . is centered at Q_2, which then represents the improved position for this atom.

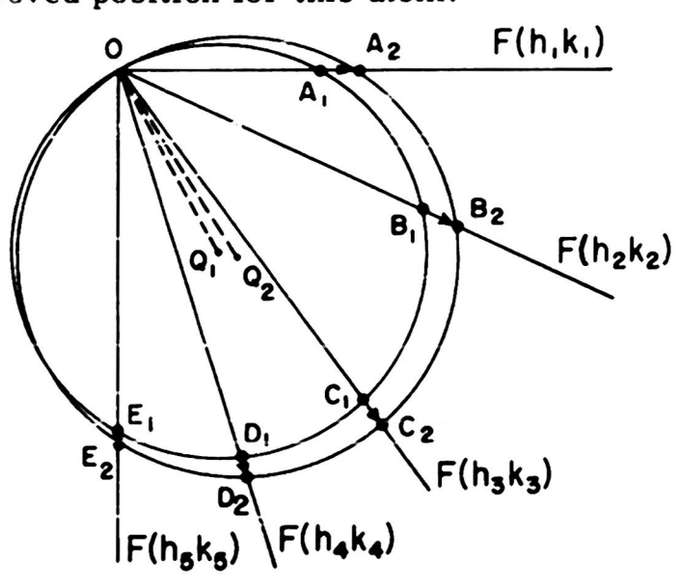

Fig. 11. Process of refining a projection.

10. General Utility of the Construction

The construction appears to have some value in the fact that it offers a very easy way of visualizing the contribution from an atom or group of atoms to a large number of structure factors simultaneously without too much over-crowding of the diagram. Space-group extinctions can be readily represented, e.g., in Fig. 12. Consider the face-centered [001] projection in which the atom at the origin O is represented by the circle through A, and the atom at the face center by the circle through B. These circles cut the F(hk) line at P and Q respectively, and OQ = OP/2.

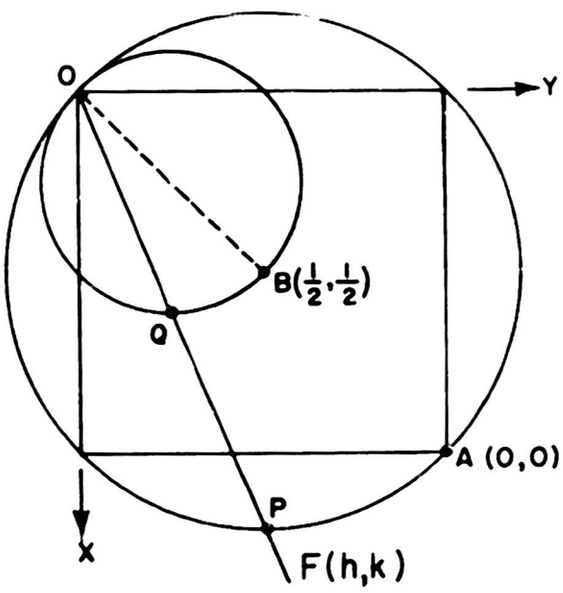

Fig. 12. Demonstration of space group extinction conditions for a face-centered projection.

In Section 3 it was shown that OP has to be graduated so as to have (h + k) equal parts with maxima at O and at P. Hence, if h + k = 2n, Q will be on a maximum, while if h + k = 2n + 1, Q will be on a minimum, and atom B will cancel out atom A's contribution. Hence, the space group condition for a centered [001] projection can be derived; namely, reflections are present only for h + k = 2n.

11. A Nomogram for Evaluating $f_T/f_o = e^{(-2B \sin^2 \theta)/\lambda^2}$

The nomogram has 4 scales A, B, C, and D. A and D are logarithmic scales with 1 cycle = 10 inches; they are equidistant from C, which is the logarithmic scale having 2 cycles = 10 inches required for multiplication.

Since

$$f_T \equiv f_o e^{(-2B \sin^2 \theta)/\lambda^2}$$

$$= f_o \, 10^{-\frac{2B}{\log_e 10} \cdot \frac{\sin^2 \theta}{\lambda^2}}$$

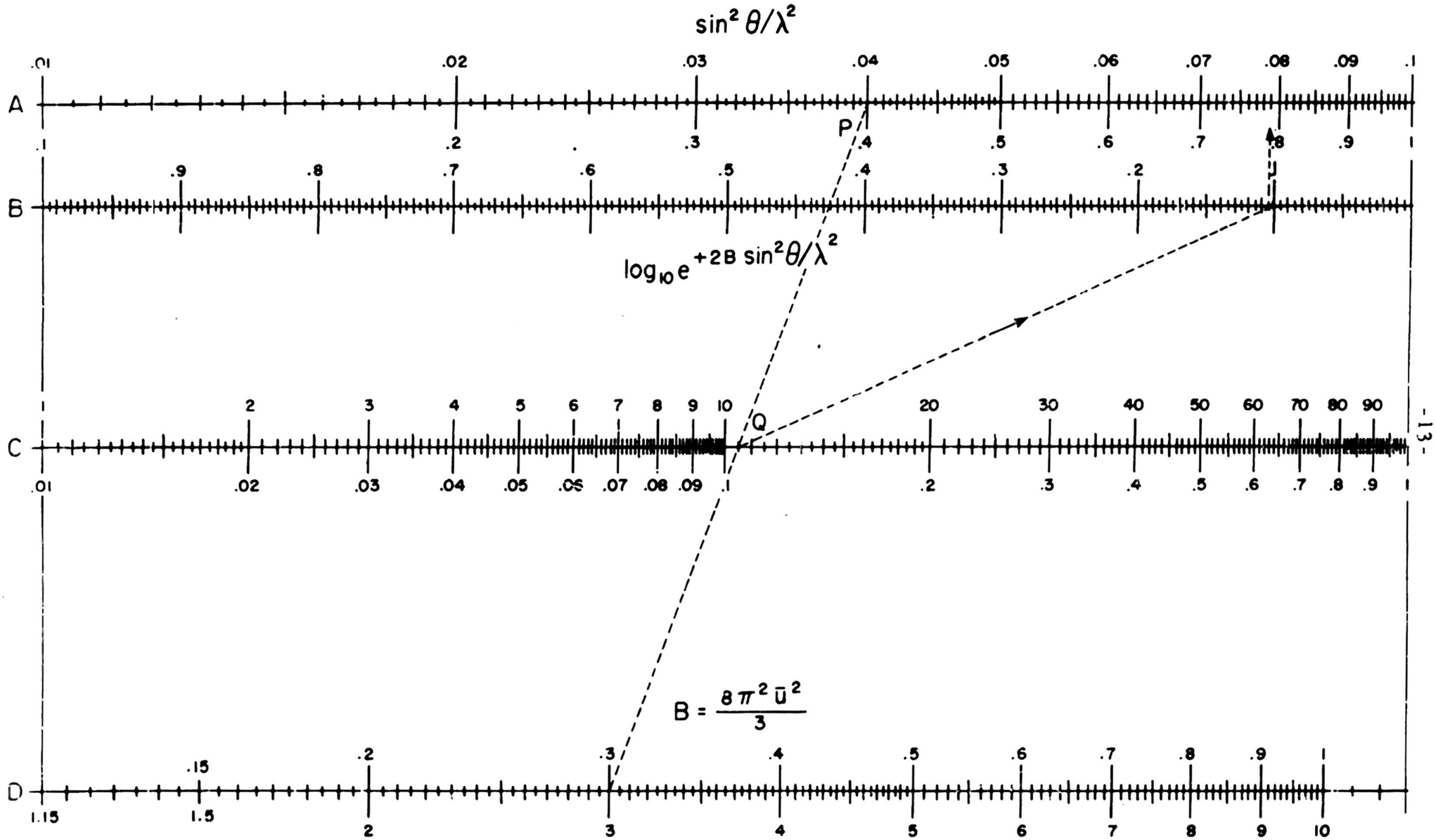

Fig. 13. Nomogram for evaluating $f_T/f_o = e^{(-2B\sin^2\theta)/\lambda^2}$.

$$= f_o \, 10^{-\frac{B}{1.15} \cdot \frac{\sin^2\theta}{\lambda^2}}$$

the D scale has its origin displaced to the left, so that the reference line carrying the origins of the A, B and C scales cuts the D scale at the value 1.15. Thus, if the value of $(\sin^2\theta)/\lambda^2$ is found on the A scale, and the value of B on the D scale, the line joining these points will cut the C scale at the point $\left[(B/1.15) \times (\sin^2\theta)/\lambda^2\right]$. The antilogarithm of this value is now required, and the B scale, which is a linear inch scale, performs this operation against the A scale. Note that the values on the B scale increase from right to left, because the original equation contains the exponent with a negative sign. An example of the use of the nomogram for evaluating f_T/f_o for particular values of B and $(\sin^2\theta)/\lambda^2$ has been sketched in on the diagram (Fig. 13): if $\sin^2\theta/\lambda^2 = 0.04$ and $B = 3$, $f_T/f_o = 0.79$.

This nomogram can also be used as follows to evaluate the temperature factor for the crystal in conjunction with the procedure described in Section 5. When a series of values of the ratio $\sum |F_{obs}| \div \sum |F_{calc}|$ has been calculated for groups having a mean value of $(\sin^2\theta)/\lambda^2 = \left[(\sin^2\theta)/\lambda^2\right]_M$, the value of each ratio, when found on the A scale, determines a point on the B scale and hence a point on the C scale. If the points on the A scale having the values $\left[(\sin^2\theta)/\lambda^2\right]_M$ are joined to their corresponding points on the C scale, these lines when produced, should converge on a particular value of the temperature factor B, which is thereby determined.

I am grateful to Professor A. von Hippel for his interest in this problem.