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'Core electrons' of bonded hydrogen atoms.

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X-ray scattering factors for bonded hydrogen atoms are derived for the case where the aspherical electron density distribution due to the chemical bonding, is approximated by additional scattering centres. It is assumed that in the vicinity of the proton the electron density does not change much when the bond is formed.

The isolated-atom model, used in conventional structure determination, can be corrected in a purely empirical way for bonding effects by approximating the excess density between atoms by additional scattering centres and the atomic cores by ions carrying some fractional charge (Brill, Dietrich & Dierks, 1971). This accounts for the plausible assumption that the electron cloud within the atomic cores will not be changed much by the chemical bonds, since the radial electric field of the nucleus dominates there. A verification of this assumption can be seen in the fact that the X-ray scattering factors of different ionic states of an atom are almost identical for the outer reciprocal space, *i.e.* the high frequency parts of the Fourier spectra of the density are nearly the same, because the density details involving large density gradients (as within the atomic cores) are almost the same.

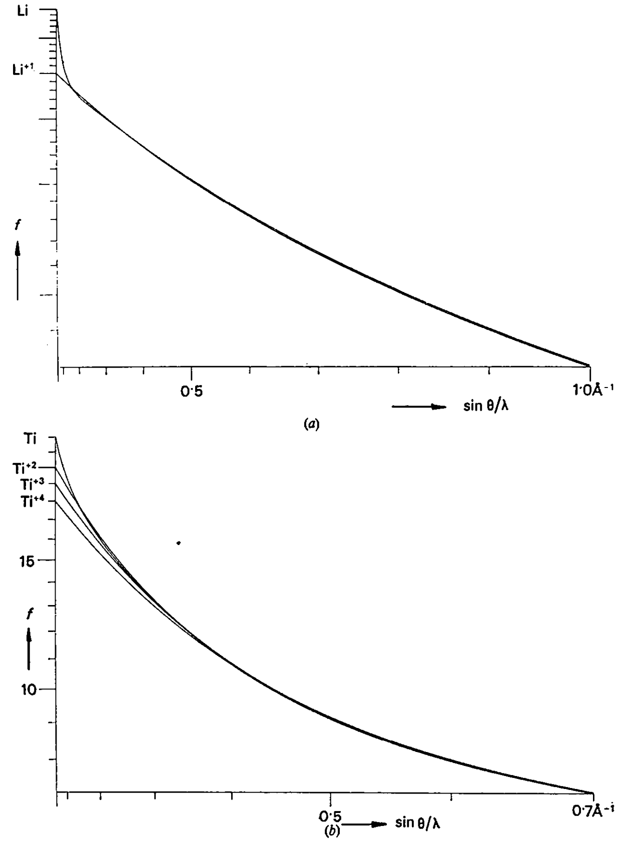

Fig. 1. Comparison of X-ray scattering factor functions for the neutral atoms to the scattering curves for the ions of (*a*) Li and (*b*) Ti. Representation log *f versus* $(\sin\theta/\lambda)^2$.

For all atoms except H the scattering factors needed for the atomic cores can be interpolated from scattering factor tables in the *International Tables for X-ray Crystallography* (1974). For first-row atoms it is more convenient to use the *L*-shell projection method of Stewart (1970).*

For the hydrogen atom an interpolation between H^+ and H would mean using just one scale factor for the whole H scattering factor. This would scale also the high-frequency part of the table, so the maximum absolute change in density would occur at the proton, which is certainly wrong. According to the above considerations a better approximation would be to keep the high-frequency part of the H scattering curve constant and reduce only the low-frequency part. For a $H^{+\delta}$ scattering factor table the maximum value, $f(0)=1-\delta$, is known. But the question is how to combine this value with the high-order tail of the H scattering curve, and where the beginning of this tail is to be assumed. Surely, any answer must be to some extent arbitrary, but this may be minimized if some general features of the *f* curves are taken into account. The curves should be considered in a coordinate system in which they show minimum curvature, especially in the low-order region. This condition is fulfilled best by the coordinates log *f* and $(\sin\theta/\lambda)^2$. In Fig. 1 the scattering curves of Li and Ti are compared to the scattering curves of their ions using the log *f versus* $(\sin\theta/\lambda)^2$ representation. It can be seen that the scattering curves of the ions either join the curve of the neutral atom tangentially from below or cross it and stay slightly above it for some interval. The latter case is typical for ions which have lost all the electrons of their outermost shell. So, for $H^{+\delta}$ a curve which does not cross the H curve is suggested.

From the shape of the curve it can be concluded that parabolic functions of the form

$$\log f(x)=a_0+a_1x+a_2x^2\,, \qquad (1)$$

with $x=(\sin\theta/\lambda)^2$, can be fitted well to the low-order region of the scattering curves.†

Table 1. *Second and third points of form factor tables for three examples and coefficients* a_i *in* (1) *computed from them*

	Second point Å^{-1}	Third point Å^{-1}	a_0	a_1	a_2
H^{-1}	0·05	0·10	0·6931	−109·4	4632
H	0·05	0·10	0·0000	−22·06	111·2
$H^{+0\cdot3}$	0·40	0·50	−0·3567	−12·96	15·21
$H^{+0\cdot5}$	0·50	0·60	−0·6931	−9·607	7·198
$H^{+0\cdot7}$	0·60	0·70	−1·204	−6·822	3·403

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* For this suggestion I am indebted to Professor R. Allmann, Marburg.

† Therefore, this type of function is also useful for accurate interpolation of scattering factor tables (Dietrich, 1976).

Using this function it is easy to find the best tangential connexion to the high order part of the H scattering curve. One has to leave out as many low-order points of this part as necessary before obtaining a $H^{+\delta}$ curve that crosses the H curve. The results for $\delta = 0{\cdot}3$, $0{\cdot}5$, and $0{\cdot}7$ are summarized in Table 1. The second point of each form factor table is the beginning of the high order part of the H table preserved. The coefficients a_i found from the first three points of each table are compared to those calculated for the first points of the H^{-1} and H tables. Fig. 2 shows the three resulting scattering curves. The scattering factor tables for H and H^{-1} plotted for comparison in Fig. 2 are taken from Vol. III of the *International Tables for X-ray Crystallography* (1962), because the tables in Vol. IV (1974) give poor curves owing to rounding effects.

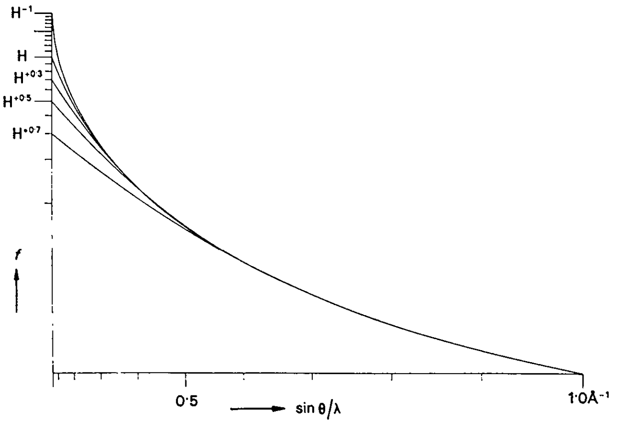

Fig. 2. Scattering factor curves for $H^{+0\cdot3}$, $H^{+0\cdot5}$, $H^{+0\cdot7}$ using high-order tails of the H curve starting at 0·4, 0·5 and 0·6 Å^{-1} respectively and using equation (1) for interpolation.

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A note on two papers by Kuntsevich & Belov.

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1237 four-dimensional space-group types of the 'low-symmetry crystal classes' have been listed by Kuntsevich & Belov [*Kristallografiya* (1971). **16**, 5–17, 268–272]. Comparison of this list with the results of Brown, Bülow, Neubüser, Wondratschek, and Zassenhaus shows that three space-group types are listed twice and one space-group type is missing. The crystal classes considered by Kuntsevich & Belov thus contain 1235 of the 4783 types of space groups of *R*4.

Crystallography in four-dimensional space *R*4 has drawn increasing interest during the last years. Reasons for this may be: possible applications in physics, better insight into dimension-independent features of crystallographic objects, mathematical interest in integer matrix groups, and the availability of large computers for the performance of the necessary calculations.

For the crystal families, crystal systems, crystal classes, and Bravais-types we refer to Wondratschek, Bülow & Neubüser (1971) and the literature quoted there. In a joint project of Brown, Bülow, Neubüser, Wondratschek, and Zassenhaus (referred to as BBNWZ) also a complete list of all affine equivalence classes of space groups of *R*4 was determined, their number being 4783.

Those space groups of *R*4 for which the linear parts of all symmetry operations have order not exceeding two, *i.e.* those corresponding to the triclinic to orthorhombic space groups in *R*3 had been derived and listed by Kunstevich & Belov (1971) (referred to as KB), using geometric arguments. They found 1237 types of such space groups.

Although KB did admirable work, errors are almost unavoidable in computations by hand. There are discrepancies in relation to the tables of BBNWZ, which contain only 1235 affinely-non equivalent space group types of this kind.

A closer inspection shows the following discrepancies. In KB crystal class VIII, X, and XI the KB numbers of space-group types exceed the BBNWZ numbers of space-group types by one, in XV BBNWZ have listed one space-group type more than have KB.

KB characterize their space-group types by certain sets of generators. The symbols used are slightly modified Hermann (1949) symbols. The generating matrices of a representation of each space-group type can be determined easily from these symbols, *e.g.* space-group type VIII, 43

$$A_1 = \left(\begin{array}{cccc|c} \bar{1} & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & \frac{1}{4} \\ 0 & 0 & 1 & 0 & \frac{1}{4} \\ 0 & 0 & 0 & 1 & 0 \\ \hline 0 & 0 & 0 & 0 & 1 \end{array}\right) \qquad A_2 = \left(\begin{array}{cccc|c} 1 & 0 & 0 & 0 & \frac{1}{4} \\ 0 & \bar{1} & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & \frac{1}{4} \\ 0 & 0 & 0 & 1 & 0 \\ \hline 0 & 0 & 0 & 0 & 1 \end{array}\right)$$