

Acta Cryst. (1961). **14**, 540

Remarks on potential peak shapes and on the detection of light atoms in the presence of heavy atoms. By JAMES A. IBERS, *Shell Development Company, Emeryville, California, U.S.A.*

(Received 7 September 1960)

In the past few years increasing use has been made of Fourier potential maps derived from electron diffraction data for the elucidation of crystal structures. Yet, the information available on X-ray peak shapes, for example quantitative data on the effects of data cut-off and thermal motion, is far more extensive than is the information available on electron diffraction peak shapes. In this note we first point out that it is possible from a consideration of the relative variations with scattering angle of electron and X-ray scattering amplitudes to make some useful qualitative predictions concerning potential peak shapes from a knowledge of electron density peak shapes. We also consider the relative heights of heavy atom and light atom electron density and potential peaks, and provide a theoretical basis for the experimental fact that, other factors being equal, the detection of light atoms in the presence of heavy atoms is easier with electrons than with X-rays.

The electrostatic potential φ of an isolated, spherically symmetric, neutral atom is related to the electron scattering amplitude $f_e(s)$ by the relation

$$\varphi = (K/2\pi^2) \int_0^{s_0} f_e(s) \exp[-Bs^2/16\pi^2] ((\sin sr)/sr) s^2 ds.$$

Here, if f_e is in \AA and φ volts, then K has the value 47.87 v.\AA^2 . In the equation s is the usual variable $(4\pi/\lambda) \sin \theta$, where θ is the Bragg angle. The temperature factor B has its usual meaning. The effects of data cut-off ($s_0 \neq \infty$) and of thermal motion ($B \neq 0$) can be computed from the above equation by numerical integration, if quantitative information is desired. On the other hand, the above equation is the direct analogue of the expression between electron density and the X-ray scattering amplitude (with $K=1$). Consider a 'scattering ratio' $f(s)/f(0)$, where the ratio is either of the electron or X-ray scattering amplitudes. (In the X-ray case this scattering ratio is what Harker & Kasper (1948) call the 'unitary atomic structure factor'.) In the range of s of interest ($s \leq 10 \text{ \AA}^{-1}$) it is usually possible, particularly for a heavy atom, to relate the electron scattering ratio of a given atom to the X-ray scattering ratio for the carbon atom through a single artificial temperature factor. In Fig. 1 we show that the electron scattering ratios for C, H, and W lie between the X-ray scattering ratios for C and H. It is possible, with reasonable accuracy, to fit the electron scattering ratios for C and H by modifying the X-ray scattering ratio of C by an artificial temperature factor of 1.8 \AA^2 , and to fit the electron scattering ratio of W by modifying the X-ray scattering ratio of C by an artificial temperature factor of about 0.9 \AA^2 . From these empirical results and from the general nature of the equation above, which applies in equivalent form to both the X-ray and electron diffraction case, it is possible to carry over X-ray results on peak shapes to electron diffraction. As an example, it is a well-known empirical result that the center of an electron density peak can be approximated by a Gaussian function. It follows from above that it should be possible

to approximate the center of a potential peak by a Gaussian. Such a possibility has apparently not been noted previously in electron diffraction work. Moreover, it is known that in the X-ray case the distance from the center over which the Gaussian approximation holds is greater the greater the thermal motion. Since most electron scattering ratios lie below the X-ray carbon scattering ratio, the range of fit of the Gaussian approximation should be greater, for a given cut-off, in the electron diffraction case. This prediction may be verified by calculation. As a second example, we showed recently (Ibers, 1961) that the electron count of the carbon atom oscillates with distance from the center of the peak, the higher the thermal motion the less severe the oscillation, and indeed the electron count exceeds the theoretical limit for certain cut-offs and temperature factors. The analogous electron diffraction quantity, the total potential, also should show oscillation, but such oscillation should be less severe than in the X-ray case. Finally we noted previously that electron density peaks are surprisingly diffuse, only about 75% of the electrons of the carbon atom lie within a sphere of radius 1 \AA surrounding the nucleus. It follows from the results shown in Fig. 1 that potential peaks will be similarly diffuse.

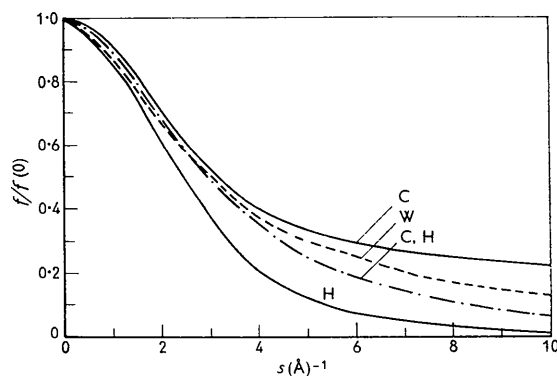


Fig. 1. Scattering ratios as a function of s . The solid lines are for $f_x(s)/Z$ (X-ray case), the dashed lines for $f_e(s)/f_e(0)$ (electron case).

One can obtain some idea of the relative merits of using electrons rather than X-rays for the detection of light atoms in the presence of heavy atoms from a comparison of the ratios of scattering amplitudes at zero scattering angle. In this way one compares the ratios of volumes of peaks which are unaffected by thermal motion or finite data. Thus, one obtains, for example,

$$\begin{aligned} \text{X-rays } H : C : W &= 1 : 6 : 74 \\ \text{electrons} &= 1 : 4.6 : 23, \end{aligned}$$

where we have taken the $f_e(0)$ values from a previous tabulation (Ibers, 1958). As a result of checks on our predictions above we had available data on X-ray and electron diffraction peak heights which permit more realistic

comparisons to be made of detectability. For example, we assume that the X-ray data go out to the copper limit ($s_0 = 8.2 \text{ \AA}^{-1}$) and that the electron diffraction data go out to a typical value of 10 \AA^{-1} . We assume that the W temperature factor is 0.5 \AA^2 , the C 1 \AA^2 , and the H 3 \AA^2 . Then we obtain for the ratios of peak heights*

| | | | |
|------------------|-----------|-----------|------------------|
| three-dimensions | X-rays | H : C : W | = 1 : 20 : ~ 480 |
| | electrons | | = 1 : 7 : 58 |
| two-dimensions | X-rays | | = 1 : 14 : 340 |
| | electrons | | = 1 : 6 : 43 |

* Our calculations on H, C, and W have verified that Vainshtein's (1956) semi-empirical method of computing central quantities such as peak heights and curvatures is reliable to within 25%.

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The crystal structure of the lanthanide oxyiodides, SmOI, TmOI and YbOI.* By F. H. KRUSE, L. B. ASPREY and BRUNO MOROSIN,† *Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico, U.S.A.*

(Received 30 September 1960)

In a program of investigation of unusual valence states of lanthanide compounds, TmOI was obtained during preparation of TmI₂ (Asprey & Kruse, 1960). Pure samples of anhydrous SmOI, TmOI, and YbOI have been prepared for purposes of identification. Subsequently, analysis of their crystal structures was carried out.

The oxyiodides are prepared by evaporation of the triiodide solution and heating the residue as described by Asprey & Kruse (1960). In a slightly different preparation, a solution of lanthanide triiodide was saturated with NH₄I and evaporated to dryness. The resultant residue was dried and annealed under vacuum in a quartz capillary at 550 °C. over night to remove NH₄I and residual lanthanide triiodide. The X-ray powder shots were made using a standard 114.5 mm. Norelco camera and Cu K α radiation.

These lanthanide oxyiodides crystallize in the tetragonal PbFCl structure type, as do a number of other lanthanide and actinide oxyhalides (Wyckoff, 1960). The unit cell dimensions for the three oxyiodides are given in Table 1.

Table 1. *Unit-cell dimensions of lanthanide oxyiodides*

| | | |
|------|--|---|
| | Structure type: PbFCl | |
| | Tetragonal space group, $P4/nmm-D_{2h}^2$ | |
| | a_0 | c_0 |
| SmOI | $4.008 \pm 0.005 \text{ \AA}$ | $9.192 \pm 0.008 \text{ \AA}$ |
| TmOI | 3.887 ± 0.001 | 9.166 ± 0.002 |
| YbOI | 3.870 ± 0.006 | 9.161 ± 0.008 |
| | Previously reported oxyiodides (Wyckoff, 1960) | |
| | BiOI | 3.985 \AA 9.129 \AA |
| | LaOI | 4.144 9.126 |
| | PuOI | 4.042 9.169 |

The sample of TmOI was of more immediate concern

* Work performed under the auspices of the U.S. Atomic Energy Commission.

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From these ratios we conclude that the advantage of using electrons rather than X-rays for the detection of light atoms in the presence of heavy atoms is striking. These ratios of peak heights seem more in keeping with experience than do the ratios of peak volumes.

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and gave the best powder patterns, consequently parameter values were determined to compare calculated with observed intensities. The final parameters obtained for TmOI are given in Table 2 along with parameters reported for LaOI, PuOI and BiOI. Table 3 presents the pertinent interatomic distances for TmOI. The distances all fall within ranges anticipated for these ions except for the relatively short I-I distance of 3.89 Å. However, the other isostructural oxyhalides show this same shortening of the halogen-halogen distances between adjacent halogen layers.

Table 2. *Atomic position parameters for TmOI and previously reported MOI structures*

| | | |
|------------------------|---------------|--|
| Space group positions: | O (a): | 0, 0, 0; $\frac{1}{2}, \frac{1}{2}, 0$ |
| | I (c): | $0, \frac{1}{2}, u; \frac{1}{2}, 0, \bar{u}$ |
| | M (c): | $0, \frac{1}{2}, u; \frac{1}{2}, 0, \bar{u}$ |
| TmOI: | $U_I = 0.680$ | $U_{Tm} = 0.125$ |
| LaOI: | $U_I = 0.660$ | $U_{La} = 0.135$ |
| PuOI: | $U_I = 0.67$ | $U_{Pu} = 0.13$ |
| BiOI: | $U_I = 0.668$ | $U_{Bi} = 0.132$ |

Table 3. *Interatomic distances in TmOI*
(In Å, all ± 0.02)

| | | | |
|-------|------------|-----|------------|
| Tm-Tm | 3.58; 3.89 | I-I | 3.89; 4.29 |
| Tm-I | 3.28 | I-O | 3.52 |
| Tm-O | 2.26 | O-O | 2.75; 3.89 |

A tabulation of the partial powder X-ray diffraction patterns of SmOI, TmOI, and YbOI is given in Table 4. The relative peak intensities are essentially the same for all three samples. The I_0 has been corrected for absorption by a cylindrical powder specimen with $\mu r = 20.0$. An isothermal overall temperature factor correction with $\beta = 2.0$ was included in the I_c .

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