Owing to the limited range in 2θ the thermal parameters are not well defined. We therefore fixed them on the best refined values of a preceding cycle without further refinement which gave considerably better standard deviations for all other parameters (see Table 2). An attempt to refine anisotropic temperature factors (Hewat, 1973*b*) gave negative temperature factors for one of the atoms as a result of the limited amount of data.

The crystallographic positional parameters are in excellent agreement with the single-crystal neutron refinement of O'Connor & Valentine (1969); the agreement is not so good with the X-ray study of Paton & Maslen (see Table 2).

The parameter varied in the least-squares refinement was in fact the occupation number of the two yttrium sites, which is linearly dependent on the scattering length. We found in fact good agreement between the scattering lengths of the two crystallographic sites.

Three values of the scattering length of oxygen are given in the literature. We carried out refinements of the yttrium occupation numbers with all three values and found the following ratios b_Y/b_O.

b_O	Reference	b_Y/b_O	b_Y
0·577	Hughes & Schwartz, 1958	1·3189	0·760
0·575	Bacon, 1962	1·3172	0·758
0·580	Bacon, 1972	1·3182	0·765

The reliability values quoted are R_{pr} which is defined above and the reliability value R_B based on the Bragg reflexions:

$$R_B = 100 \sum_i \left| F_i^2(\text{obs}) - \frac{1}{c} F_i^2(\text{calc}) \right| / \sum_i F_i^2(\text{obs})\,.$$

The final value of the scattering length of yttrium with the latest value of the oxygen scattering length of $b_O = 0{\cdot}580$ and with fixed values of the thermal parameters is $b_Y = 0{\cdot}765$ ($\sigma = 0{\cdot}007$).

Further support is given by our single crystal study of yttrium iron garnet (YIG) by the polarized neutron technique (Bonnet, Delapalme & Fuess, 1975).

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The calculation of peak heights on Fourier maps.

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(*Received* 7 *October* 1974; *accepted* 7 *November* 1974)

The paper describes a method for the rapid calculation of expected peak heights on Fourier maps for each atom type over a range of temperature factors, given the crystal data and the number of independent reflexions collected. An algorism is presented for assigning unidentified peaks to specific atom types.

Scattering factors, f, for atoms at rest can be approximated by the series $f = \sum A_j \exp(-a_j s^2)$ over j terms, where $s = \sin\theta/\lambda$ (Forsyth & Wells, 1959; Moore, 1963; Cromer, Larson & Waber, 1968; Lee & Pakes, 1969). Usually, $j = 3$, and $a_3 = 0$, so that the correction for the real component of anomalous dispersion can be added algebraically to A_3. Sakurai (1967) pointed out that this representation of f enabled the height, H_i, of a peak on a Fourier map due to an atom of type i to be calculated independently of the production of the map. If reflexions are collected out to a limiting value, l, for $\sin\theta/\lambda$, and the temperature factor, U_i, is known, then, since the effective radius of the limiting sphere is $2l$,

$$H_i = 8\int_0^l 4\pi s^2 \sum_j A_{i,j} \exp\left[-(a_{i,j} + 8\pi^2 U_i)s^2\right] ds\,. \qquad (1)$$

Sakurai published a table of values for H for all atoms over a range of values for $B(=8\pi^2 U)$ with values for l of infinity, and the values for the limiting spheres for Cu $K\alpha$, and for Mo $K\alpha$ radiations. This paper presents a routine solution for equation (1) for any limiting value for $\sin\theta/\lambda$, and any values for U.

It is convenient to drop subscripts temporarily, and to use the substitutions:

$$E = (a + 8\pi^2 U)\,; \quad x = 2Es^2\,; \quad \chi^2 = 2El^2$$

so that equation (1) is converted into (2*a*):

$$H = (8\pi/\sqrt{2}) \sum A E^{-3/2} \int_{x=0}^{x=\chi^2} \left[x^{1/2} \exp(-x/2)\right] dx\,. \qquad (2a)$$

The integral is a standard one, of value $\sqrt{2\pi}P(\chi^2, 3)$, where the function P is the χ^2 integral for three degrees of freedom. Table 1, derived by linear interpolation from the values of P as a function of χ^2 (Pearson & Hartley, 1954), gives the values of χ^2 which provide an equally spaced series of values for the integral; between these values the integral can be taken as a linear function of χ^2. With obvious substitutions, and subscripts reintroduced, equation (2*a*) becomes (2*b*):

$$H_l = 8\pi^{3/2} \sum_j A_{l,j} E_{l,j}^{-3/2} P(2l^2E_{l,j}, 3)\,. \tag{2b}$$

Table 1. *Values of P, the χ^2 integral for three degrees of freedom, and of χ^2*

$P(\chi^2,3)$	χ^2
0·000	0·000
0·10	0·584
0·20	1·005
0·30	1·424
0·40	1·869
0·50	2·367
0·60	2·847
0·70	3·666
0·80	4·643
0·90	6·253
0·995	12·851
1·0	∞

Generally, the observed reflexions, including symmetry-equivalent ones, do not fill the limiting sphere, so that l is less than $1/\lambda$. Let n independent reflexions be collected, and let V be the volume of the unit cell. Considering primitive cells first, G, the number of reflexions within the limiting sphere $\simeq 32V/3\lambda^3$; and N, the number of reflexions that are accessible by the technique employed $\simeq nl$, where L is the Laue multiplicity factor for *hkl* reflexions. The expressions give values for G and N that are too high but, to the accuracy needed,

$$l^3 = N/G\lambda^3. \tag{3}$$

Equation (3) can also be used for centred lattices; for a C lattice, while the unit cell generates two reflexions for each passage through the sphere of reflexion, half of these are systematically zero, and absent from the list for a Fourier synthesis, so that N and V are related as for a primitive cell. Given a set of structure factors, and with l derived from equation (3), equation (2*b*) can be used to calculate peak heights and the dependence of these heights on U for each atom type. The difference between the observed and calculated peak heights provides a means for correcting grossly mis-set values of U.

Further, provided one peak in a Fourier map can be ascribed to a specific atom type, *e.g.* the highest peak to the heaviest atom type, a temperature factor, U_0, can be assigned to this atom. For the other peaks each chemical type i will provide a different value, U_i, for the temperature factor. It is possible to identify the atom type for each such peak by assigning the atom to the class for which U_i/U_0, or, as appropriate, U_0/U_i has the smallest value ≥ 1.0. In practice, better results are obtained by introducing a correction for differing atomic weights. The energy of a vibrating mass $\propto$ (displacement)^2; and if atoms of different weights, w_i, vibrated independently in a crystal, then for each type the product U_iw_i would be constant. Let R_iU_0 be the most probable value for the temperature factor for atoms of type i, and let $R_w = w_0/w_i$, where w_0 refers to the atom type with temperature factor U_0. Bonding causes R_i to differ from R_w; let $R_i = (R_w)^z$. Empirically, over the atom types in six compounds [(i) $C_{20}H_{17}N_2O_3.\frac{1}{2}HgCl_4.H_2O$; Ferguson, Jeffreys & Sim, 1966; (ii) $C_{35}H_{31}N_3O_4.HI.H_2O$; Jeffreys & Ferguson, 1970; (iii) $C_{16}H_{12}N_2O_2.HBr.H_2O$; Jeffreys, 1970; (iv) $C_{25}H_{18}Fe_2O_8$; Jeffreys & Willis, 1972; (v) $C_{25}H_{18}Fe_2O_8$; Jeffreys, Willis, Robertson, Ferguson & Sime, 1973; (vi) $C_6H_{10}Mo_2N_2O_6S_4.2Na.2H_2O$; Brown & Jeffreys, 1973], least-squares fits for z for each compound ranged from −0·071 to 0·305, with an overall best fit of 0·156. With this value for z, the equations were tested for the molybdenum compound (vi) above, with peaks in a Fourier map that had been computed when all the atoms had been sited and identified, and their temperature factors known, and with the analytical constants derived by Moore (1963) for Cu $K\alpha$ radiation. Table 2 compares the true chemical types with those derived after setting the highest peak as due to molybdenum. A computer program, *IDEN*, written in Fortran IV for the operations above is available from the author.

Table 2. *Peak heights and identifications for* $C_6H_{10}Mo_2N_2O_6S_4.2Na.2H_2O$

Unit cell volume, 979 Å^3; Cu $K\alpha$ radiation; number of independent reflexions, 1808.

Peak height (e Å^{-3})	Identity: True	Derived (*a*)	(*b*)
91·0	Mo	Set to Mo	
85·2	Mo	Mo	Mo
29·9	S(*c*)	S	S
27·4	S(*d*)	S	S
15·2	Na	Na	Na
13·5	Na	Na	O
11·7	O(*c*)	O	O
9·7	(*e*)	O	O
9·6	O(*d*); N(*c*)	O	N
9·3	H_2O	N	N
8·7	N(*d*)	N	N
7·8	C(*c*)	N	C
7·5	H_2O	C	C
5·9	C(*d*)	C	C

(*a*) No correction to the analytical constants for anomalous dispersion.
(*b*) Analytical constants corrected for the real component of anomalous dispersion.
(*c*) Highest peak for an atom of this type.
(*d*) Lowest peak for an atom of this type.
(*e*) Not a peak observed on the map; value inserted into the program to locate the boundary for distinction between nitrogen and carbon.

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