does the general position of the same space group, but some space groups have many special positions (*P6/mmm*, for example, has 17, and *Pm3m* has 13). It has not been thought worth while to undertake the task without a practical end in view.

I am indebted to Professors Theo Hahn and Werner Fischer for helpful correspondence.

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X-ray Scattering Factors for O^{2-} and N^{3-}

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Form factors calculated from several theoretical models show that the $X\alpha$ method is accurate to about 1%. With the latter scheme and the Watson-sphere model the atomic form factors for O^{2-} and N^{3-} are computed for varying sphere radii. To a first approximation this radial variation accounts for the different environments of such ions. Deviations of up to 25% in the scattering factors occur when compared with the results obtained from the wave functions of the corresponding neutral atom.

1. Introduction

Coherent X-ray scattering factors are available for atoms (see, for example, Fraga, Karwowski & Saxena, 1976) and some positive and negative ions (Cromer & Mann, 1968). However, free negative ions such as O^{2-} or N^{3-} are unstable and therefore the corresponding form factors are not easily obtainable. For an investigation of Li_3N (Schulz & Schwarz, 1978) we were interested in studying the effects of an ionic crystal on the form factors of ions, especially on negative ions which are otherwise unstable.

Although free O^{2-} ions are not observed experimentally, crystalline O^{2-} ions are stabilized by their environment. Watson (1958) has suggested an electrostatic model using potential wells which simulate this stabilization. Based on this calculation atomic scattering factors for O^{2-} have been reported (Suzuki, 1960; Tokonami, 1965).

In the present work this model is used for N^{3-}, for which no such calculations have been published. In order to estimate the accuracy of the present calculation, a comparison between different theoretical models is first made for neutral atoms and positive ions, and then the effect of the Watson-sphere radius on the scattering factors of negative ions is studied in detail, concentrating on N^{3-} but also including results for O^{2-}.

2. Definitions

For spherically symmetric systems the coherent X-ray scattering factor can be expressed (Fraga *et al.*, 1976) as

$$F(\mu)=\sum_{nl} N_{nl} f_{nl}(\mu), \tag{1}$$

if one assumes that the intensity of the coherently scattered X-rays can be averaged over all orientations. In (1) N_{nl} is the number of electrons in the shell with the quantum numbers n and l. The orbital contributions $f_{nl}(\mu)$ are given by

$$f_{nl}(\mu)=\int_0^\infty P_{nl}^2(r)\,j_0(\mu r)\,\mathrm{d}r, \tag{2}$$

where the radial wave function of shell nl, denoted by $R_{nl}(r)$ multiplied by the distance r from the nucleus, enters (2) as

$$P_{nl}(r)=rR_{nl}(r), \tag{3}$$

where

$$j_0(x)=\frac{\sin x}{x} \tag{4}$$

is the spherical Bessel function of zero order, and μ is related to the scattering angle 2θ for the X-rays of wavelength λ by

$$\mu=4\pi k=4\pi(\sin\theta)/\lambda. \tag{5}$$

As a first approximation the form factor of an ion can be obtained by using the wave functions of the corresponding neutral atom: *i.e.* the orbital contributions of the atom, $f_{nl}^{\text{atom}}(\mu)$, are multiplied by the orbital occupation numbers of the ion, N_{nl}^{ion}, yielding the renormalized form factor

$$F_{\text{ren}}^{\text{ion}}(\mu)=\sum_{nl} N_{nl}^{\text{ion}} f_{nl}^{\text{atom}}(\mu) \tag{6}$$

for the ion. Such values will be used to demonstrate to what extent changes in the wave functions between atoms and ions affect the corresponding form factors.

3. Different theoretical models

An evaluation of the accuracy of several theoretical models is made here, before one of the models is chosen for the study on form factors of ions. The atomic form factor of neutral C is taken as a test case, since there are results available which were obtained from configuration-interaction (CI) wave functions (Brown, 1971). The 40-term results, denoted by F_{CI}, are assumed to be accurate and are the basis for the present comparison.

The form factor of C calculated within the Hartree–Fock (HF) theory (Fraga *et al.*, 1976) deviates from F_{CI} by less than 0·15% (Fig. 1).

In band-structure calculations three local potential models are frequently used. They are studied here in order to see what effect they have on the calculation of scattering factors and are: (1) the Slater exchange (Slater, 1951); (2) the $X\alpha$ method using the 'virial-theorem' exchange parameter α_{vt} (Schwarz, 1972); and (3) the exchange correlation potential suggested by Hedin & Lundqvist (1972). These three potentials are denoted by $\alpha=1$, $X\alpha_{\text{vt}}$ and HL, respectively. The self-consistent solutions for these potentials were obtained with a modified Herman & Skillman (1963) program. The relative deviations of the corresponding form factors from the CI values, F_{CI}, are displayed in Fig. 1. The large differences (of several per cent) for the $\alpha=1$ results are to be expected, since it is now well known that the $\alpha=1$ wave functions differ significantly from the HF functions. The $X\alpha_{\text{vt}}$ and HL results agree with F_{CI} to within 1% and 1·5% respectively. For the following study the $X\alpha_{\text{vt}}$ method is chosen, which should be sufficiently accurate.

The scattering factors of positive ions agree well with the renormalized values obtained by (6) from the corresponding neutral atom. In a case such as Li^+ or even

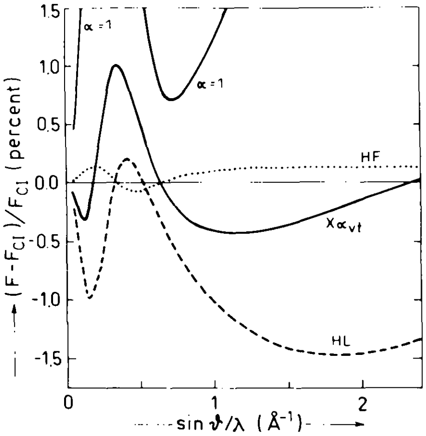

Fig. 1. The relative deviations of the atomic form factors of C with respect to the configuration-interaction (CI) results (Brown, 1971) are shown for four different theoretical models (see § 3).

Sc^{3+} the renormalized form factor differs by less than 1% from the free-ion result. This small effect on the wave functions for positive ions is in contrast to the situation found for negative ions, as will be shown in the following sections.

4. The Watson-sphere model

For O^{2-} Watson (1958) has suggested a model in which the surrounding ions in an ionic crystal are simulated by embedding the ion under consideration in a hollow sphere which carries a charge Q uniformly distributed on that sphere. This charged sphere around the ion creates a potential

$$V_W(r) = \begin{cases} \dfrac{Q}{r_W} & \text{for } r < r_W \\[2ex] \dfrac{Q}{r} & \text{for } r > r_W \end{cases} \qquad (7)$$

where r_W is the radius of the Watson sphere (Fig. 2*b*). We take Q to be the negative charge of the ion itself. The justification for this choice is that the remainder of the crystal has just this net charge. Watson himself treated Q as a parameter and took for Q the values $+1$ and $+2$ in the case of O^{2-}. For our study we fix the charge Q, but vary r_W in order to allow for a variation of the crystalline environment for a given negative ion.

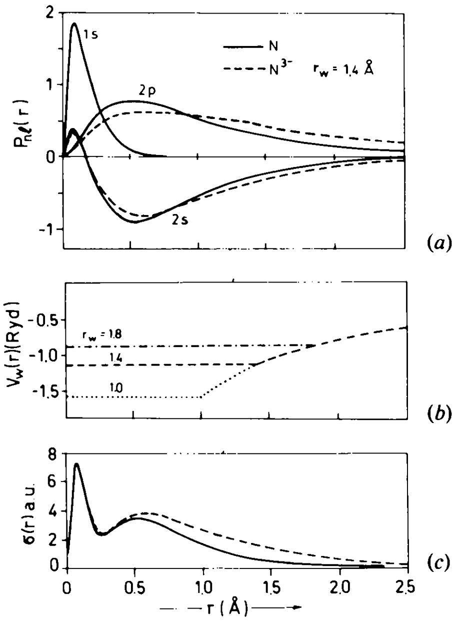

Fig. 2. Xα results (α = 0·75118) for N (solid line) and N^{3-} (dashed line, corresponding to $r_W = 1{\cdot}4$ Å): (*a*) the radial wave functions according to equation (3), (*b*) the Watson-sphere potential, according to equation (7), for three values of r_W, (*c*) the radial charge density $\sigma(r)$.

By adding this external Watson potential $V_W(r)$ to the ion potential, self-consistent solutions can be obtained for negative ions, which are otherwise unstable.

5. Results for N^{3-} and O^{2-}

Using the $X\alpha_{vt}$ method with the Watson-sphere model (as described above) atomic form factors and related quantities were computed. In Fig. 2(*a*) the radial wave functions $P_{nl}(r)$ [equation (3)] are shown for N and N^{3-}. The N^{3-} wave functions (especially the 2*p*) have a small kink at r_W, which arises from the discontinuity in the slope of the Watson potential $V_W(r)$ (Fig. 2*b*). The change from N to N^{3-} in the total radial charge density $\sigma(r)$ is displayed in Fig. 2(*c*). The decomposition of the total scattering factor into orbital contributions according to (1) is shown in Fig. 3 for neutral N.

The 1*s* radial wave function is hardly affected by the presence of the Watson sphere (Fig. 2*a*). Therefore the corresponding orbital contribution f_{1s} to the form factor is almost the same for N and N^{3-}. But for the valence states (2*s* and 2*p*) the Watson sphere strongly

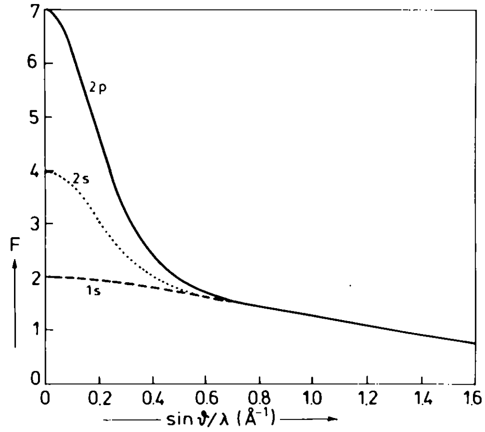

Fig. 3. Decomposition of the X-ray scattering factor of N into orbital contributions, according to equation (1).

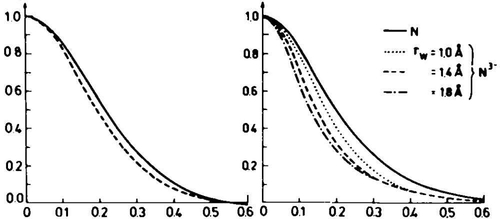

Fig. 4. The contributions f_{2s} and f_{2p} of the atomic form factor obtained according to equation (2) are shown for neutral N and for N^{3-} corresponding to different Watson radii r_W.

Table 1. *Atomic form factors for* N^{3-} *using the* $X\alpha_{vt}$ *method* ($\alpha = 0{\cdot}75118$)

Renormalized values are according to equation (6) and the results correspond to six different Watson-sphere radii.

$(\sin\theta)/\lambda$ ($Å^{-1}$)	$F_{ren}^{N^{3-}}$	Watson radius r_w (Å)					
		1·0	1·2	1·4	1·6	1·8	2·0
0·000	10·000	10·000	10·000	10·000	10·000	10·000	10·000
0·025	9·903	9·876	9·854	9·830	9·804	9·776	9·745
0·050	9·620	9·520	9·437	9·351	9·260	9·165	9·066
0·075	9·183	8·973	8·810	8·647	8·484	8·321	8·160
0·100	8·630	8·294	8·051	7·822	7·606	7·406	7·222
0·125	8·006	7·544	7·241	6·972	6·737	6·538	6·372
0·150	7·350	6·778	6·441	6·165	5·945	5·776	5·652
0·175	6·695	6·039	5·698	5·441	5·257	5·133	5·057
0·200	6·065	5·355	5·034	4·815	4·676	4·598	4·561
0·225	5·477	4·744	4·459	4·286	4·193	4·152	4·142
0·250	4·939	4·210	3·972	3·845	3·790	3·776	3·780
0·300	4·026	3·370	3·228	3·177	3·169	3·177	3·186
0·350	3·322	2·787	2·721	2·712	2·720	2·727	2·731
0·400	2·796	2·393	2·374	2·380	2·386	2·389	2·389
0·450	2·409	2·126	2·130	2·137	2·138	2·137	2·138
0·500	2·127	1·942	1·952	1·954	1·953	1·952	1·953
0·550	1·922	1·809	1·817	1·816	1·815	1·815	1·815
0·600	1·771	1·708	1·712	1·710	1·710	1·710	1·710
0·650	1·658	1·627	1·628	1·627	1·627	1·627	1·626
0·700	1·570	1·558	1·558	1·558	1·559	1·558	1·558
0·800	1·438	1·443	1·444	1·446	1·446	1·446	1·446
0·900	1·336	1·344	1·347	1·348	1·348	1·349	1·349
1·000	1·244	1·251	1·254	1·255	1·256	1·256	1·257
1·100	1·156	1·161	1·163	1·164	1·165	1·166	1·167
1·200	1·070	1·072	1·074	1·075	1·076	1·078	1·078
1·300	0·987	0·986	0·988	0·989	0·990	0·991	0·992
1·400	0·906	0·904	0·905	0·906	0·908	0·909	0·910
1·500	0·829	0·826	0·827	0·828	0·829	0·831	0·832
1·600	0·757	0·753	0·754	0·755	0·756	0·757	0·758
1·700	0·690	0·685	0·686	0·687	0·688	0·689	0·690

affects the wave functions (Fig. 2*a*) and hence also the orbital components f_{2s} and f_{2p} (see Fig. 4).

The total form factors for N^{3-} for several Watson radii are compared in Table 1 with the renormalized form factor obtained according to (6) from the neutral N. These relative differences (see Fig. 5*a*) of up to almost 25% clearly demonstrate the strong effect of the crystalline environment on the wave functions and thus on the form factors.

For O^{2-} the analogous results are presented in Table 2. Fig. 5(*b*), which also includes the earlier values obtained by Tokonami (1965), shows that the present results differ by up to 15% from the renormalized form factors.

In order to illustrate the different radii which occur in the systems N and N^{3-} we compute the total electronic charge inside a sphere of radius *r*, which is given by

$$Q(r) = \int_0^r \sigma(r')\,\mathrm{d}r', \qquad (8)$$

where $\sigma(r)$ is the radial electronic charge density (Fig. 2*c*). If the nuclear charge *Z* is included, the total charge inside a radius *r* is given by $Z - Q(r)$, as displayed in

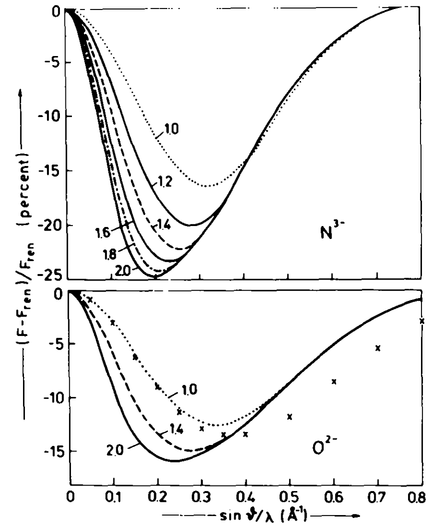

Fig. 5. The form factors corresponding to different Watson radii (between 1·0 and 2·0 Å) for the ions N^{3-} and O^{2-} are shown in the form of relative deviations with respect to F_{ren} [equation (6)], the renormalized form factor obtained from the atomic results. The earlier data by Tokonami (1965) are presented in the same form (crosses).

Table 2. *Atomic form factors for* O^{2-} *using the* $X\alpha_{vt}$ *method* ($\alpha = 0{\cdot}74367$)

Renormalized values are according to equation (6) and the results correspond to six different Watson-sphere radii.

$(\sin\theta)/\lambda$ ($Å^{-1}$)	$F_{ren}^{O^{2-}}$	Watson radius r_W (Å)					
		1·0	1·2	1·4	1·6	1·8	2·0
0·000	10·000	10·000	10·000	10·000	10·000	10·000	10·000
0·025	9·928	9·906	9·894	9·882	9·871	9·858	9·845
0·050	9·717	9·634	9·590	9·548	9·506	9·464	9·421
0·075	9·385	9·211	9·125	9·044	8·967	8·893	8·822
0·100	8·955	8·676	8·547	8·432	8·328	8·234	8·149
0·125	8·455	8·071	7·909	7·771	7·655	7·558	7·477
0·150	7·912	7·435	7·253	7·109	6·996	6·909	6·843
0·175	7·350	6·801	6·613	6·475	6·377	6·308	6·261
0·200	6·790	6·191	6·011	5·889	5·811	5·762	5·733
0·225	6·247	5·623	5·459	5·359	5·301	5·270	5·255
0·250	5·731	5·103	4·962	4·884	4·845	4·828	4·822
0·300	4·808	4·222	4·130	4·092	4·079	4·077	4·077
0·350	4·042	3·540	3·490	3·476	3·475	3·476	3·478
0·400	3·428	3·024	3·003	3·000	3·002	3·003	3·003
0·450	2·946	2·638	2·632	2·632	2·633	2·634	2·634
0·500	2·574	2·348	2·348	2·349	2·349	2·349	2·350
0·550	2·288	2·130	2·131	2·130	2·130	2·131	2·131
0·600	2·070	1·963	1·963	1·962	1·962	1·962	1·963
0·650	1·903	1·833	1·832	1·831	1·831	1·832	1·831
0·700	1·773	1·729	1·729	1·728	1·728	1·728	1·728
0·800	1·590	1·576	1·576	1·577	1·577	1·576	1·576
0·900	1·464	1·465	1·466	1·466	1·466	1·466	1·466
1·000	1·367	1·373	1·374	1·374	1·375	1·375	1·375
1·100	1·283	1·290	1·291	1·291	1·292	1·292	1·292
1·200	1·205	1·210	1·211	1·212	1·212	1·213	1·213
1·300	1·129	1·133	1·134	1·134	1·135	1·135	1·136
1·400	1·054	1·057	1·058	1·059	1·059	1·060	1·060
1·500	0·982	0·983	0·984	0·985	0·985	0·986	0·986
1·600	0·912	0·912	0·913	0·913	0·914	0·915	0·915
1·700	0·845	0·844	0·845	0·845	0·846	0·847	0·847

Fig. 6, where we see that for small radii the curves for N and N^{3-} agree, but for large radii the $Z - Q$ curves must asymptotically reach their respective ionicity (0 and 3—). Fig. 6 also shows for N the covalent radius (Pauling, 1960) outside which about 2·0 electrons are found, and the atomic radius (Pauling, 1960) (*i.e.* the metallic radius for coordination number 12) for which about 1·3 electrons are outside the corresponding sphere. In the case of N^{3-} about 1·7 and 0·9 electrons are outside the Watson radius and the ionic radius $r_{N^{3-}}$ (Pauling, 1960) respectively. The last two radii, though related to each other, are not the same.

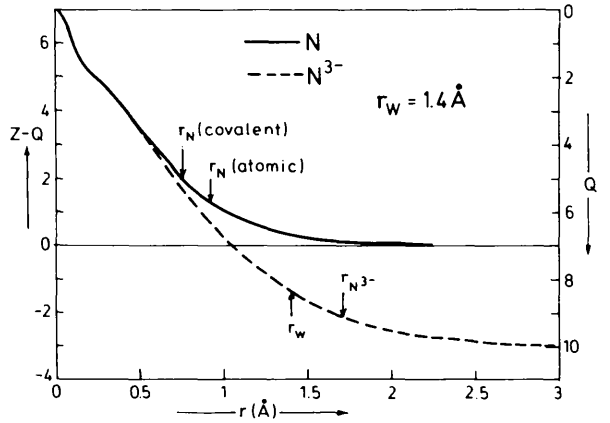

Fig. 6. The total electronic charge $Q(r)$ (in numbers of electrons) inside a sphere of radius r, according to equation (8), and the total charge $Z - Q$, including the nuclear charge Z, for N and N^{3-}.

6. Discussion

It should be mentioned that we have also applied the Watson-sphere model to positive ions using destabilizing potentials corresponding to a negatively charged Watson sphere. The effect on the form factors, however, is very small, unless one uses extremely small values of r_W, which seem unphysical. This result is not surprising; on the contrary, it is consistent with the observation that the free-ion results show remarkably good agreement with the renormalized form factors (§ 3).

For negative ions such as N^{3-} or O^{2-}, however, the form factors obtained by the Watson-sphere model deviate significantly from renormalized values, which do not account for changes in the wave functions between the negative ion and the neutral atom. However, the valence wave functions and consequently the total form factor (mainly for small sin θ/λ values) depend on the Watson-sphere radius and therefore on the crystalline environment. Thus there is not just *one* form factor for a negative ion, but a variation with r_W. The importance of this variation is demonstrated in the structure investigation of Li_3N in the following paper.

In the calculation of scattering factors for C the $X\alpha_{vt}$ method has been found (§ 3) to be accurate to about 1%. This seems to be sufficiently accurate for the present work, since we discuss larger differences. Recently, however, in connection with a study of the ionization potentials of atoms, it has been pointed out (Schwarz, 1978) that there is a fundamental difference between the HF and $X\alpha$ methods in that the instability for free negative ions is always found at smaller ionicities in the $X\alpha$ method (leading to more diffuse wave functions) than is the case with HF theory. [A similar statement has been made for H^- by Shore, Rose & Zaremba (1977).] The stabilization of the negative ions provided by the Watson sphere makes this problem less critical here. In addition it seems likely that a small reduction of r_W (*i.e.* an increasing stabilization) will effectively compensate for this difference between the $X\alpha$ and HF wave functions to a large extent.

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Is there an N^{3-} Ion in the Crystal Structure of the Ionic Conductor Lithium Nitride (Li_3N)?

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The structure parameters of Li_3N in the temperature range −120 to 20°C were refined both for neutral atoms (Li^0 and N^0) and for ions (Li^+ and N^{3-}). For N^{3-} new scattering curves were used which were calculated by applying stabilizing Watson-sphere potentials for different radii. All structure parameters depend critically on the scattering curves used. However, only on the assumption of ions, and only for N^{3-} scattering curves corresponding to a small range of Watson radii, were physically meaningful structure parameters and R values down to 0·9% obtained. These structure refinements demonstrate that Li_3N can be considered as an ionic crystal in which the N^{3-} ion, though unstable as a free ion, is stabilized by the surrounding Li^+ ions.