SHORT COMMUNICATIONS

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Acta Cryst. (1973) **B29**, 2314

The crystal structure of 2,4,7-trinitro-9-fluorenone. A correction.

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(*Received* 25 *May* 1973; *accepted* 25 *May* 1973)

In Table 3 of *Acta Cryst.* (1972). **B28**, 3122–3127 the following corrections should be noted: for C(4*a*), $U_{23} = -3$; for C(4*b*), $X = 1034$; for N(1), $U_{22} = 36$.

Three errors have been discovered in the parameters listed in Table 3 in our paper on the structure of 2,4,7-trinitro-9-fluorenone (Dorset, Hybl & Ammon, 1972). The corrections are: for C(4*a*), $U_{23} = -3$; for C(4*b*), $X = 1034$; for N(1), $U_{22} = 36$. I am grateful to Dr N. Yasuoka of Osaka University for bringing the C(4*b*) error to my attention.

References

Dorset, D. L., Hybl, A. & Ammon, H. L. (1972). *Acta Cryst.* **B28**, 3122–3127.

Acta Cryst. (1973). **B29**, 2314

A monoclinic form of $K_{0.27}WO_3$.

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(*Received* 30 *April* 1973; *accepted* 1 *May* 1973)

Crystals of $K_{0.27}WO_3$ grown at high temperature are found to exhibit long-range ordering, unlike the well known low-temperature form. Comparative use of X-ray and electron diffraction has indicated the nature of the ordering.

A hexagonal structure of the composition K_xWO_3 where $x = 0{\cdot}27$ belonging to the group of tungsten bronzes was described by Magnéli & Blomberg (1951) and later by Magnéli (1953). These bronzes are usually electronic conductors of a dark bluish colour. In this note, data are presented for monoclinic crystals of the same composition which are formed by vapour-phase reaction above 1300°C. They have a clear yellow colour and are similar in appearance to WO_3 crystals. They are therefore assumed to be semi-conducting like WO_3 rather than electronically conducting like the Magnéli bronzes.

The crystals present two distinct morphologies of needles and plates. The needles are too small for detailed observation by optical microscopy, but optical goniometry indicates a sixfold needle axis. However, scanning electron micrographs show how the needles are formed by multiple twinning of platelets (see Fig. 1) and diffraction studies show in fact that both morphologies are structurally identical. Evidence for a high electrical conductivity comes from the lack of charging up experienced in the scanning electron microscope and probe analyser.

The needle crystals were most suitable for mounting on an X-ray goniometer. An oscillation photograph about the needle axis gave a repeat of 3·83 Å, suggesting a single-layer structure of corner-sharing octahedra. Zero and first layer Weissenberg photographs about this axis gave sub-lattice intensities consistent with the hexagonal packing of tungsten octahedra described by Magnéli (see Table 1).

Table 1. *A summary of unit-cell data*

Symbols in parentheses indicate the multiplicity of the super-cells.

Type of cell	System	Parameters
WO_3 subcell	Hexagonal	$a = 7{\cdot}3$, $c = 3{\cdot}8$ Å
X-ray supercell	Monoclinic	$a = 29{\cdot}24 \pm 0{\cdot}04$, $b = 7{\cdot}36 \pm 0{\cdot}01$, (4*a*) (*b*) $c = 7{\cdot}7 \pm 1$ Å, $\gamma = 60 \pm 2°$ (2*c*)
Electron supercell	Monoclinic	$a = 29{\cdot}2$, $b = 14{\cdot}6$, $c = 7{\cdot}6$, $\frac{3}{4} = 60°$ (4*a*) (2*b*) (2*c*)

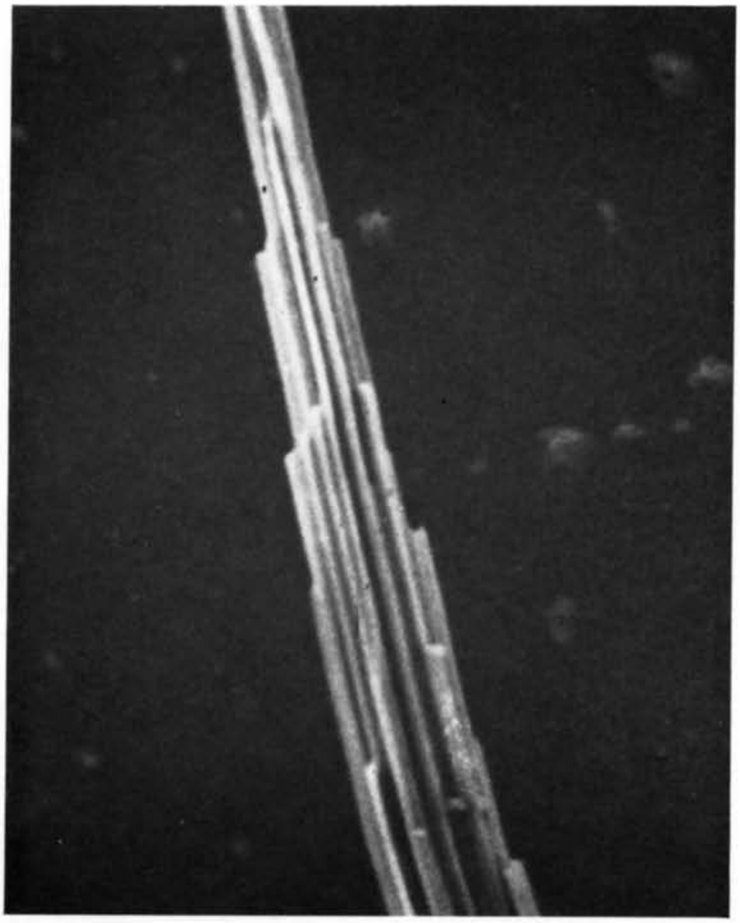

Fig. 1. Scanning electron micrograph of $K_{0\cdot27}WO_3$ needles.

They also exhibited a hexagonal super-lattice based on the cell $4a$, $4b$, c with the condition that hkl reflexions were absent unless $h=4n$, or $k=4n$, $h-k=4n$. In view of the scanning electron micrographs, the photographs were interpreted as patterns from a twinned supercell of $4a$, b, c. This is confirmed by a splitting of the sublattice reflexions in the direction of increasing 2θ consistent with a slight deviation from hexagonal symmetry in the subcell. From the degree of splitting a discrepancy of about 0·05 Å between $a/4$ and b could be deduced and using a copper powder line for calibration the values $7{\cdot}31\pm0{\cdot}01$ and $7{\cdot}36\pm0{\cdot}01$ Å were obtained respectively. The doubling of the c axis in the manner reported by Magnéli was not observed.

Electron diffraction from the platelets established the hexagonal subcell and a monoclinic superlattice of a larger cell $4a$, $2b$, $2c$. This apparent discrepancy between the X-ray and electron diffraction data was attributed to a second superstructure with a very low scattering power for X-rays. Further investigation included electron diffraction from ground needle fragments, X-ray diffraction from a platelet and finally some very long oscillation and Weissenberg exposures from a needle crystal. This established definitely that both morphologies had the same monoclinic crystal structure. In particular, some very weak X-ray reflexions were detected from the first layer about an axis corresponding to $2c$.

The combined X-ray and electron-diffraction evidence indicates that the high-temperature form of $K_{0{\cdot}27}WO_3$ is monoclinic with a cell of $a=29{\cdot}24\pm0{\cdot}04$, $b=14{\cdot}72\pm0{\cdot}02$, $c=7{\cdot}7\pm0{\cdot}1$ Å and $\gamma=60\pm2°$, which is based on the hexagonal subcell of Magnéli with two types of long-range ordering. Comparison of the intensities of the electron and X-ray diffraction patterns suggest that the quadrupling of the subcell a parameter is due to ordering of the interstitial vacancies that arise when for K_xWO_3, $x<\frac{1}{3}$; the doubling of the subcell b and c parameters is consistent with a complicated arrangement of WO_6 octahedra possessing a strong dipole moment. Aspects of the electron-diffraction analysis requiring interpretation of dynamic and disorder scattering will be reported elsewhere by one of the authors.

The authors wish to thank Dr D. Sewell of the School of Geology, Melbourne University for assistance with scanning electron microscopy and electron-probe analysis, which together with spectroscopic analysis established the composition of the material.

References

Magnéli, A. (1953). *Acta Chem. Scand.* **7**, 315–324.
Magnéli, A. & Blomberg, B. (1951). *Acta Chem. Scand.* **5**, 372–378.

Acta Cryst. (1973). **B29**, 2315

Crystallographic data for 2,4-dinitroaniline.

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(*Received* 26 *December* 1972; *accepted* 30 *March* 1973)

The morphologically plate-shaped and parallelepiped variety of 2,4-dinitroaniline has the cell constants $a=7{\cdot}603\pm0{\cdot}001$, $b=12{\cdot}914\pm0{\cdot}005$, $c=9{\cdot}146\pm0{\cdot}002$ Å and $\beta=122{\cdot}09\pm0{\cdot}01°$, the space group being $P2_1/a$ with $Z=4$. Groth's choice of unit cell is shown to be wrong. From cleavage and the strongest reflexion, the molecule seems to be planar and parallel to the 200 plane.

In Sanger's famous method for the identification of amino acid residues in polypeptide chains, 2,4-dinitrofluorobenzene is reacted with the amino group to produce tagged amino acids. Thus it is important to know the molecular structure of any 2,4-dinitrophenyl-tagged residue as well as that of 2,4-dinitroaniline. With this end in view the molecular structure determination of this complex was undertaken. This paper is a short report of the preliminary work on the structure determination of 2,4-dinitroaniline with particular reference to cell dimensions. The cell dimensions given in the present paper are different from those reported by Groth (1917), Lasheen (1963) and Siddiq, Saraogi & Ali (1959). It is shown here that the discrepancy arises from a wrong choice of the unit cell.

Groth (1917) described a variety of 2,4-dinitroaniline with $a:b:c=0{\cdot}9913:1:0{\cdot}6985$ and $\beta=95°\,58{\cdot}5'$, crystallized from a mixture of acetone and chloroform, the crystals being six-sided and prismatic. Lasheen (1963) confirmed this variety with an X-ray study. The cell dimensions are: $a=12{\cdot}8$, $b=12{\cdot}9$, $c=9{\cdot}07$ Å and $\beta=95°$, *i.e.* $a:b:c=0{\cdot}992:1:0{\cdot}703$, in good agreement with those described by Groth. Siddiq *et al.* (1959) reported a variety morphologically similar to that obtained by Groth, as shown in their clinographic diagram, having cell constants: $a=8{\cdot}46$, $b=12{\cdot}50$, $c=7{\cdot}4$ Å and $\beta=101{\cdot}54°$, $Z=4$, space group $P2_1/m$.

The present work describes the morphologically plate shaped and parallepiped variety of 2,4-dinitroaniline, obtained from acetone as solvent (2,4-dinitroaniline powder of laboratory B.D.H. was used). The variety morphologically similar to that of Groth is obtained with acetone and chloroform (1:1) as solvent.

The cell constants of the present variety obtained from three oscillation and zero-layer Weissenberg photographs calibrated with Al-powder lines are: $a=7{\cdot}603\pm0{\cdot}001$, $b=12{\cdot}914\pm0{\cdot}005$, $c=9{\cdot}146\pm0{\cdot}002$ Å and $\beta=122{\cdot}09\pm0{\cdot}01°$. Thus $a:b:c=0{\cdot}5886:1:0{\cdot}7072$. The density determined from flotation is 1·615 g cm^{-3}, which agrees well with the calculated density of 1·601 g cm^{-3} assuming the presence of four molecules in the cell. The systematic absences from the Weissenberg photographs show that the space group of the new variety is $P2_1/a$.

Powder photographs of Lasheen's and the present variety showed similar cell constants. Single-crystal Weissenberg