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SHORT-FORMAT PAPERS

Structures of RbD and CsD by Time-of-Flight Neutron Diffraction

By NATHANIEL E. BRESE AND MICHAEL O'KEEFFE

Department of Chemistry, Arizona State University, Tempe, AZ 85287-1604, USA

Abstract. Rubidium deuteride, RbD, $M_r = 87.47$, cubic, $Fm\bar{3}m$, $a = 5.9705\,(2)$ Å (10K), $a = 6.0210\,(2)$ Å (300K), $V = 212.83$ Å^3 (10K), $V = 218.27\,(2)$ Å^3 (300 K), $Z = 4$, $D_x = 2.66$ g cm^{-3} (300 K), neutron time-of-flight, Rietveld refinement, wR_p, R_p, reduced χ^2 are 0.045, 0.031, 3.99 (10K), respectively, and 0.052, 0.037, 2.19 (300 K), respectively. Caesium deuteride, CsD, $M_r = 134.92$, cubic, $Fm\bar{3}m$, $a = 6.3741\,(3)$ Å, $V = 258.97\,(4)$ Å^3, $Z = 4$, $D_x = 3.46$ g cm^{-3}, 300 K, neutron time-of-flight, Rietveld refinement, wR_p, R_p, reduced χ^2 are 0.070, 0.048, 1.30, respectively. RbD and CsD were confirmed to have the *B*1 (rocksalt) structure.

Experimental. Rb metal (Alfa 99·9%) was melted into a copper crucible in an argon-filled drybox. The crucible was placed into a copper pipe which was lightly capped. The copper pipe was quickly transferred to an alumina tube fitted with ground-glass ends, evacuated and filled with D$_2$ (Matheson, 99·7%). The alumina tube was inside a tube furnace, but the copper pipe extended beyond the ends of the furnace. The D$_2$ was passed through a cold trap and over a boat of P$_2$O$_5$. The assembly was heated to 763 K under a very slow flow of D$_2$. After 3 d, the furnace was cooled, and the copper pipe was quickly transferred to a drybox. Fluffy masses of white needles grew slightly downstream of the copper boat. CsD was prepared in an analogous fashion. The metals and their hydrides are extremely pyrophoric. X-ray diffraction analysis confirmed the presence of single-phased materials.

Pulsed neutron diffraction data were collected at room temperature on the High Intensity Powder Diffractometer (HIPD) of the Manuel Lujan, Jr, Neutron Scattering Center at Los Alamos National Laboratory. The powder data were refined with use of the General Structure Analysis System (*GSAS*), a Rietveld profile analysis code which minimizes $\sum w(I_o - I_c)^2$ (Larson & Von Dreele, 1990).

Data from the highest resolution detector banks ($\pm 153.43°$, $-90°$) were used. Collection times were kept to a minimum (2–4 h); this noisy data resulted in rather high residuals. The quality of the data determined the usable range. For RbD at 10 K and 300 K, 169 reflections in the range $0.54 < d < 3.2$ Å and 76 reflections in the range $0.80 < d < 3.2$ Å were used, respectively. For CsD, 78 reflections were available in the range $0.8 < d < 3.3$ Å.

The only possible structures for an *AB* compound with a face-centered cubic cell and with $Z = 4$ are the *B*1 (rocksalt) (Bragg & Bragg, 1913) and *B*3 (sphalerite) (Bragg, 1912) ones. The neutron data clearly showed that the former was correct for both compounds.

The scattering lengths used were 7·08, 5·42 and 6·67 fm for Rb, Cs and D, respectively. Since these are all similar, the difference reflections (h,k,l all odd)

Table 1. *Refinement variables, statistics and derived structural parameters*

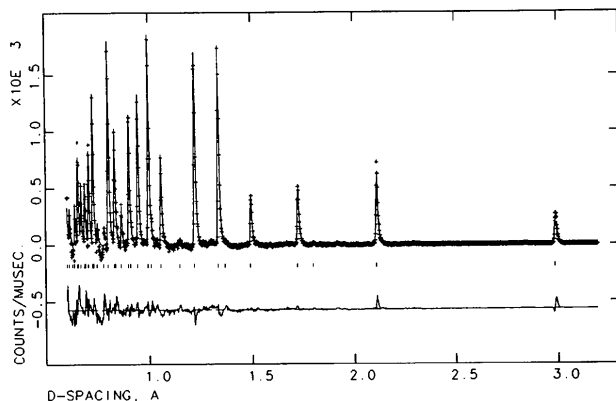|	RbD (10 K)	RbD (300 K)	CsD (300 K)
Background coeffs	32	35	27
Profile coeffs	$\beta_0, \beta_1, \sigma_1$	σ_1	σ_1
Variables	45	39	38
Profile points	10345	8279	8419
wR_p	0·04	0·05	0·07
R_p	0·03	0·04	0·05
χ^2	3·99	2·19	1·30
Cell edge, a (Å)	5·9705 (2)	6·0210 (2)	6·3741 (3)
U_{iso} (Å^2)	0·0136 (1)	0·0404 (2)	0·0461 (5)

Fig. 1. Neutron diffraction profile fit for RbD at 10 K (+ 153·4° detector bank). The data points are shown as ' + ', and the solid line is the calculated profile. The difference curve at the bottom is on the same scale. The background has been subtracted.
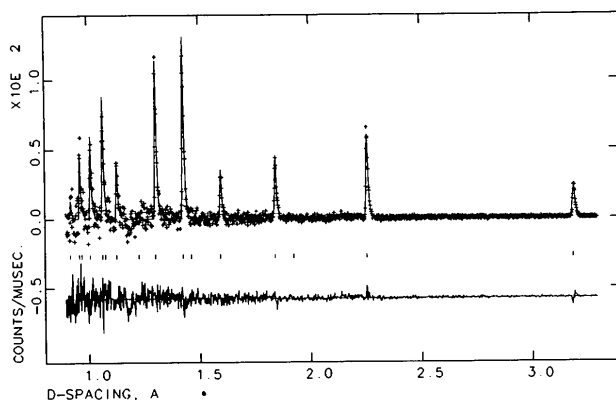

Fig. 2. Neutron diffraction profile fit for CsD at 300 K (+ 153·4° detector bank).

were weak, so that only average thermal parameters were determined.

The variables refined included scale factors, background coefficients used in a cosine Fourier series technique, profile coefficients (Von Dreele, Jorgensen & Windsor, 1982), diffractometer zero constants, lattice parameters and isotropic thermal parameters.

The refinements all converged. $(\Delta/\sigma)_{max} = 0·1$. Specific variables are given in Table 1 together with the derived structural results.* Figs. 1 and 2 display typical diffraction profiles.

Related literature. Zintl and Harder originally reported the structure of RbH and CsH (Zintl & Harder, 1931). However, using X-ray diffraction they could not locate the H atoms and could not distinguish between the $B1$ (six-coordinated atoms) and $B3$ (four-coordinated atoms) structures. They reported cell edges at room temperature of 6·049 (2) Å for RbH and 6·389 (1) Å for CsH. Neutron diffraction has shown that NaD has the $B1$ structure as well (Shull, Wollan, Morton & Davidson, 1948).

The observed bond lengths [3·0105 (1) Å in RbD and 3·1871 (2) Å in CsD] are longer than predicted (2·92 Å in RbD and 3·10 Å in CsD) from recently derived bond valence parameters (Brese & O'Keeffe, 1991). This observation was a motivation for determining the structures unambiguously. It is noted, however, that anomalously long bonds are also found in the corresponding oxides (McGuire & O'Keeffe, 1984).

* Lists of diffraction profiles correspondings to Figs. 1 and 2 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53967 (128 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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