Acta Cryst. (1962). **15**, 620

On the effect of more than one anomalous scattering atom in the unit cell.

By J. M. Bijvoet,
Laboratorium voor Kristalchemie der Rijksuniversiteit, Utrecht, The Netherlands

(*Received* 15 *February* 1962)

The recent paper by Partasarathy (1961) on the determination of the anomalous scattering $\Delta f''$ for chlorine prompts me to make come comments on the question whether the presence of more than one anomalous scattering atom in the unit cell invalidates the usual calculation of the anomalous effect.

The theoretical deduction of such an effect referred to in *Acta Cryst.* (Harrison, Jeffrey & Townsend, 1958) was incorrect, as shown by calculations of my colleague Van Laar, the same conclusion being reached independently by Townsend. Using the complete set of tight-binding approximation wave-functions, the terms which might give rise to an angular dependence of $\Delta f''$ disappear. This was briefly reported by Bijvoet (1960*a*).

As to the *experimental data*—amongst which accurate measurements by Canadian investigators may be added to the literature usually cited (Kartha, Ahmed & Barnes, 1962; Przybylska & Marion, 1959)—there is agreement that the usual calculation with constant $\Delta f''$ is a sufficient basis for crystals which contain a large number of atoms besides the anomalous scatterers.

Anomalies are reported in the case of ZnO (Harrison *et al.*, 1958) whilst a rather poor numerical agreement has been established for $NaClO_3$ (Ramachandran & Chandrasekharan, 1957; Aravindakshan, 1959). Current experiments by Townsend and co-workers, however, show that the reported anomalies are either characteristic of particular ZnO crystals or arose from some unknown systematic errors in their measurements (private communication). In the case of $NaClO_3$ our measurements are consistent again with $\Delta f''$ constant within the limits of experimental accuracy (Beurskens-Kerssen, 1961). It is true that these results are remarkable in so far as opposite configuration is found for crystals of $NaClO_3$ and $NaBrO_3$ of same rotation sign. This can be accounted for by the strong dependence of the rotatory power on small changes in the atomic parameters for this type of structure, as shown by calculations of Van Laar & Endeman (Bijvoet, 1960*b*). Our X-ray result, therefore, does not point to any doubt as to the usually accepted basis of the anomalous scattering calculations.

References

Aravindakshan, C. (1959). *Z. Kristallogr.* **111**, 241.

Beurskens-Kerssen, G. (1961). *Acta Cryst.* Thesis Utrecht. (To be published.)

Bijvoet, J. M. (1960*a*). *Acta Cryst.* **13**, 1100.

Bijvoet, J. M. (1960*b*). *Versl. Afd. Nat. K. Ned. Akad. Wet. Amst.* **69**, 122.

Harrison, P., Jeffrey, G. A. & Townsend, J. R. (1958). *Acta Cryst.* **11**, 552.

Kartha, G., Ahmed, F. R. & Barnes, W. H. (1962). *Acta Cryst.* **15**, 326.

Parthasarathy, R. (1961). *Acta Cryst.* **15**, 41.

Przybylska, M. & Marion, L. (1959). *Canad. J. Chem.* **37**, 1843.

Ramachandran, G. N. & Chandrasekharan, K. S. (1957). *Acta Cryst.* **10**, 671.

Acta Cryst. (1962). **15**, 620

Symmetry and unit-cell dimensions of selenium trioxide.

By F. C. Mijlhoff and C. H. MacGillavry,
Laboratory for Crystallography, University of Amsterdam, The Netherlands

(*Received* 26 *February* 1962)

Several authors (Toul & Dostál, 1951, 1952; Lehmann & Krüger, 1952) have published X-ray powder diffraction data on SeO_3. A tabulated survey is given by Dostál & Cernohorský (1956).

We have investigated the diffraction of a single crystal, prepared by one of us (F. C. M.), at the Laboratory for Inorganic Chemistry of the University of Amsterdam. By Weissenberg and precession methods it was found that the structure is tetragonal with cell dimensions

$$a = 9\cdot636 \pm 0\cdot005,\quad c = 5\cdot28 \pm 0\cdot02\ \text{Å}\ .$$

It is possible to index the published powder diagram data with these cell constants, and so the material is presumably identical with ours.

Assuming 8 units SeO_3 per cell, one calculates the plausible density of 3·44 g.cm.$^{-3}$; for liquid SeO_3, a density of 2·75 g.cm.$^{-3}$ is given by Lehmann & Krüger (1952).

From extinctions the space-group $P\bar{4}2_1c$ is unambiguously determined. This suggests puckered rings of four SeO_4 tetrahedra about the $\bar{4}$ axes. This idea has been preliminarily confirmed. The structure thus resembles more closely the trimeric γSO_3 (Westrik & MacGillavry, 1941) than the polymeric α-form, as suggested by Lehmann & Krüger (1952).

Mixed crystals with SO_3, obtained from an SO_3 solution of SeO_3 exhibit the same structural features, the S and Se atoms being presumably statistically distributed among the possible sites. The unit-cell dimensions of the mixed crystals decrease with increasing SO_3 content.

References

Dostál, K. & Cernohorský, M. (1956). *Chem.listy*, **50**, 702.

Lehmann, H. A. & Krüger, G. (1952). *Z. anorg. Chem.* **267**, 324.

Toul, F. & Dostál, K. (1951). *Collection Czech. Chem. Comm.* **16**, 531.

Toul, F. & Dostál, K. (1952). *Chem.listy*, **46**, 132.

Westrik, R. & MacGillavry, C. H. (1941). *Rec. Trav. Chim. Pays-Bas*, **60**, 794.