BROWN, I. D. & CALVO, C. (1970). *J. Solid State Chem.* **1**, 173–179.
BROWN, I. D., CRUMP, D. B. & GILLESPIE, R. G. (1971). *Inorg. Chem.* **10**, 2319–2323.
BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* A**29**, 266–282.
CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5504.
CRUICKSHANK, D. W. J. (1964). *Acta Cryst.* **17**, 682–683.
CRUMP, D. B. (1971). Ph.D. Thesis, McMaster Univ., p. 75.
DE VRIES, R. & MIJLHOFF, F. C. (1969). *Acta Cryst.* B**25**, 1696–1699.
LOUISNATHAN, S. J. & GIBBS, G. V. (1972). *Mater. Res. Bull.* **7**, 1281–1292.
LYNTON, H. & TRUTER, M. R. (1960). *J. Chem. Soc.* pp. 5112–5118.
MCDONALD, W. S. & CRUICKSHANK, D. W. J. (1967). *Acta Cryst.* **22**, 48–51.
NELMES, R. J. (1971). *Acta Cryst.* B**27**, 272–281.
PIERCE, L. & HAYASHI, M. (1961). *J. Chem. Phys.* **35**, 479–485.
PRINGLE, G. E. & BROADBENT, T. A. (1965). *Acta Cryst.* **19**, 426–432.
TAESLER, I. & OLOVSSON, I. (1968). *Acta Cryst.* B**24**, 299–304.

Acta Cryst. (1973). B**29**, 1983

Effect of Neglect of Dispersion in Centrosymmetric Structures: Results for OsO_4

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(*Received* 26 *March* 1973, *accepted* 27 *April* 1973)

The 0·03 Å difference between the Os–O bond lengths reported for crystalline and gaseous OsO_4 is shown not to be caused by neglect of anomalous dispersion corrections in the crystallographic refinement of a centrosymmetric structure. Small shifts in the scale factor and vibration parameters caused by anomalous dispersion are explained by a simple theory.

The crystal structure of OsO_4 (space group $C2/c$) was determined and refined by Ueki, Zalkin & Templeton (1965), who showed that it contains nearly tetrahedral molecules OsO_4, with average Os–O bond distance $1{\cdot}74 \pm 0{\cdot}02$ Å, uncorrected for the thermal motion. The same molecule was studied by gas electron diffraction (Seip, 1967) and the bond distance R_g was $1{\cdot}712 \pm 0{\cdot}002$ Å. We have examined whether this disagreement could be due to the lack of allowance in the X-ray investigation for the anomalous dispersion of Os ($\Delta f' = -1{\cdot}55$ and $\Delta f'' = 8{\cdot}60$ for Mo $K\alpha$ radiation). Despite the theoretical arguments (Cruickshank & McDonald, 1967) that no significant shifts in atomic positions are to be expected for a centrosymmetric structure, we thought it worth while to undertake actual refinement in a case with a very large anomalous contribution.

Refinement

The cell dimensions of OsO_4 are $a = 9{\cdot}379$, $b = 4{\cdot}515$, $c = 8{\cdot}632$ Å, $\beta = 116{\cdot}6°$. The data used were the observed structure factors of Ueki, Zalkin & Templeton, with unit weight assigned to each of the 479 reflexions as in the original paper. The refinement was carried out with the *CRYLSQ* program of F. A. Kundell, in which the anomalous dispersion terms are included in all structure-factor and derivative calculations. Four different full-matrix refinements of two cycles each were carried out, starting from the original parameters:

(1) without any dispersion term. The maximum shift/error in the refinement was 0·1 with no change in R. The reference parameters in the first column of Table 1 are from this refinement;

(2) correcting only for $\Delta f'' = 8{\cdot}60$ on Os;

(3) correcting only for $\Delta f' = -1{\cdot}55$ on Os;

(4) correcting for $\Delta f''$ and $\Delta f'$ on Os.

The results are shown in Table 1. No significant shifts in coordinates occur for the three refinements with dispersion correction. Thus lack of correction for dispersion cannot explain the difference between the X-ray and electron-diffraction values of the Os–O bond length. (The individual lengths from the fourth refinement are 1·760 and 1·715 Å. The mean is $1{\cdot}738 \pm 0{\cdot}020$ Å, to which a rotational correction of about 0·02 Å must be added. The difference from the electron-diffraction value of $1{\cdot}712 \pm 0{\cdot}002$ Å would be significant at between the 5% and 1% levels if the rotational correction were reliable.)

The only noticeable changes in the refinements are to the scale factor and the vibration parameters of the heavy atom. Moreover, in this structure, the error produced by neglecting $\Delta f''$ is about the same, and in the opposite direction, as the error produced by neglecting $\Delta f'$.

Scale and vibration-parameter errors

The small shifts in the scale factor and vibration parameters can be explained by simple theoretical considera-

tions. In the following discussions, the expressions for the effect of neglecting $\Delta f''$ are derived for an atom in which $\Delta f'$ is zero, and *vice versa*.

Scale factor

If $f=f^\circ+\Delta f'+i\Delta f''$ is the scattering factor of the anomalous scatterer (H) and its contribution to the mean intensity is predominant (as in OsO_4), the mean fractional contribution of $\Delta f'$ to the F's can be estimated as $\langle \Delta F\rangle/\langle |F|\rangle \simeq x'$ and of $\Delta f''$ as $\langle \Delta F\rangle/\langle |F|\rangle \simeq x''^2/2$, where $x'=\Delta f'/f^\circ$ and $x''=\Delta f''/f^\circ$. The errors due to neglect of anomalous scattering will be taken up both in a change of calculated scale factor and in the vibration amplitudes. Since all exponential terms are unity at $s=0$, the change of scale can be determined on its own by consideration of behaviour as $s\rightarrow 0$. Hence if the F_c scale factor with allowance for anomalous scattering is 1, the scale factor expected neglecting $\Delta f'$ is

$$F_c \text{ scale factor} \simeq 1+x_0' \qquad (1)$$

or neglecting $\Delta f''$

$$F_c \text{ scale factor} \simeq 1+x_0''^2/2 \qquad (2)$$

where $x_0'=(\Delta f'/f^\circ)_{s\rightarrow 0}$, $x_0''=(\Delta f''/f^\circ)_{s\rightarrow 0}$ and $s=2\sin\theta/\lambda$. The expressions (1) and (2) give the maximum change of scale factor. The change will be less for a reduced fractional contribution of H to the main intensity.

Vibration parameters

In a centrosymmetric structure with anomalous scatterers H and non-anomalous scatterers L the structure factor, ignoring $\Delta f'$, is

$$F(\mathbf{h})=\sum (f_H^0+i\Delta f_H'') \cos 2\pi \mathbf{h}\,.\,\mathbf{x}_H + \sum f_L \cos 2\pi \mathbf{h}\,.\,\mathbf{x}_L\,.$$

As the phase angle of $F(\mathbf{h})$ is usually near 0 or π, $|F|$ is approximately

$$|F(\mathbf{h})| \simeq |\sum (f_H^{02}+\Delta f_H''^2)^{1/2} \cos 2\pi \mathbf{h}\,.\,\mathbf{x}_H + \sum f_L \cos 2\pi \mathbf{h}\,.\,\mathbf{x}_L| \,. \qquad (3)$$

If the term $\Delta f''$ is neglected in the refinement, the least-squares procedure will try to force a fit multiplying f_H^0 by a pseudo-vibrational factor and shifting the scale factor so that

$$|F(\mathbf{h})| \simeq K|\sum f_H^0 \exp(-2\pi^2 U'' s^2) \cos 2\pi \mathbf{h}\,.\,\mathbf{x}_H + \sum f_L \cos 2\pi \mathbf{h}\,.\,\mathbf{x}_L\,. \qquad (4)$$

The value of U'' by comparison of (3) and (4) is given from

$$(f_H^{02}+\Delta f_H''^2)^{1/2}=Kf_H^0 \exp(-2\pi^2 U'' s^2)\,.$$

By expanding $\exp(-2\pi^2 U'' s^2) \simeq 1-2\pi^2 U'' s^2$, and using $K=1+x_0''^2/2$ as determined earlier, we get

$$U'' \simeq \langle -(x''^2-x_0''^2)/4\pi^2 s^2\rangle \qquad (5)$$

where the brackets indicate a weighted average over the range of s, depending on the method of refinement

Table 1. *Results of refinement of* OsO_4

The x and z fractional coordinates of Os, which is in a special position, are respectively 0·0 and 0·25. The U_{ij} values are in Å^2. No significant changes in e.s.d.'s were observed in the different refinements.

		Parameters without $\Delta f'$ and $\Delta f''$	E.s.d.'s	Shifts with $\Delta f''$ correction	Theoretical shifts due to $\Delta f''$	Shifts with $\Delta f'$ correction	Theoretical shifts due to $\Delta f'$	Shifts with $\Delta f''$ and $\Delta f'$ correction
	R	0·081		0·081		0·082		0·081
F_c scale factor		1·000	0·008	−0·008	−0·008	0·023	0·022	0·015
Os	y	0·2601	0·0004	−0·00003	from (2)	0·00000	from (1)	−0·00004
	U_{11}	0·0186	0·0007	0·00056		−0·00057		0·00004
	U_{22}	0·0248	0·0008	0·00057	0·00054	−0·00057	−0·00059	0·00005
	U_{33}	0·0232	0·0007	0·00056	from (5)	−0·00043	from (7)	0·00004
	U_{13}	0·0068	0·0005	0·00025		−0·00025		0·00002
O(1)	x	0·121	0·003	−0·0004		0·0001		−0·0004
	y	0·037	0·007	−0·0003		−0·0001		−0·0005
	z	0·190	0·004	−0·0003		−0·0001		−0·0004
	U_{11}	0·052	0·015	−0·0015		0·0023		0·0004
	U_{22}	0·052	0·016	−0·0030	−0·0012	0·0017	0·0022	−0·0015
	U_{33}	0·065	0·017	−0·0015	from (6)	0·0025	from (8)	0·0011
	U_{12}	0·011	0·013	−0·0006		0·0005		−0·0001
	U_{13}	0·039	0·014	−0·0008		0·0018		−0·0008
	U_{23}	0·002	0·014	0·0000		0·0000		0·0002
O(2)	x	0·115	0·003	−0·0003		0·0000		−0·0004
	y	0·477	0·006	0·0004		0·0000		0·0005
	z	0·425	0·003	−0·0004		0·0001		−0·0003
	U_{11}	0·048	0·014	−0·0017		0·0018		0·0000
	U_{22}	0·047	0·015	−0·0035	−0·0012	0·0015	0·0022	−0·0020
	U_{33}	0·037	0·012	−0·0011	from (6)	0·0014	from (8)	0·0004
	U_{12}	−0·011	0·012	0·0003		−0·0002		0·0001
	U_{13}	0·004	0·011	−0·0005		0·0002		−0·0004
	U_{23}	−0·015	0·011	0·0007		−0·0003		0·0003

and on the least-squares weights. The effect of neglecting $\Delta f''$ is thus to decrease isotropically the value of U of the anomalous scatterer since $x'' > x_0''$. As also a scale shift occurs, and if it is the only effect acting, the U values of the L atoms are increased by an amount, which for $K = 1 + x_0''^2/2$ can be estimated as

$$U_L'' \simeq \langle x_0''^2/4\pi^2 s^2 \rangle . \quad (6)$$

The effect of neglecting $\Delta f'$ can be evaluated with the same method, for $K = 1 + x_0'$, from

$$f_H^0 + \Delta f_H' = K f_H^0 \exp(-2\pi^2 U' s^2)$$

as

$$U' \simeq \langle -(x' - x_0')/2\pi^2 s^2 \rangle . \quad (7)$$

The effect of neglecting $\Delta f'$ is thus to increase isotropically the vibration parameters of the anomalous dispersor if $\Delta f' < 0$ or to decrease them if $\Delta f' > 0$. A reversed effect can be observed on the U values of the L atoms, which for a scale shift of $1 + x_0'$, can be estimated as roughly

$$U_L' \simeq \langle x_0'/2\pi^2 s^2 \rangle . \quad (8)$$

Discussion

Columns 5 and 7 of Table 1 show the theoretical shifts from the uncorrected values on the inclusion of anomalous dispersion. These shifts have been calculated from equations (1)–(8) with reversed signs. The agreement with the refinement calculations is good for the scale factor and the isotropic vibration parameters of Os, and is of the correct magnitude for the oxygen vibration parameters.

The effect of anomalous dispersion on the vibration parameters caused by the neglect of $\Delta f'$ and $\Delta f''$ is rather small. It depends on the atom type and on the radiation, as well as on the range of s of the data. For Cu $K\alpha$ radiation, the correction required if $\Delta f'$ is neglected can be estimated in some of the larger cases as $U' \simeq -0{\cdot}0061$ for Co, $-0{\cdot}0078$ for Ni and $-0{\cdot}0104$ Å^2 for Sm, and if $\Delta f''$ is neglected as $U'' \simeq 0{\cdot}0028$ for Co, 0·0047 for Sm and 0·0020 Å^2 for U. These values for Cu $K\alpha$ are several times those shown in Table 1 for Os with Mo $K\alpha$ radiation. In a hypothetical two-dimensional structure with one cobalt and ten carbon atoms, Parthasarathy, Sabesan & Venkatesan (1970), using least-squares, found the correction required for Co with Cu $K\alpha$ radiation if $\Delta f''$ is neglected to be $U'' = 0{\cdot}0029$ Å^2. Their calculated scale correction was $-0{\cdot}0117$ in comparison with $-0{\cdot}0123$ evaluated from (2) above. [It may be added that these authors discuss also the presence of spurious peaks in electron-density maps due to neglect of $\Delta f''$; spurious peaks are discussed also by Del Pra, Ferraris & Mammi (1972).]

An abstract of this work (Gilli & Cruickshank, 1972) inadvertently reported the theoretical U shifts as 100 times larger than the correct values shown in Table 1.

Wilson (1972) has also considered the effect of incorrect dispersive atomic scattering factors on refinement of scale and temperature parameters. His general expression for the error in the apparent scale-*cum*-overall-temperature factor is consistent with the particular results derived here.

We thank Professor A. J. C. Wilson for stimulating correspondence on this topic.

References

CRUICKSHANK, D. W. J. & MCDONALD, W. S. (1967). *Acta Cryst.* **23**, 9–11.

DEL PRA, A., FERRARIS, G. & MAMMI, M. (1972). *Acta Cryst.* A**28**, 65–69.

GILLI, G. & CRUICKSHANK, D. W. J. (1972). *Acta Cryst.* A**28**, S10.

PARTHASARATHY, S., SABESAN, M. N. & VENKATESAN, K. (1970). *Z. Kristallogr.* **131**, 443–454.

SEIP, H. M. (1967). *Selected Topics in Structure Chemistry*, Edited by P. ANDERSEN, O. BASTIANSEN & S. FURBERG, p. 25. Oslo: Universitetsforlaget.

UEKI, T., ZALKIN, A. & TEMPLETON, D. H. (1965). *Acta Cryst.*, **19**, 157–160.

WILSON, A. J. C. (1972). *Acta Cryst.* A**28**, S9.