X-ray Scattering Factors of Ions in Crystals

P. C. Schmidt and Alarich Weiss
Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Darmstadt

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The atomic scattering factors for X-Rays are given for the ions Li®, Be®, B®, C®, N®, O®, F®, Ne®, Mg®, Al®, Si®, P®, S®, Cl®, Ar®, K®, Ca®, Sc®, Ti®, V®, Cr®, Mn®, Fe®, Co®, Ni®, Cu®, Zn®, Ga®, Ge®, As®, Se®, Br®, Rb®, Sr®, Y®, Zr®, Nb®, Mo®, Tc®, Ru®, Rh®, Pd®, Ag®, Cd®, In®, Sn®, Sb®, Te®, I®, Xe®, Cs®, Ba®, Po®, At®. The atomic form factors of the free ions, especially the twofold and threefold ionized negative ions, which are unstable in the gaseous phase, are determined by quantum mechanical calculations.

Introduction

In todays crystal structure determinations the point positions of the atoms in the unit cell and their thermal vibrations are optimized on the basis of the reliability factor $R$. Whatever approach one chooses, $R$ is minimized and thereby the method relates to the given “theoretical” atomic scattering factors. The atomic scattering factors $f_{\text{theor}}$ are gained from the spherical charge distribution of the atoms determined by quantum mechanical calculations. Any nonspherical charge distribution is neglected in $f_{\text{theor}}$. For solids in which covalent bonds between the atoms are present, this problem was recognized since a long time. McWeeny [1, 2, 3] first pointed out, that the free atom approach to $f_{\text{theor}}$ has to be improved by more elaborate models, which take the chemical bond into account. Effective scattering factors were introduced by him to describe the x-ray scattering of “bonded” atoms. Further improvement of the theory of x-ray scattering on bonded atoms was made since, see e.g. the discussions given by Coppens [4].

A different situation arises in coherent x-ray scattering of ionic crystals. Dawson [5] has introduced the expansion of the atomic charge distribution in cubic harmonics around the nuclei. Further progress along this line is due to Kurki-Suonio and Ruuskanen [6, 7, 8]. Several approaches have been made, to take the deformation of the electronic distribution of ions in crystals into account. An important step was done by Löwdin [9, 10] in introducing the overlap model, Yamashita and Kojima [11] account for the crystal field by considering overlap and Madelung potential. A very simple model for ions in crystals was introduced by Watson [12].

The most famous example for the influence of the crystal field on ions is the ion $^{0}_{2}$O. Elaborate Hartree-Fock calculations show, that the free ion is unstable [13]. Either by the approach of Yamashita [14, 15] or by the use of the Watson sphere model [12, 16] this ion becomes stable by incorporation into the solid. The use of the Watson sphere potential for ions in crystals has shown up to be very useful in calculating physical properties which depend strongly on the charge distribution around the nucleus, such as the diamagnetic susceptibility [16, 17], the dipole polarizabilities [16, 18] and the Sternheimer antishielding factors [16, 19]. We therefore propose the application of this model to calculate the $f_{\text{theor}}$ for ions in crystals. Thereby a set of $f_{\text{theor}}$-values is available, which in general should lead to a better starting point in judging the reliability and accuracy of crystal structure data by minimizing $R \sim |f_{\text{theor}} - f_{\text{exp}}|$. 

Theory

The atomic scattering factor is calculated from the spherical charge distribution of atoms and ions by

$$f(k) = \int \rho(r) \exp \{i \mathbf{k} \cdot \mathbf{r} \} d\mathbf{r}, \quad (1)$$

where $\rho(r)$ is the electron density of the isolated atom (ion) and $k = 4\pi \sin \theta/\lambda$ is the magnitude of the vector $\mathbf{k}$ in the reciprocal space. Since we assume...
the electronic charge density to be spherical symmetric, \( q(r) = U(r) \), (1) reduces to
\[
 f(k) = \int_0^\infty U(r) \frac{\sin kr}{k r} \, dr
\]
(2)

\( U(r) \) is taken from self consistent field treatments of the atoms (ions). By changing the free ion approach by application of the Watson-sphere model [12] we put around the spherical ion a charged hollow sphere of radius \( R_0 \). For compensation the charge \( q_e \) of the sphere has opposite sign but equal magnitude to the charge of the ion. The system: (ion + sphere) is now neutral. In Fig. 1 the model is shown. The model crystal potential is given by the form [16]
\[
 V_w(r) = \begin{cases} 
 q/R_0 & \text{for } r \leq R_0 \\
 q/r & \text{for } r > R_0 
\end{cases}
\]
(3)

and \( q_{\text{sphere}} = -q_{\text{ion}} \).

The resulting Hamiltonian of the ion in the crystal is then
\[
 \mathcal{H} = -\sum_{l=1}^\infty \left[ \frac{1}{2} \Lambda_l + \frac{Z}{r_l} + V_w(r_l) + \sum_{j>i} \frac{1}{r_{ij}} \right]
\]
(4)

(\( N \) is the number of electrons, \( Z \) the nuclear charge).

In the frame of the SCF-HF-Roothaan theory the one electron wave functions are given by
\[
 \begin{align*}
 \varphi_{nlm} &= \sum_p c_{nlp} R_{lp}(r) Y_{lm}(\theta, \phi) \\
 R_{lp}(r) &= N_{lp} r^{n_{lp}-1} \exp \left\{ -\zeta_{lp} r \right\} \\
 N_{lp} &= \left[ (2n_{lp})! \right]^{1/2} \left( 2\zeta_{lp} \right)^{n_{lp}+1/2}
\end{align*}
\]
(5)

The radial electron distribution functions of the ions in the crystal is easily found. The radial electron density for closed shell ions is
\[
 P^2(r) = \sum_{nl} 2(2l + 1) \sum_{pp'} c_{nlp} c_{nlp'} r^2 R_{lp}(r) R_{lp'}(r) 
\]
(6)

From (6) and (2) for \( k = 0 \) the atomic scattering factors are given by the expression
\[
 f(k) = \frac{1}{k} \sum_{nl} 2(2l + 1) \sum_{pp'} c_{nlp} c_{nlp'} (\zeta_{lp}^2 + \zeta_{lp'}^2)^{-n_{lp} + n_{lp'}} S_{n_{lp} + n_{lp'} - 1} \left( \frac{k}{\zeta_{lp}^2 + \zeta_{lp'}^2} \right)
\]
(7)

where the integral
\[
 S_m(x) = \int_0^\infty t^m \sin(x t) \exp \{-t\} \, dt
\]
(8)
is not calculated numerically but by a simple recurrence formula.

Results

The electron distribution, respectively the radial distribution functions of ions, changes considerably through the influence of the spherical potential. In general cations expand, anions shrink [16]. The radial density distribution depends on the radius of the charged sphere. We have chosen the ionic radii of Pauling, but \( P^2(r) \) was also calculated for \( R_0 = R_{\text{Pauling}} \). There is no doubt, that the arbitrariness in selecting \( R_0 \) is a major disadvantage of the model. Nevertheless the \( R_0 \)-dependence at \( R_0 \approx r_{\text{Pauling}} \) is small compared with the total effect of the charged sphere on \( P^2(r) \). In Fig. 2 the radial distribution function \( P^2(r) \) is shown for \( Fe^2+ \). The difference in the radial charge density for the ion in the Watson sphere for different radii \( R_0 \), \((P^2(r))_{R_0} \), can not be resolved within the plot of Fig. 2. In Fig. 3 the differences
\[
 P^2(r) = (P^2(r))_{R_0=\infty} - (P^2(r))_{R_0}
\]
are listed for \( Fe^{2+}, Br^{2-} \) and \( Rb^{+} \).

In Table 1 the \( f_{\text{theor}} \) are given for 33 ions. For comparison the data calculated from HF- radial distribution functions for free ions as used in todays crystal structure determination are listed too. No approval has been made to include \( f_{\text{theor}} \) based on
Table 1. Atomic scattering factors $f$ for free ions and ions in the crystal potential based on Hartree-Fock-Rothaan wave functions. The first line of the table gives the chemical symbol and the charge $q_{\text{ion}}$ of the ion. The first column gives the value of $X = \sin \theta / \lambda$ in Å$^{-1}$. In the further columns the $f$ values for each ion are given for three different radii $R_0$ of the Watson sphere. The first column for one ion is calculated with $R_0 = \infty$ (free ion). The second and third column for the same ion are calculated for two different radii, which are given in Å in the second line of the table. Besides $Pd^{0}$ and $N^{0}$ the charge of the Watson sphere $q_{\text{w}}$ is equal to $-q_{\text{ion}}$.

For $Pd^{0}$ and $N^{0}$ there are five columns. The first column gives the free atom result, the second and third column the crystal atom result for two values $R_0$ with $q_{\text{w}} = -1$, and the last two columns the $f$-values for two values $R_0$ and for $q_{\text{w}} = +1$.

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Fig. 3. Difference in the total radial charge density

\[ P^2(r) = (P^2(r))_{\text{free}} - (P^2(r))_{\text{Watson sphere}} \]

for F\(^-\), Br\(^-\) and Rb\(^+\) for two different Watson sphere radii \( R_0 \).
more sophisticated quantum mechanical calculation which take configuration interaction into account [20] nor were relativistic effects considered [21]. In good approximation the corrections for anomalous dispersion can be applied to $f_{\text{theor, crystal}}$ in the usual way [22].

**Discussion**

Comparison of the charge density $P^2(r)$ for the free ions and the ions within the hollow charge sphere shows that the model crystal potential causes an expansion of the electron cloud in the cations and a shrinkage of it in the anions (see Figs. 2 and 3). The influence of the crystal potential on the electron distribution is larger for anions than for cations, an effect which is due to the more loosely bonded valence shell electrons of the anions in comparison with the cations.

The shrinkage of the anion electron cloud within the crystal potential induces an increase of the atomic scattering factor $f$ for small $\sin \vartheta / \lambda$. This is shown in Fig. 4 for $F^\ominus$.

In contrast, the atomic scattering factors $f_{\text{cation}}$ are lowered by the Watson-sphere potential (see Table 1 and Figure 5). Analogously with the density function $P^2(r)$ the effect of the crystal potential on the atomic scattering factor is larger for anions than for cations. Considering for example the ion $F^\ominus$ the maximum of the relative deviation

$$\frac{\Delta f}{f} = \frac{(f_{\text{theor, free}} - f_{\text{theor, crystal}})}{f_{\text{theor, free}}}$$

is found at $\sin \vartheta / \lambda = 0.16$ Å$^{-1}$ and is equal to $-2\%$, whereas for $Na^\oplus(\Delta f/f)_{\text{max}}$ at $\sin \vartheta / \lambda = 0.40$ Å$^{-1}$ is 0.1 to 0.2%, depending on the choosen Watson sphere radius (see Table 1).

Table 2 gives $(\Delta f)_{\text{max}}$ and $(\Delta f/f)_{\text{max}}$ for some ions. It shows that for equally charged ions $(\Delta f)_{\text{max}}$ increases with increasing atomic number. For single charged negative ions $(\Delta f/f)_{\text{max}}$ is decreasing with increasing atomic number $Z$ because $f(\sin \vartheta / \lambda = 0)$ $= Z + 1$ increases linearly with $Z$, whereas the spherical crystal potential influences mainly the valence shell electrons, which are constant in number within this series. Therefore $f$ is increasing faster with $Z$ than $\Delta f$.

For single charged positive ions the (small) change of $f_{\text{crystal}}$ compared to $f_{\text{free}}$ is sensitive to the chosen Watson sphere radius, and no general trend for $(\Delta f/f)_{\text{max}}$ for these ions is found. Twofold (and three fold) positive ions show larger $(\Delta f/f)_{\text{max}}$ than singly ionized ions because of the stronger crystal potential (see Figure 3). The large changes $\Delta f$ for the multiple charged ions is somewhat surprising. One reason for this effect may be that the Watson sphere model overestimates the true crystal potential for these ions. This assumption is supported by the fact that for the multiple charged ions considerable electron density (between 1.5 to 3 electrons) is found outside the hollow charged sphere.

The strongest effect of the crystal potential on the atomic scattering factors is experienced by the twofold and threefold negative ions. The free ion atomic scattering factor for these ions, given in Table 1, has no physical meaning because they are unstable in the gaseous phase. A comparison of the $f_{\text{free}}$ and $f_{\text{crystal}}$ for multiple charged negative ions is therefore of no use. The two- and threefold negative ions have extremely weakly bonded electrons in the outermost shell, where from a distinct difference up to 10% in the atomic scattering factors for the same ion within different crystal potentials (different Watson sphere radii in our model) results.

It will be of interest to apply $f_{\text{theor, crystal}}$ to experimentally well investigated ionic crystals, such as the alkali halides and oxides and other halides with simple crystal structures.
Fig. 5. Difference in the atomic scattering factor $\Delta f = f_{\text{free}} - f_{\text{Watson sphere}}$ for $F^-$, $Br^-$ and $Rb^+$ for two different Watson sphere radii $R_0$.

Table 2. Differences ($f_{\text{free ion}} - f_{\text{ion crystal}}$) $= \Delta f$ at the point $(\sin \theta/\lambda)_{\max}$ where the relative deviation $\Delta f/f_{\text{free}}$ is a maximum; $\lambda$ in Å.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$(\sin \theta/\lambda)_{\max}$</th>
<th>$\Delta f \cdot 10^2$</th>
<th>$\Delta f/f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F^-$</td>
<td>0.15</td>
<td>-0.148</td>
<td>1.91</td>
</tr>
<tr>
<td>$Cl^-$</td>
<td>0.15</td>
<td>-0.177</td>
<td>1.29</td>
</tr>
<tr>
<td>$Br^-$</td>
<td>0.12</td>
<td>-0.250</td>
<td>0.63</td>
</tr>
<tr>
<td>$Na^+$</td>
<td>0.35</td>
<td>0.007</td>
<td>0.11</td>
</tr>
<tr>
<td>$K^+$</td>
<td>0.20</td>
<td>0.028</td>
<td>0.17</td>
</tr>
<tr>
<td>$Rb^+$</td>
<td>0.15</td>
<td>0.032</td>
<td>0.10</td>
</tr>
<tr>
<td>$Mg^{2+}$</td>
<td>0.45</td>
<td>0.062</td>
<td>0.64</td>
</tr>
<tr>
<td>$Ca^{2+}$</td>
<td>0.25</td>
<td>0.070</td>
<td>0.78</td>
</tr>
<tr>
<td>$Sr^{2+}$</td>
<td>0.18</td>
<td>0.080</td>
<td>0.26</td>
</tr>
<tr>
<td>$Al^{3+}$</td>
<td>0.45</td>
<td>0.101</td>
<td>1.62</td>
</tr>
<tr>
<td>$Sc^{3+}$</td>
<td>0.25</td>
<td>0.121</td>
<td>0.89</td>
</tr>
<tr>
<td>$Y^{3+}$</td>
<td>0.20</td>
<td>0.244</td>
<td>0.80</td>
</tr>
</tbody>
</table>
Acknowledgement

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