

SHORT COMMUNICATIONS

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X-ray structure analysis and molecular conformation of *tert*-butyloxycarbonyl-L-prolylproline (Boc-Pro-Pro): errata. By M. E. KAMWAYA, O. OSTER and H. BRADACZEK, *Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-1000 Berlin 33, Federal Republic of Germany*

(Received 6 November 1981)

Abstract

Two errors in the paper by Kamwaya, Oster & Bradaczek [*Acta Cryst.* (1981), B37, 1564–1568] are corrected: On p. 1565, left column, line 5 from the top should read ' C_5-C^{γ} -endo (C^{β} -exo) for ring I and C_5-C^{γ} -exo (C^{β} -exo) for

ring II.' On p. 1567, right column, line 11 from the top should read 'prolyl residue can, therefore, be regarded as C_5-C^{γ} -endo (C^{β} -exo) for ring I and C_5-C^{γ} -exo (C^{β} -exo) for ring II.'

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All relevant information is given in the *Abstract*.

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Refinement of the Nd_2O_3 and Nd_2O_2S structures at 4 K. By M. FAUCHER, *ER 210, CNRS, 92190 Meudon-Bellevue*, J. PANNETIER, *Institute Laue–Langevin, BP n° 156, 38042 Grenoble CEDEX*, Y. CHARREIRE, *ER 211, CNRS, 92190 Meudon-Bellevue*, and P. CARO, *ER 210, CNRS, 92190 Meudon-Bellevue, France*

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Abstract

Structural parameters of polycrystalline Nd_2O_3 and Nd_2O_2S were refined at 4 K from neutron powder diffraction data to provide accurate atomic positions for the *ab initio* calculation of crystal-field parameters. The 4 K and 300 K structures of Nd_2O_3 are not significantly different. The parameters of Nd_2O_2S are close to those of Ho_2O_2S and La_2O_2S at room temperature.

Linares (1972) were compared with calculated values utilizing the room-temperature structure of Ce_2O_2S (Zachariasen, 1949).

In the present study, we have redetermined the structural parameters of the two compounds at 4 K from neutron powder diffraction data using both a conventional (integrated intensities) and a profile refinement method (Rietveld, 1969). The results were subsequently used to calculate (presumably) more accurate electrostatic c.f.p. (point charge + dipolar contribution).

1. Introduction

Spectroscopic experiments are often performed at low temperature so that calculation of *ab initio* crystal-field parameters (c.f.p.) requires structural data at the same temperature. However, c.f.p. of Nd^{3+} in Nd_2O_3 (Caro, Derouet, Beaury & Soulié, 1979) were derived from absorption spectra at 4 K and compared (Faucher, Dexpert-Ghys & Caro, 1980) with *ab initio* values based on the room-temperature structure of Boucherle & Schweizer (1975). In the same way, experimental c.f.p. of Nd^{3+} in Nd_2O_2S determined at 1.6 K by Soullat, Rossat-Mignod &

2. Experimental and refinement

Polycrystalline Nd_2O_3 (99.99% from Pechiney) was heated for 12 h at 1300 K to eliminate hydroxide and oxycarbonates. Nd_2O_2S was prepared from the oxide by the flux technique proposed by Ozawa, Forest, Jaffe & Ban (1971): a mixture of Nd_2O_3 , sulfur and sodium carbonate in the molar ratio 1:3:1 was fired at 1370 K for 2 h in an argon atmosphere. The sample was then washed with water and dried.

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Table 1. *Positional and thermal parameters of Nd₂O₃ at 4 K, compared with room-temperature values*

	<i>a</i> (Å)	<i>c</i> (Å)	<i>u</i>	<i>v</i>	<i>B</i> _{Nd} (Å ²)	<i>B</i> _{O(1)} (Å ²)	<i>B</i> _{O(2)} (Å ²)	<i>R</i> _p or <i>R</i> _N
This work (neutrons; 4 K)	3.8272 (1) 3.8277 (3)	5.9910 (2) 5.9908 (4)	0.2473 (3) 0.2463 (9)	0.6464 (3) 0.6469 (8)	0.04 (3) 0.02 (11)	0.42 (5) 0.28 (20)	0.88 (8) 0.69 (23)	8.2 (Profile refinement) 4.7 (Integrated intensities)
Boucherle & Schweizer (1975) (neutrons; 300 K)			0.2462 (3)	0.6466 (3)	0.25 (4)	0.59 (5)	0.85 (8)	6.8 (Profile refinement) 1.9 (Integrated intensities)

Following Pauling's (1928) model, the space group of both compounds is $P3m1$; $Z = 1$. The atomic positions are: Nd, $2(d)$, $\pm(\frac{1}{3}, \frac{2}{3}, u)$; O(1), $2(d)$, $\pm(\frac{1}{3}, \frac{2}{3}, v)$; O(2) or S, $1(a)$, (0,0,0).

The neutron diffraction patterns were recorded at 4 K on the D1A high-resolution diffractometer of the Institut Laue-Langevin with $\lambda = 1.909$ Å; the powdered sample was inserted in a 15 mm diameter vanadium tube. Data were collected from $\theta = 5$ to 78° in steps of 0.05° , the measurement time being about 30 s per step. The data from the ten counters were subsequently summed with ILL programs (Wolfers, 1970). The integrated intensities were determined by fitting the shape of the Bragg peaks to Gaussian distributions and the background to a first-order polynomial.* Refinement was carried out by integrated-intensity and profile-analysis (Rietveld, 1969) methods. No preferred orientation was observed. The expression for the reliability factor was: $R_{p \text{ or } N} = 100 \sum_i |Y_o(i) - s_q^2 Y_c(i)| / \sum_i Y_o(i)$. The following scattering lengths were used: $b(\text{Nd}) = 7.69$ (Boucherle & Schweizer 1975), $b(\text{O}) = 5.8$, and $b(\text{S}) = 2.8$ fm (Bacon, 1972).

(a) Nd₂O₃

25 lines were observed between 9 and 70° . The starting values for u and v were those of Boucherle & Schweizer (1975) for both profile and conventional refinements. Final parameters are reported in Table 1. B values are corrected

* The scattering angles and observed integrated intensities for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36229 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

for absorption (Hewat, 1979),* the values of μr ($=0.452$) being obtained experimentally by measuring the transmission coefficient of the sample.

(b) Nd₂O₂S

26 peaks recorded in the range 6 to 76° were used in the refinement. Spurious lines revealed the presence of an unidentified impurity distinct from the starting materials. The initial u and v values were those of Ce₂O₂S (Zachariassen, 1949). The refined parameters are given in Table 2, together with the room-temperature values for La₂O₂S (Morosin & Newman, 1973), Ho₂O₂S (Boucherle, Quezel, Schweizer & Tch  ou, 1979) and Ce₂O₂S. Thermal parameters are corrected for absorption (experimental $\mu r = 0.498$); however, B_{Nd} from the profile refinement as well as B_{O} from the normal refinement were negative. This anomalous behaviour is probably related to the presence of a second phase in the sample. The lines due to this impurity were indexed on the basis of an hexagonal lattice with $a = 7.544$ (6), and $c = 9.257$ (18) Å. This precludes it from being another type of lanthanide oxide sulfide such as Ln₂O₂S₂ (Dugu   1978). Some lines of the impurity most likely overlap with those of Nd₂O₂S at high angles which thus artificially decreases the thermal parameters. The differences between the results of the two refinement methods then reflect the different way they handle the data. Therefore, the thermal parameters of Nd₂O₂S must be considered as very uncertain [the thermal parameters given by Boucherle *et al.* (1979) for Ho₂O₂S are also poorly defined]. It is worth noting, however, that the positional parameters as determined by the two methods agree within one standard deviation.

* Note that the correction ΔB given in Hewat (1979) must be divided by 2 because the transmission factor A_{hkl} applies to the intensities and not to the structure factor.

Table 2. *Positional and thermal parameters of Nd₂O₂S at 4 K, and La₂O₂S, Ho₂O₂S, Ce₂O₂S at 300 K*

	<i>a</i> (Å)	<i>c</i> (Å)	<i>u</i>	<i>v</i>	<i>B</i> _{Ln} (Å ²)	<i>B</i> _{O(1)} (Å ²)	<i>B</i> _S (Å ²)	<i>R</i> _p or <i>R</i> _N
This work (neutrons; Nd ₂ O ₂ S; 4 K)	3.9470 (2) 3.9456 (6)	6.7801 (1) 6.7804 (9)	0.2805 (3) 0.2798 (6)	0.6288 (4) 0.6284 (8)	-0.17 (5)* 0.08 (13)	0.33 (8) 0.41 (17)	0.55 (15) -0.51 (31)*	9.6 (Profile refinement) 4.4 (Integrated intensities)
Boucherle <i>et al.</i> (1979) (neutrons; Ho ₂ O ₂ S; 300 K)	3.7804 (5)	6.5837 (5)	0.2812 (5)	0.6297 (6)	0.40 (10)	0.24 (20)	0.28 (24)	11.1 (Profile refinement) 4.1 (Integrated intensities)
Morosin & Newman (1973) (X-rays; La ₂ O ₂ S; 300 K)	4.049 (1)	6.939 (2)	0.27929 (6)	0.6287 (8)		Anisotropic		3.1 (Integrated intensities)
Zachariassen (1949) (X-rays; Ce ₂ O ₂ S; 300 K)	4.00 (1)	6.82 (3)	0.29 (2)	0.64				

* See text for explanation of these values.

Table 3. Calculated crystal-field parameters: point-charge (PCEM) and dipolar (ID) contributions; corrected parameters: ES $(1 - \sigma_k) \langle r'^k \rangle / \langle r^k \rangle$

Experimental values are after Caro *et al.* (1979) and Souillat *et al.* (1972). Earlier calculations (Faucher *et al.*, 1980) are in parentheses.

Parameter (cm ⁻¹)	Nd ₂ O ₃				Nd ₂ O ₂ S				Experimental	
	PCEM	ID	PCEM + ID (ES)	ES(1 - σ_k) × $\langle r'^k \rangle / \langle r^k \rangle$	PCEM	ID	PCEM + ID (ES)	ES(1 - σ_k) × $\langle r'^k \rangle / \langle r^k \rangle$		
B ₀ ²	-1541	-451	-1992	-580 (-575)	-836	-44	546	502	146 (207)	194
B ₀ ⁴	424	17	441	759 (754)	634	536	1	537	925 (1274)	912
B ₂ ⁴	1184	-21	1163	2002 (2092)	1606	798	11	809	1393 (1037)	924
B ₄ ⁰	283	-31	252	584 (590)	752	211	37	248	574 (595)	512
B ₄ ²	-169	-8	-177	-410 (-372)	-237	-139	3	-136	-315 (-320)	-300
B ₆ ⁰	261	12	273	632 (640)	672	205	-12	193	447 (484)	256

3. Discussion

The refined coordinates and cell parameters were used to recalculate *ab initio* electrostatic c.f.p. In Table 3 are reported for both compounds the point-charge distribution (PCEM), the induced-dipoles correction (ID), the total electrostatic parameters corrected for the shielding factor σ_k and the wave-function expansion, and the experimental c.f.p. as determined by Caro *et al.* (1979) for Nd₂O₃ and Souillat *et al.* (1972) for Nd₂O₂S. Compared with our earlier work (Faucher *et al.*, 1980), the results of *ab initio* calculations for Nd₂O₃ are not much changed since the 4 K structure is not significantly different from the room-temperature structure. Concerning Nd₂O₂S, the results are different since the coordinates of Ce₂O₂S (Zachariasen, 1949) were used previously. In fact, the coordinates of Nd₂O₂S at 4 K are very close to those of Ho₂O₂S (Boucherle *et al.*, 1979) and La₂O₂S (Morosin & Newman, 1973) at 300 K.

The dipolar correction to B₀² yields a sign and magnitude consistent with the experimental value. The influence of the dipolar corrections on higher-order c.f.p. is quite small while B₀⁴ and B₂⁴ are quite varied owing to changes in the point-charge contributions. However, one must conclude that the agreement between calculated and experimental c.f.p. is not significantly improved by the use of more accurate structural data; the origin of the observed discrepancies is

thus to be found in multipolar effects of higher order or a possible covalency contribution.

References

- BACON, G. E. (1972). *Acta Cryst.* A **28**, 357–358.
 BOUCHERLE, J. X., QUEZEL, S., SCHWEIZER, J. & TCHÉOU, F. (1979). *Acta Cryst.* A **35**, 818–820.
 BOUCHERLE, J. X. & SCHWEIZER, J. (1975). *Acta Cryst.* B **31**, 2745–2746.
 CARO, P., DEROUET, J., BEAURY, L. & SOULIÉ, E. (1979). *J. Chem. Phys.* **70**, 2542–2549.
 DUGUÉ, J. (1978). Thèse de Doctorat d'Etat ès Sciences Physiques, Paris VI.
 FAUCHER, M., DEXPERT-GHYS, J. & CARO, P. (1980). *Phys. Rev. B*, **23**, 607–617.
 HEWAT, A. W. (1979). *Acta Cryst.* A **35**, 248.
 MOROSIN, B. & NEWMAN, D. J. (1973). *Acta Cryst.* B **29**, 2647–2648.
 OZAWA, L., FOREST, H., JAFFE, P. M. & BAN, G. (1971). *J. Electrochem. Soc.* **118**, 482–486.
 PAULING, L. (1928). *Z. Kristallogr.* **69**, 415.
 RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
 SOUILLAT, J. C., ROSSAT-MIGNOD, J. & LINARES, C. (1972). *Phys. Status Solidi B*, **52**, 601–608.
 WOLFERS, P. (1970). Unpublished programs.
 ZACHARIASEN, W. H. (1949). *Acta Cryst.* **2**, 60–62.

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A neutron diffraction study of Cr₃Si. By J.-E. JØRGENSEN and S. E. RASMUSSEN, *Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark*

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Abstract

Cr₃Si, cubic, *Pm*3*n*, $a = 4.5599$ (3) Å, $Z = 2$, $V = 94.8$ Å³, $D_c = 6.448$ Mg m⁻³, $\mu = 0.01048$ mm⁻¹, $R = 1.8\%$ for 21 reflexions [$I > 3\sigma(I)$] and 4 parameters. $U_{\text{iso}}^{\text{Cr}} = 0.0036$ (4) Å² and $U_{\text{iso}}^{\text{Si}} = 0.0050$ (6) Å².

Single crystals of Cr₃Si have been grown by zone melting in our laboratory (Jørgensen & Rasmussen, 1979). Cr₃Si has

the *A15* or β -tungsten structure and many intermetallic compounds with this structure are high-temperature superconductors. Several *A15* compounds, e.g. V₃Si (Batterman & Barrett, 1964), exhibit a cubic to tetragonal phase transition at low temperature. Cr₃Si has no superconduction transition down to 0.015 K (Blaugher, Hein, Cox & Waterstrat, 1969) and neutron powder diffraction experiments at room temperature and 6 K (Jørgensen, 1979) showed that Cr₃Si remains cubic at low temperature. A neutron diffraction

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