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## Atomic Scattering Factors for Mixed Atom Sites

BY KEITH D. SALES

*Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, England*

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### Abstract

A method is presented for the calculation of analytical coefficients for scattering factors at mixed atom sites. The importance of the concept of compatible coefficients for the separate atoms is stressed and examples of the problems that can arise when trying to find coefficients for mixed atom sites are given. A computer program and its use are described. Two errors in *International Tables for X-ray Crystallography* [(1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht)] are noted, for  $\text{Ru}^{4+}$  and  $\text{Bi}^{5+}$ , for which revised coefficients are given. For  $\text{N}$ ,  $\text{O}^-$  and  $\text{Sr}^{2+}$  analytical coefficients are given which fit the tabulated scattering factors significantly better than the coefficients in *International Tables for X-ray Crystallography*.

### 1. Introduction

The atomic scattering factor is used to describe the coherent scattering of X-rays by an atom. It is a function of the electron density of the atom and the finite size of this density causes the scattering factor to depend upon the Bragg angle  $\theta$  and the wavelength of the X-rays  $\lambda$  through the parameter  $x = \sin\theta/\lambda$ . The electron density of an atom is known only by theoretical calculation so the scattering factor is approximate and depends upon the reliability of the theory; various calculations have been used and the resulting factors tabulated for a range of  $x$  values between 0 and 2 (*International Tables for X-ray Crystallography*, 1974, pp. 82-98).

Tables of such values were used in older X-ray computer programs, scattering factors for non-tabulated  $x$  values being obtained by linear interpolation. More recent programs use an analytical expression

of the form:

$$f_c(x) = \sum_{i=1}^4 a_i \exp[-b_i x^2] + c, \quad (1)$$

with values of  $\mathbf{a}$  ( $= a_i, i = 1$  to 4),  $\mathbf{b}$  ( $= b_i, i = 1$  to 4) and  $c$  being tabulated for different atoms (*International Tables for X-ray Crystallography*, 1974, pp. 99-101). The  $\mathbf{a}$ ,  $\mathbf{b}$  and  $c$  for a particular atom are obtained by minimizing the difference between  $f_c(x)$ , the value calculated from such an expression, and  $f(x)$ , the tabulated value. The statistic used here to obtain this best fit is

$$\chi^2 = \sum_{i=1}^n [f(x_i) - f_c(x_i)]^2 / (n - 9),$$

where  $n$  is the number of  $x$  values used in the fitting, those used here being  $x_i = 0.0$  (0.01) 0.20 (0.02) 0.50, 0.55, 0.60, 0.65, 0.70 (0.10) 2.00, a maximum of 53 values, although for some cases  $f(x)$  is quoted for only the first 48 values.

Some structures contain a mixture of two different atoms occupying the same type of site as, for instance, NO and CO groups or  $\text{Na}^+$  and  $\text{K}^+$  ions disordered in a lattice. In these cases an average scattering factor has to be used:

$$f(x) = x_A f_A(x) + x_B f_B(x), \quad (2)$$

where  $x_A$  is the mole fraction of atom  $A$  with scattering factor  $f_A$  and similarly for  $B$ . With tabulated values of  $f_A$  and  $f_B$  this averaging is trivial, but with the analytical expression for  $f$  there is a complication in existing computer programs which require coefficients for each 'atom', regardless of whether that 'atom' is a mixture of two atoms or not. Thus the problem is to express  $x_A f_A(x) + x_B f_B(x)$  in the form of (1).

Table 1. *Coefficients for mixtures of C and N starting from pure C*The coefficients of the mixture of next higher  $x_A$  have been used to begin each calculation.

| $x_A$ | $a_1$    | $a_2$   | $a_3$   | $a_4$    | $b_1$    | $b_2$   | $b_3$   | $b_4$   | $c$        |
|-------|----------|---------|---------|----------|----------|---------|---------|---------|------------|
| 1.00  | 1.59217  | 1.39793 | 2.15991 | 0.636729 | 0.567485 | 11.1793 | 23.8251 | 57.3470 | 0.212972   |
| 0.90  | 1.58486  | 1.25760 | 2.32489 | 0.713653 | 0.552649 | 10.0157 | 21.9017 | 54.3586 | 0.218597   |
| 0.80  | 1.57838  | 1.24101 | 2.41398 | 0.742646 | 0.537745 | 9.31626 | 20.8839 | 52.6317 | 0.223543   |
| 0.70  | 1.57287  | 1.28006 | 2.46706 | 0.751716 | 0.522874 | 8.87302 | 20.2215 | 51.3354 | 0.227822   |
| 0.60  | 1.56855  | 1.36431 | 2.49405 | 0.741035 | 0.508305 | 8.61937 | 19.8448 | 50.4459 | 0.231606   |
| 0.50  | 1.56534  | 1.46392 | 2.51075 | 0.724903 | 0.493814 | 8.44845 | 19.5571 | 49.6218 | 0.234663   |
| 0.40  | 1.56331  | 1.57576 | 2.51954 | 0.704053 | 0.479421 | 8.33513 | 19.3410 | 48.8463 | 0.236953   |
| 0.30  | 1.56251  | 1.69663 | 2.52223 | 0.679889 | 0.465114 | 8.26038 | 19.1765 | 48.0834 | 0.238397   |
| 0.20  | 1.56288  | 1.76787 | 2.54401 | 0.686929 | 0.450032 | 8.11120 | 18.6948 | 46.5252 | 0.237962   |
| 0.10  | 1.56489  | 1.95700 | 2.51317 | 0.626343 | 0.436686 | 8.18109 | 18.9462 | 46.4561 | 0.238374   |
| 0.00  | 1.56822  | 2.09369 | 2.50215 | 0.599096 | 0.422538 | 8.16299 | 18.8601 | 45.5169 | 0.236688   |
|       | [12.2126 | 1.16630 | 3.13220 | 2.01250  | 0.005700 | 0.58260 | 9.89330 | 28.9975 | -11.5290]* |

\* Tabulated coefficients for pure N.

## 2. Method and problems

Marquardt's (1963) method, which is simple and efficient provided, as is the case here, the derivatives of  $\chi^2$  with respect to the coefficients can be evaluated analytically, has been used to find the best fit. A Fortran program to find the best coefficients for a mixture of atoms is given in the deposited material, together with an explanation of its use.\* The method is iterative, requiring starting values of  $a_0$ ,  $b_0$  and  $c_0$  and, as with any iterative method, the rate of convergence depends upon these starting values. Problems occur in the minimization because the surface of  $\chi^2$  plotted against  $a$ ,  $b$  and  $c$  is, in some cases, rather complicated: it appears to be flat in parts, to be pitted with local minima which are higher than the global minimum, and to contain more than one global minimum. Thus, depending upon the choice of  $a_0$ ,  $b_0$  and  $c_0$ , it is possible either to fall into a local minimum, when the method will make no further progress, or to reach a flat region near the global minimum, when progress becomes very slow. There is no easy way round the latter problem and whereas the former can, in principle, be circumvented by restarting from a different point, in practice this is difficult to programme for the general case and would result in a time consuming procedure. The fact that there can be more than one global minimum means that several sets of quite different coefficients may give an equally good fit to the data.

The choice of  $a_0$ ,  $b_0$ ,  $c_0$  is therefore a matter of importance. The most obvious reasonable one would seem to be:

$$a_0 = x_A a_A + x_B a_B \quad (3)$$

with similar expressions for  $b_0$  and  $c_0$ . The first problem is that whereas  $a_i$  and  $b_i$  for a particular atom

are paired the order of the pairs is arbitrary, so it is not clear for a mixture how to order the relative pairs for averaging in (3). A second problem, which is in some ways related to the first, is that the coefficients of atom  $A$  may not be compatible with those of  $B$  in the sense that if the coefficients for a series of mixtures of  $A$  and  $B$  are calculated starting from pure  $A$  and always using as starting values the final values for the previous mixture, the coefficients for pure  $B$  may be completely different from the tabulated values. An example, for carbon and nitrogen, is shown in Table 1; the coefficients found here for pure nitrogen actually give a better fit to the  $f$  data.

## 3. Applications

The coefficients for the free atoms and chemically significant ions have been recalculated in an attempt to make them more compatible in the sense defined above. There can be no absolute guarantee that a set of coefficients is completely compatible for that would require calculations on a series of mixtures for all possible pairs of atoms – a very large amount of computation. Furthermore, it is quite probable that no one set of coefficients would be compatible for all possible pairs. In the course of this work two errors were found in the tabulated values: the coefficients for  $Ru^{4+}$  and  $Bi^{5+}$  are incorrect (usable values are given in Table 2). The species with the bigger changes in their coefficients, relative to the tabulated values, are shown in Table 2 together with the errors for the two sets; the compatible coefficients for  $N$ ,  $O^-$  and  $Sr^{2+}$  happen also to give rather smaller errors. Some typical results for equimolar mixtures of atoms, which might be expected to be the most difficult ones to fit, are given in Table 3 and illustrate the points made above. Thus for the pairs (C,N) and ( $Na^+$ ,  $K^+$ ) the old coefficients require many more iterations than the new but arrive at the same minimum, whereas for ( $O^-$ ,  $Cl^-$ ) a worse result is obtained after more iterations. Similarly poor results are obtained for ( $Y^{3+}$ ,  $Sm^{3+}$ ) and ( $Ca^{2+}$ ,  $Sr^{2+}$ ). It is interesting to note

\* The Fortran program *MARQ* and its accompanying documentation have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 42963 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Compatible coefficients with the bigger differences from tabulated values*

The row for each species contains the coefficients in the order *a*, *b*, *c*, the maximum error, *x* value at which it occurs, and the mean error, with corresponding values for the tabulated coefficients in brackets.

|                  |         |         |          |          |            |          |         |         |           |        |      |        |         |      |         |
|------------------|---------|---------|----------|----------|------------|----------|---------|---------|-----------|--------|------|--------|---------|------|---------|
| N                | 1.56822 | 2.09515 | 2.50171  | 0.598040 | 0.422558   | 8.16516  | 18.8703 | 45.5445 | 0.236715  | 0.0010 | 2.00 | 0.0003 | [0.0066 | 0.11 | 0.0029] |
| O <sup>-</sup>   | 1.39094 | 3.27082 | 3.08788  | 0.766192 | 0.442884   | 7.01110  | 20.0770 | 66.4949 | 0.482356  | 0.0026 | 1.30 | 0.0013 | [0.0114 | 1.50 | 0.0044] |
| Ar               | 6.19120 | 7.26462 | 7.12086  | 1.90010  | 0.0106084  | 0.949902 | 15.3801 | 39.3024 | -4.47684  | 0.0108 | 0.80 | 0.0021 | [0.0292 | 2.00 | 0.0029] |
| K <sup>+</sup>   | 3.83963 | 3.59059 | 7.73888  | 1.41577  | 0.771452   | 0.772122 | 12.4399 | 29.5307 | 1.41618   | 0.0129 | 0.90 | 0.0026 | [0.0112 | 2.00 | 0.0033] |
| Ti <sup>4+</sup> | 7.93953 | 7.95478 | -1.61398 | 2.26933  | 0.565339   | 6.19280  | 1.93746 | 11.8272 | 1.45011   | 0.0006 | 0.14 | 0.0003 | [0.0018 | 1.50 | 0.0004] |
| Sr <sup>2+</sup> | 8.30615 | 17.8518 | 8.65338  | 1.97393  | 0.078529   | 1.51796  | 13.1749 | 26.4711 | -0.784920 | 0.0018 | 0.80 | 0.0005 | [0.0085 | 2.00 | 0.0011] |
| Y <sup>3+</sup>  | 14.8649 | 17.7993 | 9.18957  | 1.70509  | 0.0349503  | 1.36526  | 11.2808 | 22.8260 | -7.55888  | 0.0021 | 1.10 | 0.0005 | [0.0049 | 2.00 | 0.0006] |
| Zr <sup>4+</sup> | 25.4279 | 17.8868 | 10.0699  | 0.946880 | 0.0168489  | 1.23581  | 10.2292 | 21.7825 | -18.3310  | 0.0047 | 0.90 | 0.0011 | [0.0036 | 2.00 | 0.0010] |
| Ru <sup>4+</sup> | 14.9890 | 18.5004 | 13.0735  | 2.29059  | 0.0109554  | 0.845303 | 8.09074 | 20.3722 | -8.85346  | 0.0082 | 1.00 | 0.0018 | [—]     |      |         |
| Rh <sup>3+</sup> | 13.5476 | 18.7909 | 14.1496  | 3.28190  | 0.00663111 | 0.769059 | 7.87065 | 21.3575 | -7.77126  | 0.0076 | 2.00 | 0.0022 | [0.0134 | 2.00 | 0.0022] |
| Rh <sup>4+</sup> | 7.13262 | 18.7752 | 13.8916  | 2.61762  | 0.0111264  | 0.763980 | 7.60410 | 19.0217 | -1.41710  | 0.0083 | 1.80 | 0.0019 | [0.0134 | 2.00 | 0.0021] |
| Bi <sup>5+</sup> | 12.0277 | 32.5234 | 19.7004  | 6.24141  | 0.125629   | 0.945056 | 5.86539 | 13.2823 | 7.50562   | 0.0038 | 0.90 | 0.0014 | [—]     |      |         |

Table 3. *Errors for equimolar mixtures of A and B atoms*

| A                | B                | Tabulated coefficients |          |        |      | Compatible coefficients |          |        |     |
|------------------|------------------|------------------------|----------|--------|------|-------------------------|----------|--------|-----|
|                  |                  | max.                   | <i>x</i> | mean   | its* | max.                    | <i>x</i> | mean   | its |
| C                | N                | 0.0028                 | 2.00     | 0.0006 | 390  | 0.0028                  | 2.00     | 0.0006 | 12  |
| Na <sup>+</sup>  | K <sup>+</sup>   | 0.0027                 | 0.80     | 0.0010 | 156  | 0.0027                  | 0.80     | 0.0010 | 9   |
| O <sup>-</sup>   | Cl <sup>-</sup>  | 0.0109                 | 0.65     | 0.0058 | 261  | 0.0063                  | 1.50     | 0.0021 | 148 |
| Ti <sup>4+</sup> | Mn <sup>4+</sup> | 0.0013                 | 1.40     | 0.0004 | 86   | 0.0014                  | 1.40     | 0.0003 | 23† |
| Ca <sup>2+</sup> | Sr <sup>2+</sup> | 0.0077                 | 2.00     | 0.0020 | 236  | 0.0011                  | 0.70     | 0.0005 | 204 |
| Y <sup>3+</sup>  | Sm <sup>3+</sup> | 0.0290                 | 2.00     | 0.0088 | 500‡ | 0.0013                  | 0.24     | 0.0005 | 53  |
| Mn <sup>4+</sup> | Zr <sup>4+</sup> | 0.0077                 | 1.30     | 0.0027 | 157  | 0.0026                  | 1.40     | 0.0007 | 80  |
| Cr <sup>3+</sup> | Rh <sup>3+</sup> | 0.0028                 | 0.80     | 0.0010 | 500‡ | 0.0053                  | 0.90     | 0.0022 | 182 |

\* its = number of iterations taken.

† Takes 275 iterations if the Ti<sup>4+</sup> coefficients are re-ordered.

‡ 500 was the maximum number of iterations allowed.

Table 4. *Errors for equimolar mixtures of A and B atoms using calculated atomic scattering factors*

The errors are relative to the tabulated factors, not the calculated ones.

| A                | B                | max.   | <i>x</i> | mean   | its* |
|------------------|------------------|--------|----------|--------|------|
| C                | N                | 0.0031 | 2.00     | 0.0006 | 9    |
| Na <sup>+</sup>  | K <sup>+</sup>   | 0.0067 | 0.90     | 0.0014 | 36   |
| O <sup>-</sup>   | Cl <sup>-</sup>  | 0.0098 | 0.80     | 0.0040 | 95   |
| Ti <sup>4+</sup> | Mn <sup>4+</sup> | 0.0025 | 1.20     | 0.0004 | 7    |
| Ca <sup>2+</sup> | Sr <sup>2+</sup> | 0.0052 | 0.90     | 0.0012 | 177  |
| Y <sup>3+</sup>  | Sm <sup>3+</sup> | 0.0013 | 0.24     | 0.0005 | 56   |
| Mn <sup>4+</sup> | Zr <sup>4+</sup> | 0.0024 | 1.40     | 0.0007 | 472  |
| Cr <sup>4+</sup> | Rh <sup>4+</sup> | 0.0059 | 1.40     | 0.0016 | 364  |

\*its = number of iterations taken.

that if the compatible *b* coefficients for Ti<sup>4+</sup> (see Table 2) are re-ordered to be in increasing size then 275 iterations are required to produce the same result, another indication of the importance of obtaining compatible coefficients.

The technique for finding the coefficients as explained so far requires not only the coefficients of the two constituent atoms and their mole fractions but also the scattering factors for the atoms. The scattering factors for the mixture are found from (2) and the starting values *a*<sub>0</sub>, *b*<sub>0</sub> and *c*<sub>0</sub> for the iterative procedure from (3). However, it is more convenient, especially when *x*<sub>A</sub> is an unknown quantity and has

itself to be optimized during the general crystallographic fitting, to calculate the scattering factors from the stored coefficients for the atoms and to use these values for *f*<sub>A</sub> and *f*<sub>B</sub> in (2). This procedure will, in general, be less accurate but appears to give satisfactory results, as the typical data in Table 4 show.

#### 4. Concluding remarks

The recommended procedure to obtain coefficients for a mixture is to use the tabulated atomic coefficients as input to the computer program: if the computed error limits are acceptable then use the derived coefficients. If the mole fraction is not known, when the number of iterations may be important, or if the errors are not acceptable then compatible coefficients for the pair of atoms should be found as described in the text (see Table 1). Thereafter the coefficients for all mixtures should be obtainable quickly and accurately.

#### References

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