Redetermined Crystal Structures of $NiTe_2$, $PdTe_2$, PtS_2, $PtSe_2$, and $PtTe_2$

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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 $NiTe_2$ and $PdTe_2$. (The $Cd(OH)_2$ type structure is described in terms of space group $P\bar{3}m1$ with metal atoms in 0,0,0 and metalloid atoms in $\frac{2}{3},\frac{1}{3},z$ and $\frac{1}{3},\frac{2}{3},\bar{z}$ with $z \approx \frac{1}{4}$.) The previous determination of the crystal structure of $PdTe_2$ by Thomassen [1] was based on the assumption of an ideal z value of $\frac{1}{4}$, whereas Tengnér [2] used a rotation diagram to estimate $z = 0.25 \pm 0.01$ for $NiTe_2$. The isostructural compounds PtS_2, $PtSe_2$, and $PtTe_2$ have recently been reinvestigated by Grønvold *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 99.999+ %) in the stoichiometric ratio 1:2 in evacuated, sealed silica tubes, as previously described by Grønvold *et al.*,[3] Westrum *et al.*,[4] and Grønvold and Røst.[5]

All samples were crushed and X-ray powder photographs taken with filtered CuK radiation ($\lambda(\alpha_1) = 1.54050$ Å) in cameras with 114.6 mm effective diameter and asymmetric film mounting. Photographs were also taken with strictly monochromatized Cu$K\alpha_1$ 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 $K\alpha_1\alpha_2$ doublets were carried out according to the method of Rae and Barker.[6] F_o^2 values were obtained by multiplication of the corrected intensities with $(Lp \times \nu)^{-1}$. (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

$$R^* = \Sigma|F_o^2 - F_c^2| / \Sigma F_o^2$$

has been used in order to judge the accordance between the observed and calculated data. (F_c^2 represents the sum of the squares of the structure factors for reflections with equal $\sin^2\Theta$. The observed intensities of the strong, high-angle reflections ($\Theta > 75°$) 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 MX_2 compounds $NiTe_2$, $PdTe_2$, PtS_2, $PtSe_2$, and $PtTe_2$.

Compound	$NiTe_2$	$PdTe_2$	PtS_2	$PtSe_2$	$PtTe_2$
a (Å)	3.8542	4.0365	3.5432	3.7278	4.0259
c (Å)	5.2604	5.1262	5.0388	5.0813	5.2209
z	0.254 ± 0.004	0.247 ± 0.005	0.227 ± 0.010	0.255 ± 0.003	0.254 ± 0.005
$M - 6M$ (Å)	3.854	4.037	3.543	3.728	4.026
$M - 6X$ (Å), $X - 3M$ (Å)	2.596 ± 0.011	2.652 ± 0.013	2.34 ± 0.03	2.513 ± 0.009	2.676 ± 0.013
$X - 3X$ (Å)	3.41 ± 0.04	3.49 ± 0.04	3.43 ± 0.08	3.29 ± 0.02	3.46 ± 0.04
$X - 3X$ (Å)	3.48 ± 0.04	3.44 ± 0.04	3.07 ± 0.08	3.37 ± 0.02	3.53 ± 0.04
$X - 6X$ (Å)	3.854	4.037	3.543	3.728	4.026

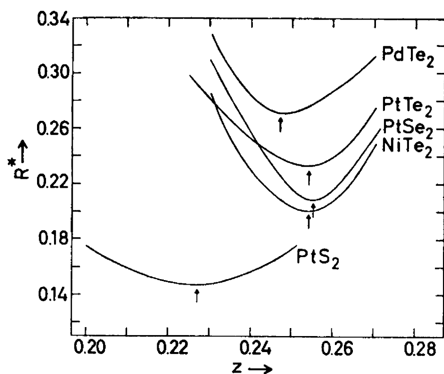

Fig. 1. The R^* *versus* z curves for $NiTe_2$, $PdTe_2$, PtS_2, $PtSe_2$, and $PtTe_2$.

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 Grønvold *et al.*,[3] 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 $R^{**} = \Sigma||\sqrt{F_o^2}|-|\sqrt{F_c^2}||/\Sigma|\sqrt{F_o^2}|$ 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 [1-4] we here report the results of magnetic susceptibility measurements carried out on the existing phases Nb_5Se_4, Nb_3Se_4, $Nb_{1+x}Se_2$ ($0.00 \leq x \leq 0.29$ at 25°C), "$NbSe_4$", Nb_5Te_4, Nb_3Te_4, $NbTe_2$, and $NbTe_4$.

Purity of the materials and preparation of the samples have previously been described.[1-4] The magnetic measurements were made according to the Gouy method at temperatures between 90 and 725°K and at three different maximum field strengths (H_{max} = 4015, 4700, and 5110 Ø, respectively). The samples were enclosed