Redetermined Crystal Structures of NiTe₂, PdTe₂, PtS₂, PtSe₂, and PtTe₂

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The present study was originally started with the purpose of reinvestigating the variable z parameter in the Cd(OH)₂ type crystal structure of NiTe₂ and PdTe₂. (The Cd(OH)₂ type structure is described in terms of space group P3m1 with metal atoms in 0,0,0 and metalloid atoms in ⃗r,⃗x,⃗z and ⃗r,⃗y,⃗z with z = 1/4.) The previous determination of the crystal structure of PdTe₂ by Thomassen 1 was based on the assumption of an ideal z value of 1/4, whereas Tengnér 2 used a rotation diagram to estimate z = 0.25 ± 0.01 for NiTe₂. The isostructural compounds PtS₂, PtSe₂, and PtTe₂ have been recently reinvestigated by Grenvold et al. 3 As only a qualitative criterion was used to compare observed and calculated intensities of the X-ray powder photographs, these compounds were also included in the present study.

Samples were prepared by treating the mixed powders of metal (of purity 99.9 % or better) and chalcogen (of purity 88.999+ %) in the stoichiometric ratio 1:2 in evacuated, sealed silica tubes, as previously described by Grenvold et al., 3WESTRUM et al., 4 and Grenvold and Ræst. 5

All samples were crushed and X-ray powder photographs taken with filtered CuKα radiation (λ(α₁) = 1.54050 Å) in cameras with 114.6 mm effective diameter and asymmetric film mounting. Photographs were also taken with strictly monochromatized CuKα₁ radiation in a Guinier type camera with KCl as internal standard. The relative intensities of the reflections on multiple-film Debye-Scherrer photographs were determined from photometric recordings of the films. Corrections for the resolution of Kα₂,α₁ doublets were carried out according to the method of Rae and Barker. 6 F₀,₁ values were obtained by multiplication of the corrected intensities with (Lp × ν)⁻¹. (No corrections for absorption and temperature factors were used.) In the calculation of F_c values, atomic scattering factors were taken from International Tables. 7 The reliability index

\[ R* = \frac{\sum |F_o|^2 - |F_c|^2|}{\sum F_o^2} \]

has been used in order to judge the accordance between the observed and calculated data. (F₀,₁ represents the sum of the squares of the structure factors for reflections with equal sin Θ. The observed intensities of the strong high-angle reflections (Θ > 75°) are, probably because of systematic errors, considerably lower than calculated, and these reflections are not taken into account in the calculation of R*.)

Sets of F_c values were calculated for each compound for values of z between 0.20 and 0.28. The z,R* curves are shown in Fig. 1. The minima of the curves indicate the most probable values of z. Unit cell dimensions, z parameters with correspond-

Table 1. Structural data for the MX₂ compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>NiTe₂</th>
<th>PdTe₂</th>
<th>PtS₂</th>
<th>PtSe₂</th>
<th>PtTe₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>3.854</td>
<td>4.0365</td>
<td>3.5432</td>
<td>3.7278</td>
<td>4.0259</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.2804</td>
<td>5.1262</td>
<td>5.0388</td>
<td>5.0813</td>
<td>5.2209</td>
</tr>
<tr>
<td>z</td>
<td>0.254 ± 0.004</td>
<td>0.247 ± 0.005</td>
<td>0.227 ± 0.010</td>
<td>0.255 ± 0.003</td>
<td>0.254 ± 0.005</td>
</tr>
<tr>
<td>M - 6 M (Å)</td>
<td>3.854</td>
<td>4.037</td>
<td>3.543</td>
<td>3.728</td>
<td>4.026</td>
</tr>
<tr>
<td>X - 6 X (Å)</td>
<td>2.596 ± 0.011</td>
<td>2.652 ± 0.013</td>
<td>2.34 ± 0.03</td>
<td>2.513 ± 0.009</td>
<td>2.676 ± 0.013</td>
</tr>
<tr>
<td>X - 3 X (Å)</td>
<td>3.41 ± 0.04</td>
<td>3.49 ± 0.04</td>
<td>3.43 ± 0.08</td>
<td>3.29 ± 0.02</td>
<td>3.46 ± 0.04</td>
</tr>
<tr>
<td>X - 3 X (Å)</td>
<td>3.48 ± 0.04</td>
<td>3.44 ± 0.04</td>
<td>3.07 ± 0.08</td>
<td>3.37 ± 0.02</td>
<td>3.53 ± 0.04</td>
</tr>
<tr>
<td>X - 6 X (Å)</td>
<td>3.854</td>
<td>4.037</td>
<td>3.543</td>
<td>3.728</td>
<td>4.026</td>
</tr>
</tbody>
</table>

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ing uncertainties estimated from the curvature of the $z_{R^*}$ curves, and the shortest interatomic distances are listed in Table 1.

Some comments on the results should be appropriate:

(i) All samples used for collecting the intensity data in this study, suffered from preferred orientation of the crystals in the glass capillaries. This effect was least significant for PtS$_2$ and most noteworthy for PdTe$_2$. Our first sample of PdTe$_2$, prepared at 500°C, gave $R^* = 0.52$ as the best $R^*$ value; the second sample, heated at 300°C for four days, gave the $z_{R^*}$ curve shown in Fig. 1. Within the limited accuracy the position of the minimum was the same for the two sets of intensity data. This indicates that the determinations of $z$ in Table 1 are quite reliable despite the relatively high values of $R^*$ shown in Fig. 1.

(ii) The only compound of this investigation having a $z$ parameter markedly different from the ideal value $z = \frac{1}{4}$, is PtS$_2$. The flatness of the $R^*$ versus $z$ curve for PtS$_2$ explains why this deviation has not been observed by Grenvold et al., so showing clearly that qualitative criteria may be insufficient for accurate structure determinations. (Because of the large difference in the X-ray scattering factors of Pt and S, $R^*$ for PtS$_2$ is rather insensitive to the variations in $z$).

(iii) The reliability index $R^{**} = \Sigma |\sqrt{F_o^2} - |\sqrt{F_c^2}||/\Sigma |\sqrt{F_c^2}|$ can more easily than $R^*$ be compared with the commonly used $R = \Sigma |F_o| - |F_c|/\Sigma |F_o|$. In the minima of the $z_{R^*}$ curves the corresponding values of $R^{**}$ are 0.12, 0.13, 0.083, 0.12, and 0.11 for NiTe$_2$, PdTe$_2$, PtS$_2$, PtSe$_2$, and PtTe$_2$, respectively. ($R^{**}$ is 0.095 for PtS$_2$ at $z = 0.250$).

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On the Magnetic Properties of Niobium Selenides and Tellurides

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As part of our continued studies of niobium selenides and tellurides we here report the results of magnetic susceptibility measurements carried out on the existing phases Nb$_2$Se$_4$, Nb$_2$Te$_4$, Nb$_{1+x}$Se$_2$ (0.00 $\leq x \leq 0.29$ at 25°C), “NbSe$_2$”, Nb$_2$Te$_4$, Nb$_2$Te$_6$, Nb$_2$Te$_8$, and NbTe$_6$.

Purity of the materials and preparation of the samples have previously been described. The magnetic measurements were made according to the Gouy method at temperatures between 90 and 725°C and at three different maximum field strengths ($H_{\text{max}} = 4015, 4700$, and 5110 $\Omega$, respectively). The samples were enclosed in 

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