INVESTIGATION OF COMPRESSION AND THERMAL EXPANSION 
OF α-MnTe USING A CUBIC-ANVIL X-RAY DIFFRACTION PRESS

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ABSTRACT
Investigation of α-MnTe was performed at high pressure-high temperature conditions at a synchrotron radiation X-ray source. The high pressures and temperatures were obtained with the help of a cubic anvil X-ray diffraction press, MAX80. Unit-cell parameters were determined at 296 °K at pressures up to 67.5 kbar and at fixed pressure of 67.5 kbar in the temperature range from 296 to 1273 °K. The obtained data allowed determination of the compressibility at 296 °K and of the thermal expansion at 67.5 kbar. The calculated value of bulk modulus agrees with earlier reported data.

INTRODUCTION
Several high-temperature and high-pressure forms of MnTe have been reported [1-4] (see Table 1): MnTe-I (or α-MnTe), stable at ambient temperature and pressure, crystallizes in NiAs-type hexagonal structure. Two high-pressure phases are known [4]: MnTe-II of a structure related to NiAs type and orthorhombic MnTe-III of MnP structure type. Table 1 is completed by data of Mn₂Te₃ and MnTe₂ compounds. Discrepancies exist between different literature sources concerning the high-pressure behaviour of α-MnTe, in particular in the most recent paper the high-pressure limit of occurrence of α-MnTe has been found to be considerably lower (73 kbar [4]) than that reported earlier (130 kbar [14]). The observed anomalies in the pressure variations of lattice-constants have been attributed to a magnetic transition [5]. There is one well known high-temperature form, β-MnTe, of NaCl structure type. The occurrence of other high-temperature forms, γ and δ of unknown structure types, reported in [2] seems to be not confirmed yet. Recently, thin MnTe films of sphalerite structure type were grown by molecular beam epitaxy (see, e.g., [9] and references therein). The films exhibit interesting physical properties because of the presence of manganese atoms exhibiting magnetic moment in a typical semiconductor structure.

EXPERIMENTAL
The investigated MnTe sample was prepared by crystallization from vapour phase. Laboratory diffractometric measurements did not show any trace of secondary phases in it. The diffraction experiments were performed using synchrotron radiation at P2.1 beamline at DESY-HASYLAB. The high pressure-high temperature conditions were obtained at a cubic anvil X-ray diffraction press, MAX80 (described, e.g., in [15]). NaCl sample located in the close vicinity of the studied sample was used as a pressure marker while a thermocouple was used to determine the temperature. The estimated uncertainty in pressure was 1 kbar. The X-ray detection system was based on a germanium solid state detector of resolution 155 eV. Peak positions were obtained by profile fitting assuming the gaussian shape. The lattice constants were calculated by least squares method from positions of nine observed peaks. The compression was studied at 296 °K in the
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pressure range up to 67.5 kbar on uploading and the thermal expansion was studied at 67.5 kbar in the temperature range from 296 to 1273 °K.

Table 1. Reported compounds in the Mn-Te system. $B_0$ and $B'$ refer to the bulk modulus and its first pressure derivative, respectively.

<table>
<thead>
<tr>
<th>compound</th>
<th>structure type</th>
<th>space group</th>
<th>lattice constants [Å]</th>
<th>$B$ [kbar]</th>
<th>$B'$ &amp; stability range</th>
</tr>
</thead>
<tbody>
<tr>
<td>(α-MnTe)</td>
<td></td>
<td></td>
<td>4.158, 6.726</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.146, 6.709</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>497</td>
<td>3.0</td>
<td>[4] $p &gt; 73$ kbar 2)</td>
</tr>
<tr>
<td>MnTe-II</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-MnTe</td>
<td>NaCl</td>
<td>Fm3m</td>
<td>6.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-MnTe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[4] $97 &lt; p &lt; 208$ kbar</td>
</tr>
<tr>
<td>MnTe</td>
<td>sphalerite</td>
<td>F-43m</td>
<td>6.343</td>
<td>151</td>
<td>[8] 7)</td>
</tr>
<tr>
<td>Mn$_2$Te$_3$</td>
<td>σ-CrFe</td>
<td>P4$_2$mmn</td>
<td>9.15, 4.80</td>
<td></td>
<td>[7]</td>
</tr>
<tr>
<td>MnTe$_2$</td>
<td>pyrite</td>
<td>Pa-3</td>
<td>6.952(1)</td>
<td>149.6</td>
<td>[10]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.795(12)</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

1) calculated from compressibility cited in [12],
2) values jointly determined for both MnTe-I and MnTe-II forms,
3) data for $T=296$ °K,
4) structure type probably related to NiAs type,
5) stable above 1312 °K or if grown from Te-rich melt,
6) structure of γ and δ phases has not been studied in [2], the authors have postulated the wurtzite and sphalerite type for them, respectively, believing that there may be an analogy with MnSe polymorphs,
7) data for thin films,
8) data derived by extrapolation from those of (Cd,Mn)Te given in [13] for thin films,
9) high pressure form being a second MnTe$_2$ form of pyrite type.
RESULTS AND DISCUSSION
In the applied conditions, i.e. at 296 °K with pressure increasing up to 67.5 kbar, and with following temperature rise from 296 to 1273 °K (at 67.5 kbar), the structure type of NiAs type is found to be conserved. Variations of the α-MnTe unit-cell constants with pressure on uploading up to 67.5 kbar are presented in Fig. 1. Compared to the previous high-pressure investigations [5,14], the experimental points obtained in this work are characterized by a much smaller scatter. This feature can be attributed to the favourable experimental conditions based on the setting of MAX80 facility at the synchrotron source (good statistics, precisely controlled temperature and pressure). With these conditions the lattice parameters could be calculated from nine peaks which gives a smaller error than if only two (as in [5]) or 4-6 (as in [14]) peaks are used, only. The results obtained do not confirm the anomalies of the lattice constant c dependence on pressure found in [5].

![Graph of lattice constants vs pressure](image1)

**Fig. 1.** Variation of lattice constants of α-MnTe as a function of pressure at 296 °K.

The compressibility dependence on pressure (Fig. 2) was used to determine the bulk modulus of the α-MnTe phase. The bulk modulus and its first pressure derivative calculated by fitting the Birch-Murnaghan equation [16] are \( B_0 = 473 \) kbar and \( dB_0/dp = 3.0 \). The \( B_0 \) value obtained in this work for α-MnTe is slightly lower than the value 497 kbar obtained jointly for this phase and MnTe-II, and it is markedly lower than that of MnTe-III (\( B_0 = 584 \) kbar), both reported in [4]. This sequence of values is in agreement with the expectation that high-pressure phases...
included in Table 1. Although the diffraction data of [4] are of a high accuracy, a full comparison with our work is not possible because the experimental points of the cited paper are located at higher pressures.

![Graph](image)

**Fig. 2.** Compressibility of $\alpha$-MnTe as a function of pressure at 296 °K. The solid line refers to the fitted Birch-Murnaghan equation.

The dependence of unit-cell constants and volume with temperature at fixed 67.5 kbar pressure is shown in Fig. 3. It completes earlier investigations performed at ambient [17] and intermediate [5] pressures. The obtained dependences may be approximated by:

\[
\begin{align*}
a &= 3.956 + 1.072 \times 10^{-4} T - 3.059 \times 10^{-8} T^2 \\
c &= 6.340 + 3.316 \times 10^{-4} T - 1.077 \times 10^{-7} T^2 \\
V &= 85.89 + 9.37 \times 10^{-3} T - 2.82 \times 10^{-6} T^2
\end{align*}
\]

with temperature expressed in °K, lattice constants in Å and the cell volume in Å³.

The magnetic transition observed in $\alpha$-MnTe occurs just above room temperature and manifests itself by a strong ($\Delta c \approx 0.01$ Å) increase of the lattice constant $c$ [17]. Electrical resistivity measurements have shown [18] that the transition temperature increases with applied pressure. More detailed investigation would be needed to reveal this transition under high temperature-high pressure conditions applied in the present work.
Fig. 3 Unit-cell constants and volume of α-MnTe at 67.5 kbar as a function of temperature. The solid lines corresponds to the approximations given by equations (1-3).
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6. ICDD© reference card No 18-814

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