

from the water molecules [0.30 (6) and 0.13 (5)] while Cu π donates 0.18 (10) e to them. We seem to see greater electron acceptance by Cr^{II} and Fe^{II} [0.8 (2) and 1.3 (3)] than Cu [0.2 (3) e].

Overall therefore we see charge transfer *via* hydrogen bonding from the sulfate ion onto the metal(II) ion. The PND experiments lend support to this conclusion. When we have spin in the metal t_{2g} orbitals more spin appears on the water protons than isolated hexaaquametal(II) ion local-density functional calculations account for, leading to the suspicion that this excess is one consequence of the hydrogen bonding. We can understand the charge movements qualitatively if we note that the minority spin metal $3d-t_{2g}$ orbitals are empty in Cr^{II}, $\frac{1}{3}$ full in Fe^{II} and filled in the Cu^{II} case. This relative electron deficiency in the Cr^{II} and Fe^{II} cases can be imagined to attract electrons from electron-rich regions, in particular the sulfate ion.

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Novel High-Temperature Polymorphs of MgBr₂ and MnBr₂ – Limits of Powder Diffraction for Structure Determination

BY MICHAEL SCHNEIDER, PETER KUSKE AND HEINZ DIETER LUTZ*

Universität Siegen, Anorganische Chemie I, W-5900 Siegen, Germany

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Abstract

High-temperature polymorphs of magnesium bromide and manganese bromide, hexagonal, $R\bar{3}m$, $Z =$

3. MgBr₂, $M_r = 184.13$, Cu $K\alpha_1$, $\lambda = 1.54051$ Å, $T = 973$ K, $a = 3.9152$ (7), $c = 19.420$ (4) Å, $V = 257.80$ (9) Å³. MnBr₂, $M_r = 214.76$, neutron radiation, $\lambda = 1.594$ (2) Å, $T = 773$ K, $a = 3.92240$ (2), $c = 19.167$ (2) Å, $V = 255.38$ (3) Å³, Rietveld

* Author to whom correspondence should be addressed.

refinement, $10 \leq 2\theta \leq 150^\circ$, $R_{wp} = 0.13$. The hitherto unknown high-temperature polymorphs of both MgBr₂ and MnBr₂ crystallize in the CdCl₂ form. The manganese compound is pseudocubic [$a = 11.0864(1) \text{ \AA}$ at 773 K] above 623 K. Distinction between the rhombohedral layered CdCl₂ structure and the cubic three-dimensional net λ -MnO₂ structure is not possible by powder diffraction experiments alone. Additional observations must be employed. The JCPDS File Nos. for MnBr₂ and MgBr₂ are 43-1499 and 43-1500 respectively.

Introduction

Both MgBr₂ and MnBr₂ crystallize in the CdI₂ structure type ($hP3$) as has been known for a long time (Ferrari & Giori, 1929). In the case of MnBr₂, it has been reported that the structure changes to the CdCl₂ type ($hR9$) by incorporation of even small amounts of LiBr (Seifert & Dau, 1972). Recently, we found previously unknown high-temperature polymorphs of these isostructural bromides by high-temperature X-ray experiments (Kuske, 1988; Kuske & Lutz, 1989*a,b*). The novel magnesium bromide polymorph was assumed to crystallize as the CdCl₂ type (Kuske, 1988), and high-temperature MnBr₂ (MnBr₂ II) was characterized as the cubic λ -MnO₂ type (Hunter, 1981) by neutron powder diffraction experiments (Kuske, 1988; Kuske & Lutz, 1989*a,b*). On cooling to ambient temperature, the reflections of cubic MnBr₂ split. The X-ray pattern thus obtained was indexed as due to the CdCl₂ structure (MnBr₂ III). CdCl₂-type MnBr₂ is only metastable at ambient temperature (Kuske, 1988; Kuske & Lutz, 1989*a,b*). In order to confirm the high-temperature polymorphs of MgBr₂ and MnBr₂ in more detail we reanalyzed the high-temperature neutron powder diffraction data of MnBr₂ and performed additional high-temperature X-ray measurements on both MgBr₂ and MnBr₂ (Schneider, 1991). The results obtained and the problems involved with Rietveld's method of structure refinement are presented in this paper.

Experimental

Anhydrous MgBr₂ and MnBr₂ were prepared by heating the hydrates MgBr₂·6H₂O and MnBr₂·4H₂O in a dry stream of HBr at 623 K and subliming the products at 823–873 K in a vacuum.

The cell parameters of MgBr₂ were refined from X-ray Guinier powder data (Enraf-Nonius high-temperature Guinier Simon FR 533 camera, Cu $K\alpha_1$ radiation, 16 reflections, silicon as internal standard, $a = 5.44434 \text{ \AA}$) by least-squares methods. The pattern of MgBr₂ was indexed with the systematic absences of space group $R\bar{3}m$ (CdCl₂ type).

Table 1. Refined profile parameters for MnBr₂ II with e.s.d.'s in parentheses

	CdCl ₂ type	λ -MnO ₂ type
Scale factor	0.290 (2)	0.01018 (9)
Number of structural parameters refined	4	4
U (deg ²)	0.15 (1)	0.19 (1)
V (deg ²)	-0.34 (2)	-0.35 (2)
W (deg ²)	0.318 (8)	0.324 (8)
Zero point (°)	-0.002 (4)	0.005 (5)
Asymmetry parameters	0.90 (5)	0.90 (5)

Table 2. Structural parameters of MnBr₂ II at 773 K with e.s.d.'s in parentheses

Site	x	y	z	U_{iso} ($\text{\AA}^2 \times 10^2$)
Space group $R\bar{3}m$ (CdCl ₂ structure)				
Mn 3(<i>a</i>)	0	0	0	5.7 (1)
Br 6(<i>c</i>)	0	0	0.2540 (2)	5.65 (6)
Space group $Fd\bar{3}m$ (λ -MnO ₂ structure)				
Mn 16(<i>d</i>)	0.5	0.5	0.5	5.6 (1)
Br 32(<i>e</i>)	u^*	u^*	u^*	5.68 (6)
$*u = 0.25394$ (7).				

The neutron diffraction intensities of MnBr₂ were collected at 773 K on the powder diffractometer D2B at the Institut Laue-Langevin in Grenoble (ILL). The neutron wavelength used was 1.594 (2) \AA . The reflections can be indexed on the basis of the cubic space group $Fd\bar{3}m$ (λ -MnO₂ type) as well as on that of the hexagonal space group $R\bar{3}m$ (CdCl₂ type). The structure was refined with a modified Rietveld program (Rietveld, 1969; Cockcroft, 1991). Neutron scattering lengths used in structure refinement were $b(\text{Mn}) = -3.73$ and $b(\text{Br}) = 6.78$ fm (Koester & Rauch, 1983). The final R values yielded are $R_{wp} = 0.130$ (expected 0.041) and $R_l = 0.078$ for the refinement in space group $R\bar{3}m$ and $R_{wp} = 0.132$ (expected 0.041) and $R_l = 0.071$ for the cubic space group $Fd\bar{3}m$. The maximum ratios of least-squares shift to e.s.d. in the final cycles were less than 0.01. The final profile parameters are given in Table 1, the structural parameters in Table 2.*

Discussion

The question arises as to what the true crystal structure of the high-temperature polymorph of manganese bromide, MnBr₂ II, is. For both CdCl₂-type and λ -MnO₂-type structures an equally good fit of the neutron powder diffraction data is obtained by Rietveld's procedure (see Fig. 1). Furthermore, X-ray intensities calculated for both structure models by LAZY PULVERIX (Yvon, Jeitschko & Parthé,

* Lists of observed and calculated profile intensities have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55240 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1977) do not differ significantly. The reason for these findings is that powder samples of compounds with cubic closest-packed anions and half of the octahedral voids occupied by metal ions produce equal powder diffraction patterns, for both X-ray and neutron data, regardless of whether the metal ions are ordered in layers [position 3(*a*) in space group $R\bar{3}m$] or in a three-dimensional manner [position 16(*d*) in space group $Fd\bar{3}m$] as already shown by Parthé & Yvon (1970) for M_2C -type carbides. The values of goodness of fit (*R*, *S* etc.) for powder diffraction data alone, even with Rietveld's method, do not enable the true crystal structure to be determined for the two cases. In order to distinguish which of the two structure models is correct a single-crystal structure determination is needed. If this is not possible additional observations must be

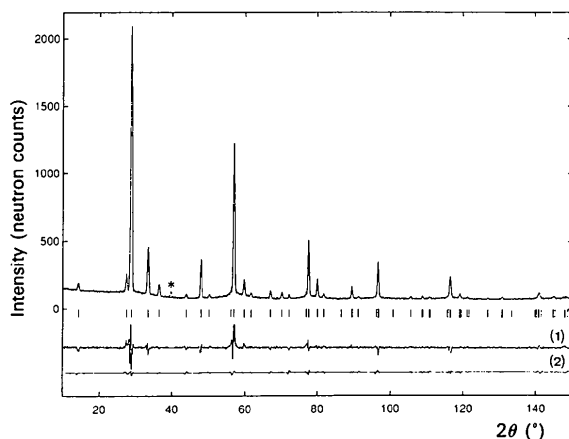


Fig. 1. Neutron diffraction patterns of $MnBr_2$ *hR9* at 773 K [experimental, calculated, difference (1), and positions of the reflections for the $CdCl_2$ -type structure; difference for λ - MnO_2 -type structure model (2)]. The asterisk denotes a reflection caused by the sample holder.

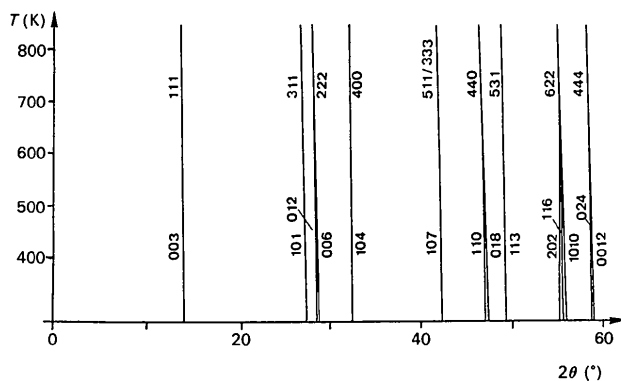


Fig. 2. High-temperature X-ray pattern of $MnBr_2$ *hR9* (cooling of the pseudocubic form to ambient temperature, splittings of the reflections are over-emphasized).

employed. Thus, in the case of Li_2MnBr_4 *oC14* Raman spectra and cohesive energy calculations were used to evaluate the true structure (Lutz, Schneider, Kuske & Steiner, 1991).

The high-temperature polymorph of manganese bromide, $MnBr_2$ II, crystallizes as pseudocubic [$a = 11.0864(4)$ Å at 773 K] in the layered $CdCl_2$ structure (space group $R\bar{3}m$). This is revealed by the continuous transition of pseudocubic $MnBr_2$ II to the rhombohedral metastable room-temperature form $MnBr_2$ III [$a = 3.856(2)$, $c = 18.74(3)$ Å] (see Fig. 2). This would not be possible if $MnBr_2$ II belonged to space group $Fd\bar{3}m$ because group theory does not allow continuous phase transition from space group $Fd\bar{3}m$ to $R\bar{3}m$ for the cell volumes under discussion (Schneider, 1991). This means that $MnBr_2$ II and $MnBr_2$ III (Kuske & Lutz, 1989*a,b*) possess equivalent crystal structures, but $MnBr_2$ *hR9* is pseudocubic above 623 K.

The pseudocubic metric of $MnBr_2$ *hR9* above 623 K means that the flattening of the occupied octahedra equals the elongation of the empty ones. In the case of $MgBr_2$ *hR9*, the c/a ratio is > 4.899 contrary to most other $CdCl_2$ -type compounds (Partin & O'Keeffe, 1991) and, hence, the empty layers are more elongated than the occupied ones are flattened. The CdI_2 - to $CdCl_2$ -type phase transitions of $MgBr_2$ and $MnBr_2$ are, to our knowledge, the first ones to be observed for this layered structure type. They are probably martensitic in nature.

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