

A Note on the Crystal Structure of MnB_4

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The existence of a phase in the Mn-B system with the composition MnB_4 was reported by Fruchart and Michel in 1960.¹ Since the published powder pattern of this phase was very similar to that of CrB_4 , the crystal structure of which has been recently determined at this Institute,² an investigation was started in order to obtain more detailed structural information. In the present note X-ray powder data for MnB_4 are given together with preliminary results from a structure determination.

Three alloys with the approximate initial composition $\text{MnB}_{4.0}$ were prepared in the following way. Pieces of manganese (from Koch-Light Laboratories, Ltd., claimed purity 99.99 %) and crystalline boron (from Borax Consolidated, Ltd., claimed purity 99.8 %) were arc-melted under a purified argon atmosphere. Two of the alloys were then annealed in evacuated and sealed silica tubes for fourteen days, one at 800°C and the other at 1000°C. The third alloy was heat-treated for nine days at 1150°C under an argon atmosphere in an induction furnace. No single crystals of MnB_4 suitable for X-ray work were obtained.

Powder diffraction patterns of the reaction products were recorded using Guinier-Hägg focussing cameras with strictly monochromatic $\text{CrK}\alpha_1$ or $\text{CuK}\alpha_1$ radiation. In the latter case an aluminium foil was used to reduce the fluorescence radiation. Unit cell dimensions were measured using silicon ($a=5.43054$ Å) as internal calibration standard and a least-squares refinement of the lattice parameters was made with a program called CELSIUS.³ Although the standard deviations indicate a rather high precision, systematic errors can possibly be of greater magnitude than those indicated by the standard deviations.

The examination of the powder diffraction films gave the following results. After melting only, the reaction products were MnB_2 and a probably very boron-rich phase. The samples annealed at 800°C and

1000°C gave rise to similar powder patterns containing lines from Mn_3B_4 and MnB_4 . These results confirmed those of Fruchart and Michel¹ showing that MnB_4 is not stable at high temperatures and that MnB_2 decomposes at low temperatures. The sample heat-treated at 1150°C, however, showed a two-phase equilibrium between MnB_2 and MnB_4 .

The powder pattern of MnB_4 could be indexed with very good agreement between observed and calculated $\sin^2\theta$ -values in terms of a monoclinic unit cell with $a=5.5029 \pm 0.0003$ Å, $b=5.3669 \pm 0.0003$ Å, $c=2.9487 \pm 0.0002$ Å, and $\beta=122.710 \pm 0.005^\circ$ (for values of $\sin^2\theta_c$ and $\sin^2\theta_o$ see Table 1). The errors given are standard

Table 1. Powder diffraction data for MnB_4 up to $\sin^2\theta=0.50$. $\text{CrK}\alpha_1$ radiation, $\lambda=2.28962$ Å.

hkl	$\sin^2\theta_o \times 10^6$	$\sin^2\theta_c \times 10^6$	I_o
1 1 0	10668	10663	vst
0 2 0	18199	18201	st
1 1 $\bar{1}$	19622	19624	st
2 0 $\bar{1}$	21084	21083	st
0 0 1	21285	21290	st
2 0 0	24444	24452	w
2 2 $\bar{1}$	39282	39284	st
0 2 1	39495	39491	st
2 2 0	42655	42653	st
3 1 $\bar{1}$	43872	43869	st
1 1 1	44286	44283	st
1 3 0	47060	47064	st

deviations obtained from the least-squares refinement. The d -values corresponding to the observed $\sin^2\theta$ -values are quite similar to those given by Fruchart and Michel.¹ Only reflexions with $h+k=2n$ were observed indicating a C -centered unit cell.

In order to determine the structure of MnB_4 the intensities of the reflexions were recorded using a Philips Powder Diffractometer PW 1050 with $\text{CrK}\alpha$ radiation. The preliminary structure analysis confirmed the composition of the phase to be MnB_4 and indicated the space group $C2/m$ with two manganese atoms in position 2(a) and eight boron atoms in position 8(j) with $x=0.20$, $y=0.34$, and $z=0.20$.

This atomic arrangement is nearly identical with that in CrB_4 . The close correspondence between the structures of CrB_4

and MnB_4 is easily seen if the C -centered MnB_4 cell is transformed to an I -centered one with $a=4.6303 \text{ \AA}$, $b=5.3669 \text{ \AA}$, $c=2.9487 \text{ \AA}$, and $\beta=90.309^\circ$. The I -centered orthorhombic CrB_4 unit cell has the dimensions $a=4.744 \text{ \AA}$, $b=5.477 \text{ \AA}$, and $c=2.866 \text{ \AA}$.

It was observed that there were marked preferred orientation effects in the MnB_4 powder specimen used for recording the intensities, and accordingly the preliminary structure data quoted above are less accurate. Efforts are now being made to obtain improved diffraction data, and the results from this work together with the results from a careful phase analysis of the region MnB_2 -B will be published later.

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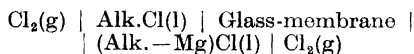
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Partial Free Energies of the Alkali Chlorides in Fused Mixtures with Magnesium Chloride

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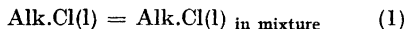
For systems of the type magnesium chloride-alkali chloride the partial molar Gibbs free energy has been measured. The data were obtained from electromotive force measurements of galvanic cells of the type:



where

Alk. = Na, K, Rb, and Cs.

The cell reaction for this galvanic cell is



In two previous papers by Førland and Østvold^{1,2} the liquid junction potential was discussed for galvanic cells of the type mentioned above. They concluded that this potential was negligible as long as $t_{\text{Alk}^+} \approx 1$. In the present investiga-

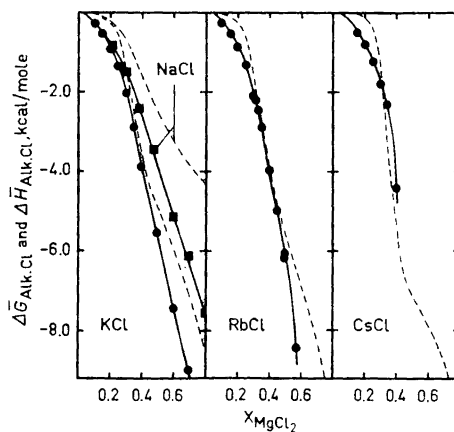


Fig. 1. Partial molar Gibbs free energies and partial molar enthalpies of mixing (dotted lines) of the alkali chlorides in mixtures with magnesium chloride. The temperatures are 1123°K, 1073°K, 998°K, and 928°K, respectively, for the sodium, potassium, rubidium, and cesium chloride systems.