Acta Cryst. (1993). **B49**, 165–169

Refinement of Atomic Positions in Bixbyite Oxides using Perturbed Angular Correlation Spectroscopy

By A. Bartos, K. P. Lieb, M. Uhrmacher and D. Wiarda

II. *Physikalisches Institut Universität Göttingen, D-*3400 *Göttingen, Germany*

(*Received* 6 *April* 1992; *accepted* 17 *July* 1992)

Abstract

In a number of isostructural sesquioxides M_2O_3 (M = Sc, In, Y, Yb, Dy, Ho, Sm, Gd) with the bixbyite structure the electric field gradients at substitutional ^{111}Cd nuclei show a regular and smooth dependence on the lattice constant. The electric field gradients allow the positions of all atoms in the unit cell to be determined with an accuracy of 0.3 pm by means of a simple point-charge model; this is typically five times better than the data available from neutron and X-ray diffraction experiments.

1. Introduction

Hyperfine interaction methods like nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR) or Mössbauer spectroscopy (MS) are widely used to study local atomic properties in solids (Recknagel, Schatz & Wichert, 1983). A method not so well known in solid-state spectroscopy is the perturbed angular correlation (PAC) technique. For example, this method has elucidated the structures, formation and annealing behaviour of point defects in metals (Pleiter & Hohenemser, 1982). Furthermore, it has been successfully applied in characterizing the electronic properties of impurities in semiconductors (Achtziger, 1992) and on surfaces (Klas *et al.*, 1988). For a large number of metal oxides, PAC has recently provided information concerning magnetic and structural phase transitions (Bartos, Bolse, Lieb & Uhrmacher, 1988; Inglot, Wiarda, Lieb, Wenzel & Uhrmacher, 1991) and chemical bonding (Wiarda, Wenzel, Uhrmacher & Lieb, 1992; Bolse, Uhrmacher & Lieb, 1987).

In the present study we report an interpretation of PAC experiments for several sesquioxides M_2O_3 (M = Sc, In, Yb, Y, Ho, Dy, Gd, Sm). While all oxides investigated share the same structure, the cubic C-form (bixbyite) with space group $Ia3$ (Wyckhoff, 1964), and show nearly pure ionic bonding (Eyring, 1964), they mainly differ in the lattice constant a, which ranges from $a(Sc_2O_3)$ = 9.8436 Å to $a(Sm_2O_3)$ = 10.9276 Å (Taylor, 1984). The unit cell contains eight cations at Wyckhoff position 8(b) having D_{3d} point symmetry (in the following referred to as site 'D'), 24 cations in position 24(d) with C_2 point symmetry (site 'C') and 48 oxygen ions in position 48(e) (see Fig. 1a). The positions of all atoms in the unit cell are determined by four parameters: the coordinate u fixes the cation position 24(d), while the oxygen positions are given by the parameters x, y and z (Wyckhoff, 1964). These oxides offer the possibility of investigating, on an atomic scale, small changes in atomic positions in an isostructural matrix.

2. The PAC method

As the PAC method has been reviewed extensively in the literature (Rinneberg, 1979; Schatz & Weidinger, 1985), only a brief description of the method and PAC apparatus used will be given here. PAC spectroscopy reflects the local electronic and/or spin environment of the probe nuclei *via* the hyperfine interaction. Information concerning the local arrangement of neighbouring atoms is often provided by the electric field gradient (e.f.g.), which is usually specified by the quadrupole coupling constant

$$\nu_Q = eQ\,V_{zz}/h$$

with Q being the electric quadrupole moment of the probing nuclear state. The asymmetry parameter is defined as

$$\eta = (V_{xx} - V_{yy})/V_{zz}$$

with $0 \leq \eta \leq 1$, where the components V_{ii} of the diagonalized e.f.g. tensor have been chosen in the order

$$|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|.$$

The coupling constant ν_Q gives information about the strength of the e.f.g., while an asymmetry parameter $\eta > 0$ reflects a deviation from axial symmetry ($\eta = 0$).

The hyperfine interaction is traced *via* a γ–γ cascade of radioactive decay. The first γ-transition populates the sensitive PAC state which is characterized by its quadrupole moment Q and lifetime τ. An interaction of the quadrupole moment Q with an e.f.g. leads to precession of the nuclear moment

0108-7681/93/020165-05$06.00

around the z axis of the e.f.g. and also to a time modulation with probability $W(\theta,t)$ of finding the second γ-ray within an angle θ with respect to the first γ-ray. In this work, all experiments were carried out with the common PAC probe ^{111}In, which decays *via* electron capture to the $7/2^+$ state of ^{111}Cd. This $7/2^+$ state decays under emission of a 171–245 keV γ-cascade to the ground state of ^{111}Cd. The PAC sensitive $5/2^+$ state is characterized by a lifetime $\tau = 122$ ns and quadrupole moment $Q = 0.83\,(13)$ b (Schatz & Weidinger, 1985). The time differential angular correlation is given by

$$W(\theta,t) = 1 + A_{22}G_{22}(t)P_2(\cos\theta)$$

where A_{22} denotes the anisotropy coefficient of the γ–γ cascade and $P_2(\cos\theta)$ is a Legendre polynomial. All solid-state information is contained in the perturbation factor $G_{22}(t)$ which in the case of static electric quadrupole interaction in polycrystalline materials is given by

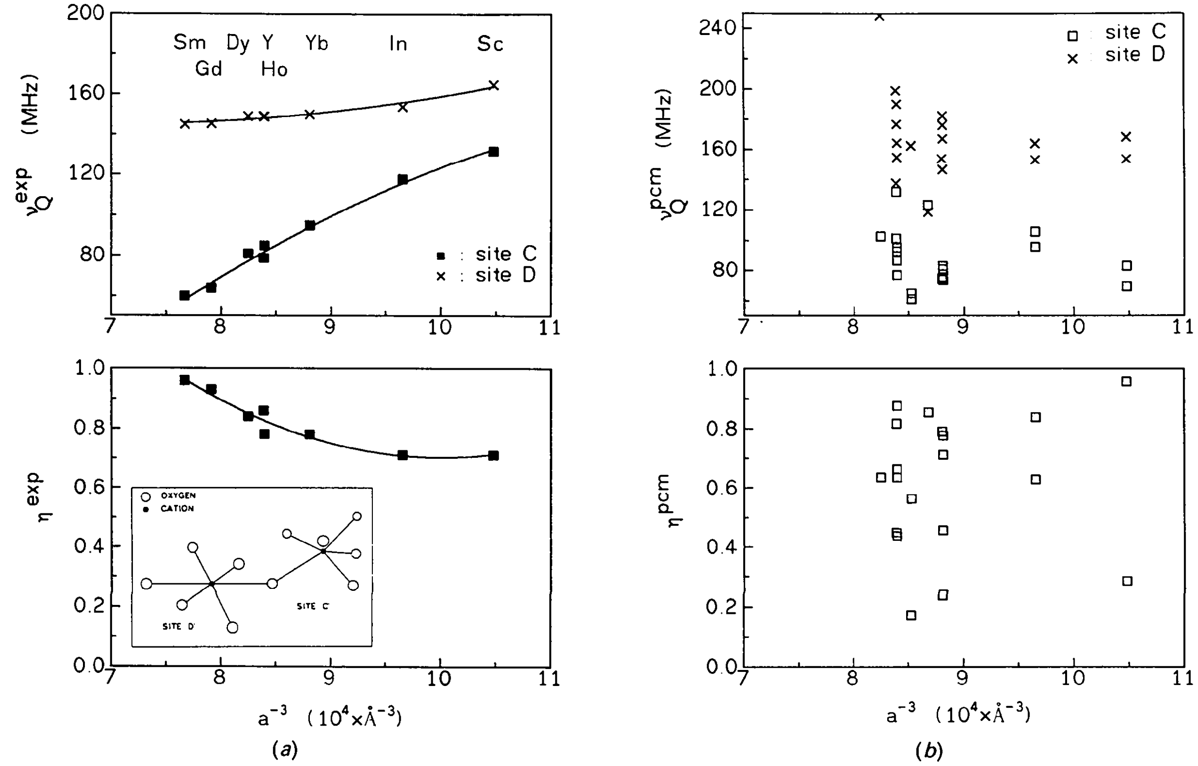
$$G_{22}(t) = \sum_{n=0}^{3} s_{2n}(\eta)\cos[g_n(\eta)\nu_Q t]\exp[-g_n(\eta)\delta t].$$

The expressions $g_n(\eta)$ and $s_{2n}(\eta)$ are given in Kajfosz (1974). Often a broadening of the e.f.g. is observed in PAC experiments that can be described by a Lorentzian distribution having a width δ.

3. The experimental data set

The experiment has been described in detail by Bartos, Lieb, Pasquevich & Uhrmacher (1991) and Shitu *et al.* (1992). About 10^{13} $^{111}\mathrm{In}^+$ cm^{-2} were implanted into powder samples (Johnson Matthey, Y_2O_3: ultrapure; Sc_2O_3: 99.99%; all others: 99.999%) at 400 keV using the Göttingen ion implanter IONAS (Uhrmacher, Pampus, Bergmeister, Purschke & Lieb, 1985). The ^{111}In-doped samples were then annealed in vacuum for $t = 1$h at $T = 975$ K in order to remove radiation damage.

Fig. 1(*a*) displays the e.f.g.'s at ^{111}Cd located at the two substitutional sites C and D *versus* a^{-3}. For both sites a nearly linear variation of the e.f.g. with a^{-3} is found, which provides the following information on the local structure around the ^{111}Cd probe (Bartos, Lieb, Pasquevich & Uhrmacher, 1991; Shitu *et al.*, 1992): for site D the deviation from linearity of ν_Q^D with a^{-3} is small and axial symmetry ($\eta^D = 0$) is observed for all oxides. For site C a dramatic non-



(*a*) (*b*)

Fig. 1. (*a*) Scaling of the experimental electric field gradients at ^{111}Cd located at substitutional sites C and D *versus* a^{-3}, a being the lattice constant. In a purely ionic picture, a linear dependence of the coupling constant ν_Q on a^{-3} and a constant asymmetry parameter η are expected if the atomic positions are kept fixed. Thus, the non-linearity of ν_Q^{exp} and the increase of the asymmetry parameter $\eta^{exp,C}$ reflect small structural changes through the series if pure ionic bonding is assumed. (*b*) The electric field gradient values at the cation sites C and D calculated with the point-charge model using the published coordinates from neutron and X-ray diffraction, which are given in Table 2.

linear increase of ν_Q^C and decrease of η^C with a^{-3} is found. Assuming a purely ionic point-charge model, one expects a linear dependence of the coupling constant ν_Q with a^{-3} and a constant asymmetry parameter if the atomic coordinates do not vary with a. Therefore, the oxygen octahedra around site D remain regular through the series, while the pronounced decrease of η^C and non-linear increase of ν_Q^C reflect a steady deformation of the irregular oxygen octahedra with increasing lattice constant.

4. Refinement of atomic positions

To understand the observed scaling of the e.f.g., it has to be compared with theoretical calculations of e.f.g.'s, which have recently become feasible for some compounds (Schwarz & Blaha, 1992; Nagel, 1985). If the bonding is supposed to be purely ionic, the point-charge model (p.c.m.) may be applied to evaluate the e.f.g. parameters at the two sites C and D. In calculating the lattice sum

$$V_{ij}^{\rm lat} = \frac{e}{4\pi\varepsilon_0} \sum_k Z_k \frac{3x_k x_{kj} - \delta_{ij} r_k^2}{r_k^5} \quad \forall r_k \le 50\ \text{Å}$$

the contribution of all ions k in a sphere with radius $R_L = 50$ Å were taken into account. Here, Z_k denotes the ionic charge ($M = 3^+$, $\mathrm{O} = 2^-$), x_{ki} the coordinates and r_k the distance for the kth ion to the probe. The lattice sum was found to converge within $R_L \simeq 30$ Å. This value $V_{ij}^{\rm lat}$ has to be corrected by the Sternheimer (1966) antishielding factor γ_∞ of ^{111}Cd *via*

$$V_{ij}^{\rm pcm} = (1 - \gamma_\infty) V_{ij}^{\rm lat}$$

with $\gamma_\infty = -31.9$ (Mahapatra, Pattnaick, Thompson & Das, 1977).

Using the published coordinates from neutron and X-ray diffraction results given in Table 2, we calculated the e.f.g. parameters displayed in Fig. 1(b). Evidently, these values do not show a systematic trend with respect to the lattice constant and even differ strongly from each other for a given oxide. The extreme sensitivity of the e.f.g. to the coordinates is also demonstrated by comparing the calculated e.f.g.'s for $\mathrm{In_2O_3}$. The two sets of coordinates obtained by precise X-ray diffraction investigations for the same $\mathrm{In_2O_3}$ single crystal, but for two different wavelengths (Marezio, 1966) yield the following values

	ν_Q^C(MHz)	η^C	ν_Q^D(MHz)	η^D
Cu $K\alpha$	106	0.84	164	0
Mo $K\alpha$	96	0.63	153	0

In conclusion, the experimental uncertainties of the available neutron and X-ray diffraction data do not allow reliable prediction of the dependence of the e.f.g.'s on the lattice constant within the framework of the p.c.m. On the other hand, the observed experimental scaling reflects the high sensitivity of PAC to small structural changes in the atomic positions. Therefore, we reversed the argument by asking which atomic positions reproduce the experimental e.f.g.'s within the limit of the p.c.m.

Table 1. *Experimental PAC data ν_Q and η for* ^{111}Cd *located at the two substitutional sites C and D*

$M_2\mathrm{O_3}$	T_m(K)	ν_Q^C(MHz)	η^C	ν_Q^D(MHz)	η^D	References
$\mathrm{Sc_2O_3}$	650	132.3 (3)	0.71 (1)	166.7 (3)	0	Bartos (1991*a*)
$\mathrm{In_2O_3}$	750	118.4 (5)	0.705 (5)	154.4 (6)	0	Bartos (1991*a*)
$\mathrm{Yb_2O_3}$	730	97.2 (4)	0.757 (8)	154.3 (5)	0	Bartos (1991*a*)
$\mathrm{Y_2O_3}$	750	87.9 (5)	0.77 (1)	149.6 (3)	0	Bartos (1991*a*)
$\mathrm{Ho_2O_3}$	793	82.8 (6)	0.81 (1)	151.7 (5)	0	Shitu (1991)
$\mathrm{Dy_2O_3}$	750	82.9 (7)	0.80 (1)	151.2 (3)	0	Bartos (1991*a*)
$\mathrm{Gd_2O_3}$	858	74.3 (7)	0.83 (5)	148.9 (6)	0	Shitu (1991)
$\mathrm{Sm_2O_3}$	773	66.8 (5)	0.88 (4)	147.1 (5)	0	Shitu (1991)

The following assumptions were made:

(1) As PAC spectroscopy is sensitive to the local atomic configuration, the crystal symmetry and lattice constants had to be provided by diffraction methods and were taken from the literature (Wyckhoff, 1964; Taylor, 1984).

(2) Pure ionic bonding was assumed and any local lattice distortions caused by the ^{111}Cd probe were neglected.

(3) As all bixbyites investigated show motional narrowing effects leading to nearly undamped PAC spectra, the refinement was carried out for the e.f.g.'s given in Table 1 for the temperatures indicated. The very weak temperature dependence of the e.f.g.'s permits the comparison with room-temperature diffraction data and does not indicate any structural changes with temperature (Bartos, Lieb, Pasquevich & Uhrmacher, 1991; Saiki, Ishizawa, Mizutani & Kato, 1985). The corresponding lattice constants were taken from the compilation of Taylor (1984).

(4) A fixed antishielding factor $\gamma_\infty = -31.9$ (Mahapatra, Pattnaick, Thompson & Das, 1977) was adopted.

The refinement was carried out in the following way. The atomic coordinates (u, x, y and z) were varied in such a way that the quadrupole coupling constants at the cation sites C and D were reproduced within 5 MHz and the asymmetry parameters within 0.01. Variation was carried out with the program *SGIT* (Bartos, 1991b) including the Monte-Carlo routine *SEEK* of the CERN code *MINUIT* (James & Ross, 1971). The (mean) atomic coordinates obtained by neutron and X-ray diffraction, given in Table 2, were used as starting parameters; in the case of $\mathrm{Gd_2O_3}$ and $\mathrm{Sm_2O_3}$, where no diffraction data are available, the average coordinates of the other oxides were chosen. The admitted deviation of $\Delta\nu_Q = 5$ MHz does not reflect the very small experimental error of $\Delta\nu_Q^{\rm exp} \simeq 1$ MHz, but includes the uncertainty of the antishielding factor, $\Delta\gamma_\infty \simeq 1$ (Feiock & Johnson, 1969; Mahapatra, Pattnaick, Thompson & Das, 1977). The error in the quadrupole moment $Q = 0.83\,(13)$ b was not taken into

Table 2. *Comparison of the atomic coordinates u, x, y and z (all* × 10^3*) obtained from X-ray and neutron diffraction with those obtained from PAC measurements at the temperatures indicated*

		PAC				X-ray and neutron diffraction					
M	*T* (K)	$-u$	*x*	*y*	*z*	*T* (K)*	$-u$	*x*	*y*	*z*	Reference
Sc	650	35.45 (5)	389.3 (3)	153.0 (2)	384.9 (4)	RT, X, sc	35.1 (2)	392.8 (7)	152.8 (7)	380.2 (7)	Geller *et al.* (1967)
						RT, X, sc	35.46 (4)	391.4 (1)	154.8 (1)	381.4 (1)	Norrestram (1968)
In	750	33.73 (5)	390.9 (3)	152.3 (2)	384.7 (4)	RT, X, sc	33.2 (1)	390.5 (15)	152.9 (11)	383.2 (13)	Marezio (1966)
						RT, X, sc	33.7 (1)	391.2 (12)	155.8 (11)	379.6 (13)	Marezio (1966)
Yb	730	32.77 (5)	390.8 (2)	152.4 (2)	383.0 (3)	RT,	32.53 (4)	391.0 (6)	152.3 (6)	380.7 (6)	Saiki *et al.* (1985)
						834	32.40 (5)	392.1 (8)	152.8 (7)	380.9 (7)	Saiki *et al.* (1985)
						RT, X, p	32.2 (1)	391.8 (9)	154.5 (8)	380.5 (9)	Will *et al.* (1987)
						RT, n,	33.6 (8)	391 (2)	151.0 (15)	380 (2)	Fert (1962)
						RT, n, sc	32.1 (8)	391 (1)	151 (1)	380 (1)	Moon (1968)
Y	750	32.75 (5)	390.7 (3)	152.6 (2)	382.4 (4)	RT, n, sc	32.7 (3)	390.7 (3)	152.0 (3)	380.4 (3)	O'Connor & Valentine (1969)
						RT, X, sc	32.8 (3)	389 (1)	154 (1)	378 (1)	Paton & Maslen (1965)
						RT, X, p	32.0 (1)	391.1 (5)	151.6 (5)	382.7 (6)	Smrcok (1989)
						RT, X, p	32.2 (3)	389 (2)	150 (2)	381 (2)	Scott (1981)
Ho	793	32.55 (5)	390.8 (3)	152.7 (2)	381.7 (4)	RT, n,	27.0 (6)	388.0 (15)	152 (1)	382.0 (15)	Fert (1962)
Dy	750	32.01 (5)	391.1 (3)	152.4 (1)	380.9 (5)	RT, n,	28 (1)	387 (3)	148 (3)	378 (3)	Hase (1963)
Gd	858	31.44 (5)	391.5 (4)	152.4 (1)	380.9 (5)						
Sm	773	31.44 (5)	391.5 (4)	152.6 (1)	380.1 (5)						

* X, X-ray diffraction; n, neutron diffraction; sc, single crystal; p, polycrystalline; RT, 293 K.

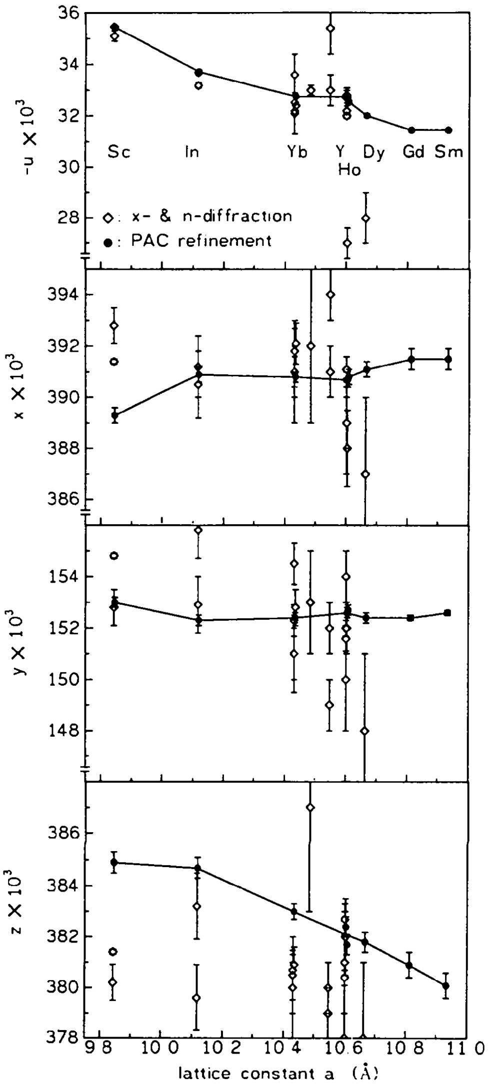


Fig. 2. Comparison of the PAC refined parameters *u*, *x*, *y* and *z* with those obtained by neutron and X-ray diffraction (see Table 2). The lines are to guide the eye.

account. The atomic parameters (*u*, *x*, *y* and *z*) were allowed to vary around the starting value within a range of ±0.010.

The results are shown in Fig. 2, which compares the final values of *u*, *x*, *y* and *z* with those from neutron and X-ray diffraction. First of all, we find that the coordinates from PAC refinement have a precision of typically 0.3 pm and agree with the less-precise coordinates from neutron and X-ray diffraction, except in the case of Sc_2O_3 and Dy_2O_3. In contrast to the diffraction data, the coordinates from PAC refinement vary systematically with the lattice constant: the oxygen coordinates *x* and *y* are nearly independent of *a*, while the cation coordinate *u* and the oxygen coordinate *z* decrease with increasing lattice constant. In the case of Gd_2O_3 and Sm_2O_3, where to our knowledge no diffraction analysis exists, this PAC analysis predicts the atomic parameters. Finally, we note that the results of the PAC refinement for Sc_2O_3 do not match the very precise coordinates given by Norrestram (1968). Because of the small bond length of $d_{M-O} \simeq 2.11$–2.12 Å the assumption of pure ionic bonding, *i.e.* a purely ionic antishielding factor γ_∞, may not be valid any more and covalency may contribute to the e.f.g. (Wiarda, Wenzel, Uhrmacher & Lieb, 1992).

To summarize, accurate PAC measurements with the same nuclear probe (^{111}Cd) in a class of essentially isostructural ionic compounds have for the first time allowed quantitative determination of atomic coordinates in polycrystalline solids.

This work has been supported by Deutsche Forschungsgemeinschaft.

References

Achtziger, N. (1992). *Submicroscopic Investigations of Defects in Semiconductors*, edited by G. Langouche, pp. 101–122. Amsterdam: North-Holland.

Bartos, A. (1991*a*). PhD thesis, Univ. of Göttingen, Germany.
Bartos, A. (1991*b*). *SGIT*. Unpublished.
Bartos, A., Bolse, W., Lieb, K. P. & Uhrmacher, M. (1988). *Phys. Lett. A*, **130**, 177–183.
Bartos, A., Lieb, K. P., Pasquevich, A. F. & Uhrmacher, M. (1991). *Phys. Lett. A*, **157**, 513–518.
Bolse, W., Uhrmacher, M. & Lieb, K. P. (1987). *Phys. Rev. B*, **36**, 1818–1830.
Eyring, L. (1964). *Handbook on the Physics and Chemistry of the Rare Earths*, edited by K. A. Schneider & L. Eyring, pp. 339–399. Amsterdam: North-Holland.
Feiock, F. D. & Johnson, W. R. (1969). *Phys. Rev.* **187**, 39–45.
Fert, A. (1962). *Bull. Soc. Fr. Mineral. Cristallogr.* **85**, 267–270.
Geller, S., Romo, P. & Remeika, J. P. (1967). *Z. Kristallogr.* **124**, 136–143.
Hase, W. (1963). *Phys. Status Solidi*, **3**, K446–447.
Inglot, Z., Wiarda, D., Lieb, K. P., Wenzel, Th. & Uhrmacher, M. (1991). *J. Phys. Condens. Matter*, **3**, 4569–4585.
James, F. & Ross, M. (1971). *MINUIT*. CERN Program Library, France.
Kajfosz, J. (1973). Report 858/PM. Institute Nuclear Physics, Krakow, Poland.
Klas, T., Fink, R., Krausch, G., Platzer, R., Voigt, J., Wesche, R. & Schatz, G. (1988). *Europhys. Lett.* **7**, 151–154.
Mahapatra, M. C., Pattnaick, P. C., Thompson, M. D. & Das, T. P. (1977). *Phys. Rev. B*, **16**, 3001–3009.
Marezio, M. (1966). *Acta Cryst.* **20**, 723–728.
Moon, R. M. (1968). *Phys. Rev.* **176**, 722–725.
Nagel, S. (1985). *J. Phys. Chem. Solids*, **46**, 743–756.
Norrestram, R. (1968). *Ark. Kemi*, **29**, 343–353.
O'Connor, B. H. & Valentine, T. M. (1969). *Acta Cryst.* **B25**, 2140–2144.
Paton, M. G. & Maslen, E. N. (1965). *Acta Cryst.* **19**, 307–310.
Pleiter, F. & Hohenemser, C. (1982). *Phys. Rev. B*, **25**, 106–125.
Recknagel, E., Schatz, G. & Wichert, Th. (1983). *Hyperfine Interactions of Radioactive Nuclei*, edited by J. Christiansen, pp. 133–204. Heidelberg: Springer.
Rinneberg, H. H. (1979). *At. Energy Rev.* **17**, 477–501.
Saiki, A., Ishizawa, N., Mizutani, N. & Kato, M. (1985). *Yogyo Kyokai Shi*, **93**, 649–654.
Schatz, G. & Weidinger, A. (1985). *Nukleare Festkörperphysik*, pp. 77–115. Stuttgart: Teubner.
Schwarz, K. & Blaha, P. (1992). *Z. Naturforsch. Teil A*, **47**, 197–202.
Scott, H. G. (1981). *Acta Cryst.* **A37**, 456–461.
Shitu, J. (1991). Personal communication.
Shitu, J., Wiarda, D., Wenzel, Th., Uhrmacher, J., Lieb, K. P., Bedi, S. & Bartos, A. (1992). *Phys. Rev. B*, **46**, 7987–7993.
Smrcok, L. (1989). *Cryst. Res. Technol.* **24**, 607–611.
Sternheimer, R. M. (1966). *Phys. Rev.* **146**, 140–148.
Taylor, D. (1984). *Br. Ceram. Trans. J.* **83**, 92–98.
Uhrmacher, M., Pampus, K., Bergmeister, F. J., Purschke, D. & Lieb, K. P. (1985). *Nucl. Instrum. Methods*, **B9**, 234–255.
Wiarda, W., Wenzel, Th., Uhrmacher, M. & Lieb, K. P. (1992). *J. Phys. Chem. Solids*, **53**, 1199–1209.
Will, G., Masciocchi, N., Hart, M. & Parrish, W. (1987). *Acta Cryst.* **A43**, 677–683.
Wyckhoff, R. W. G. (1964). *Crystal Structures*, Vol. II, pp. 2–6. New York: Interscience.

Acta Cryst. (1993). **B49**, 169–171

High-Pressure Phases in the System W–O. II. Structure Determination of $WO_{2.625}$ by HRTEM and X-ray Powder Diffraction Analysis

By Yu. A. Barabanenkov, N. D. Zakharov and I. P. Zibrov

Institute of Crystallography, Academy of Sciences of Russia, Leninsky prospekt 59, *Moscow* 117333, *Russia*

V. P. Filonenko

Institute of High-Pressure Physics, Academy of Sciences of Russia, Troitsk, Moscow Region, Russia

P. Werner

Institute of Solid State Physics and Electron Microscopy, Halle/Sale, Germany

and A. I. Popov and M. D. Valkovskii

Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of Russia, Moscow, Russia

(*Received* 12 *September* 1991; *accepted* 13 *July* 1992)

Abstract

A new type of tungsten oxide has been synthesized from a mixture of W and WO_3 by a solid-phase sintering method under high-pressure conditions. The crystal structure of the new oxide was investigated by HRTEM, selected-area electron diffraction and X-ray powder diffraction. The structure belongs to space group *Pbam* or $P2_12_12$ and has the following unit-cell parameters: $a = 21.431\ (9)$, $b = 17.766\ (7)$, $c = 3.783\ (2)$ Å, $V = 1440$ Å^3, $Z = 32$, $D_x = 8.33$ g cm^{-3}. The structural model and W-cation positions were determined by HRTEM and image processing. X-ray powder analysis and the *SHELX* computer program were used to prove the proposed structural model: $N = 158$, $R = 0.075$, $U_{\rm iso}(\rm W) =$

0108-7681/93/020169-03$06.00