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Far-Infrared and X-Ray Investigations of the Mixed Platinum Dichalcogenides $PtS_{2-x}Se_x$, $PtSe_{2-x}Te_x$, and $PtS_{2-x}Te_x$

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Polycrystalline samples of the CdI_2-type mixed crystals $PtS_{2-x}Se_x$, $PtSe_{2-x}Te_x$, and $PtS_{2-x}Te_x$ were prepared and characterized by far-infrared (4000–40 cm^{-1}) and X-ray techniques. A change in the behavior of the *c*/*a*-ratio and in the *x* dependence of the plasma resonance frequency of the free carriers present is observed in the system $PtS_{2-x}Se_x$ near $PtS_{0.6}Se_{1.4}$, which is interpreted as a critical composition for (*p*,*d*)-band overlap in the platinum dichalcogenides. Optical phonon frequencies are given for the two-mode system $PtS_{2-x}Se_x$.

1. Introduction

The platinum dichalcogenides PtS_2, $PtSe_2$, and $PtTe_2$ are CdI_2-type layer compounds (*1*). The electrical properties range from semiconducting PtS_2 (*2, 3*) to metallic $PtTe_2$ (*4, 5*) and it is expected that the conductivity can be slowly modified by anionic substitution within the alloys $PtS_{2-x}Se_x$ and $PtSe_{2-x}Te_x$. From the literature only few electrical and optical data are available for such mixed crystals. Soled *et al.* (*2*) investigated some selenium-rich alloys $PtS_{2-x}Se_x$ ($1.1 \leq x \leq 1.8$), Hulliger (*6, 7*) and Ruchkin *et al.* (*8*) prepared PtSSe and PtSeTe ($x = 1$). But the position of the metal–semiconductor transition point in these compounds is still an open question: Hulliger (*7*) set this point near the composition PtSeTe, whereas Soled *et al.* (*2*) found a nearly zero band gap already for $PtS_{0.3}Se_{1.7}$, i.e., the metal–semiconductor transition may occur in the $PtS_{2-x}Se_x$ alloys.

In this work we studied the X-ray and far-infrared properties of the alloys $PtS_{2-x}Se_x$, $PtSe_{2-x}Te_x$, and $PtS_{2-x}Te_x$ and found a discontinuous behavior of the *c*/*a* ratio and in the *x*-dependence of the plasma resonance frequency of the free carriers near the composition $PtS_{0.6}Se_{1.4}$, which we assume to be critical for (*p*,*d*)-band overlap.

2. Experimental

The mixed platinum dichalcogenides $PtS_{2-x}Se_x$ and $PtSe_{2-x}Te_x$ were obtained in form of flowing polycrystalline, metallic grey powders by annealing stoichiometric mixtures of the elements in evacuated quartz tubes at 600–700°C, the annealing times varied from 14 days for the tellurium-rich compounds to 120 days for the sulfur-rich compounds.

Lattice constants were determined from X-ray powder photographs using $CrK\alpha_1$-radiation and SiO_2 as internal standard.

The infrared spectra were recorded in the

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range from 4000–180 cm^{-1} on a Perkin–Elmer Model 580 grating spectrophotometer (CsI-technique in the case of absorption spectra) and in the range from 700 to 30 cm^{-1} on a Bruker Model IFS 114 Fourier-transform interferometer. Reflection spectra were measured at near-normal incidence from pellets pressed at ambient temperature, an aluminum mirror was used as reference.

3. Experimental Results and Discussion

All alloys of the two systems $PtS_{2-x}Se_x$ and $PtSe_{2-x}Te_x$ can be obtained in the CdI_2-structure. The X-ray pattern of the sulfur-rich compounds $PtS_{2-x}Se_x$ ($0.1 \leq x \leq 0.8$) showed very broad reflexes even after a long-time annealing (120 days) at 600°C. Higher preparation temperatures must be avoided because of a decomposition of these alloys into PtS + S + $PtS_{2-x}Se_x$ with higher selenium content. (From high-temperature X-ray photographs it was seen that in an evacuated quartz tube PtS_2 decomposes into PtS + S above 850°C.) In some cases a splitting of some broad reflexes into two sharper ones (i.e., a structural distortion) may occur, but this effect was small and difficult to reproduce. Attempts to prepare the mixed crystals $PtS_{2-x}Te_x$ failed, only small amounts of sulfur and tellurium can be solved in $PtTe_2$ and PtS_2, respectively, as seen from the obtained lattice constants (see Table I). A compound PtSTe, as claimed by Ruchkin *et al.* (*8*), was not observed in our experiments. But from the *d*-values given for "PtSTe" by Ruchkin *et al.* it can be seen that these authors had obtained also only a mixture of $PtS_{2-\delta}Te_\delta$ and $PtTe_{2-\delta}S_\delta$, as found in this work. It is unintelligible that the strong (100) reflexes are omitted in the table of Ruchkin *et al.*

TABLE I

LATTICE CONSTANTS [Å] AND *c/a* RATIOS OF MIXED PLATINUM DICHALCOGENIDES

	a	*c*	*c/a*	Ref.
PtS_2	3.5432	5.0388	1.442	*1*
	3.542	5.043	1.424	*2*
	3.51	5.03	1.433	*3*
	3.542	5.040	1.423	
$PtS_{1.9}Se_{0.1}$	3.551	5.062	1.426	
$PtS_{1.6}Se_{0.4}$	3.577	5.102	1.426	
$PtS_{1.5}Se_{0.5}$	3.587	5.114	1.426	
$PtS_{1.2}Se_{0.8}$	3.619	5.144	1.421	
$PtS_{1.0}Se_{1.0}$	3.59	5.06	1.401	*8*
$PtS_{0.9}Se_{1.1}$	3.638	5.148	1.415	*2*
$PtS_{0.8}Se_{1.2}$	3.647	5.154	1.413	*2*
	3.652	5.148	1.410	
$PtS_{0.7}Se_{1.3}$	3.657	5.153	1.409	*2*
$PtS_{0.6}Se_{1.4}$	3.665	5.153	1.406	*2*
	3.664	5.153	1.406	
$PtS_{0.5}Se_{1.5}$	3.673	5.156	1.404	
$PtS_{0.4}Se_{1.6}$	3.684	5.152	1.398	
$PtS_{0.3}Se_{1.7}$	3.692	5.141	1.392	
$PtS_{0.2}Se_{1.8}$	3.707	5.114	1.380	*2*
	3.706	5.122	1.382	
$PtS_{0.1}Se_{1.9}$	3.717	5.110	1.375	
$PtSe_2$	3.728	5.081	1.363	*1*
	3.727	5.083	1.364	*2*
	3.727	5.082	1.364	
$PtSe_{1.75}Te_{0.25}$	3.766	5.101	1.354	
$PtSe_{1.5}Te_{0.5}$	3.793	5.123	1.351	
$PtSe_{1.25}Te_{0.75}$	3.836	5.138	1.339	
$PtSe_{1.0}Te_{1.0}$	3.89	5.11	1.314	*7, 8*
	3.884	5.154	1.327	
$PtSe_{0.75}Te_{1.25}$	3.925	5.171	1.317	
$PtSe_{0.5}Te_{1.5}$	3.964	5.193	1.310	
$PtSe_{0.25}Te_{1.75}$	3.993	5.207	1.304	
$PtTe_2$	4.0259	5.2209	1.297	*1*
	4.025	5.224	1.297	
"PtSTe"				
Sulfur-rich	3.560	5.113	1.436	
Tellurium-rich	4.017	5.218	1.299	

Table I gives the obtained lattice constants of the mixed platinum dichalcogenides, literature data are included. In Fig. 1 the *a* and *c* lattice constants and the *c/a*-ratios are plotted vs *x*.

The *a* lattice constants show a linear dependence on *x* in both $PtS_{2-x}Se_x$ and $PtSe_{2-x}Te_x$ with a slightly changed slope due to the different radii of the chalcogens substituted. The behavior of the *c* lattice constant is nearly linear only in $PtSe_{2-x}Te_x$ (an

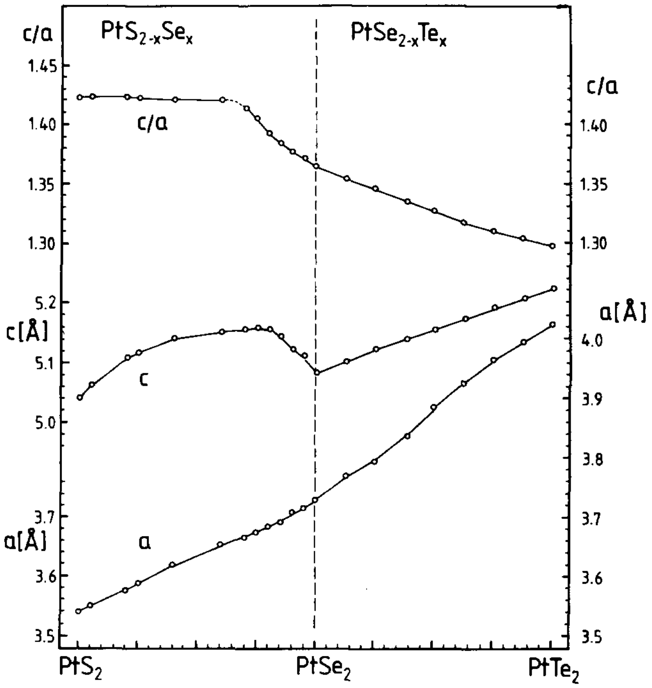

FIG. 1 Lattice constants [Å] and *c*/*a*-ratios of mixed platinum dichalcogenides $PtS_{2-x}Se_x$ and $PtSe_{2-x}Te_x$.

"unusual" (*9*) negative deviation from Vegard's rule in $PtSe_{2-x}Te_x$, derived from the lattice constants of PtSeTe given by Hulliger (*7*) or Ruchkin *et al.* (*8*), cannot be confirmed), but is more complicate in $PtS_{2-x}Se_x$, where a positive deviation from Vegard's rule occurs. Considering the *c*/*a*-ratios is more instructive in this case.

The *c*/*a*-ratios remain nearly constant from PtS_2 to $PtS_{0.8}Se_{1.2}$ but fall in a parabolic curve from $PtS_{0.6}Se_{1.4}$ to $PtSe_2$ and fall further from $PtSe_2$ to $PtTe_2$. A constant *c*/*a*-ratio is typical for solid solutions of two ionic compounds (compare, e.g., $SnS_{2-x}Se_x$, (*10*)), whereas the decrease of the *c*/*a*-ratio found here is assumed to be due to an increase on metallic bonding contributions caused by (*p*,*d*)-band overlap in the selenium richer alloys.

The behavior of the far-infrared spectra gives evidence for an increased metallicity of the selenium- (and tellurium) rich alloys. Group theory predicts two ir-active lattice vibrations of species A_{2u} and E_u for the CdI_2-type platinum dichalcogenides (*11*), but in the absorption spectrum of PtS_2 only the E_u mode is observed at 326 cm^{-1} ($PtS_2 : E_u$) (see Fig. 2). Substitution of sulfur by selenium results in a second mode near 230 cm^{-1} due to the E_u-mode of $PtSe_2$, i.e., the infrared spectra of the $PtS_{2-x}Se_x$ alloys show a two-mode (*12*) behavior. The weak mode near 350 cm^{-1} observed at the high-wavenumber side of the $PtS_2 : E_u$ mode in the sulfur-rich alloys is assigned to the $PtS_2 : A_{2u}$ mode, its intensity may be defect enhanced. (Because of the anisotropy of CdI_2-type layered compounds the A_{2u} modes are expected to be at higher energies than the E_u modes (*13*).)

An increase of the selenium content leads to a small low-wavenumber shift of the PtS_2 absorption bands caused by a softening of the lattice (*14*) and to a variation of the relative intensities. Some mode splittings are observed indicating a clustering effect (*15*)

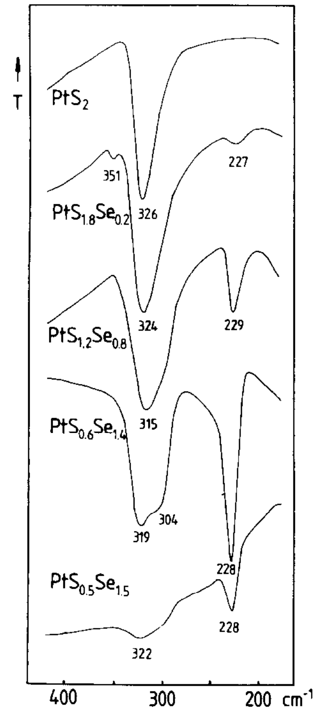

FIG. 2. Infrared absorption spectra (PE 580, CsI-disks) of sulfur-rich alloys $PtS_{2-x}Se_x$.

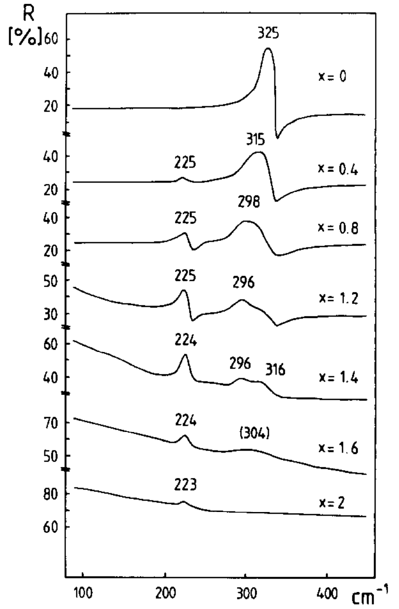

FIG. 3. Far infrared reflection spectra (Bruker IFS 114) of sulfur-rich alloys $PtS_{2-x}Se_x$.

in accordance with reflex splittings in some X-ray pattern (see above).

At $x \approx 1.4$ the $PtS_2:E_u$ band broadens and the $PtS_2:A_{2u}$ mode is no longer observable. Further substitution of sulfur leads to a development of a broad plasma mode of free carriers, free carrier absorption dominates in the spectra with $x > 1.5$ and in those of $PtSe_{2-x}Te_x$. From the far-infrared reflection spectra more detailed informations are available in this case.

Figures 3 and 4 show the reflection spectra of some $PtS_{2-x}Se_x$ and $PtSe_{2-x}Te_x$ mixed crystals. The sulfur-rich alloys show no free carrier contributions to the fir reflec-

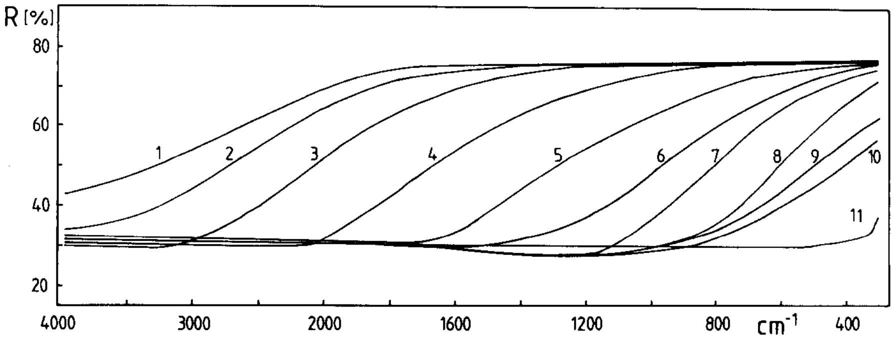

FIG. 4. Infrared reflection spectra (PE 580) of selenium-rich alloys $PtSe_{2-x}Te_x$ (1–4: $x = 1.0$, 0.75, 0.5, 0.25) and $PtS_{2-x}Se_x$ (5–11: $x = 2$, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4). The spectra are normalized to reach 80% reflectivity in the far-infrared region.

tivity, but with increasing selenium content plasma contributions become more and more important and broad plasma modes are observed. In order to compare the spectra of the different samples studied the reflectivities were normalized to reach 80% in the far-infrared region, the value observed for the most metallic compounds. This normalizing influences the position of the plasma frequencies only little (contrary to the plasma-damping constant of the classical Drude theory). Measurements on different samples show that the obtained values are reproducible within an error of ≈5%, i.e., the observed free carriers are intrinsic and not caused by deviations from the stoichiometry of the samples. The plasma resonance frequencies ω_P', defined as

$$\omega_P'^2 = \frac{4\pi e^2 n_0}{\varepsilon_\infty m^*} \qquad (1)$$

(*16*) were obtained from the maxima of the dielectric-loss functions $Im(-1/\hat{\varepsilon})$ calculated from the observed reflectivities by means of Kramers-Kronig analyses (*17*).

TABLE II

PLASMA RESONANCE FREQUENCIES, ω_P'[cm^{-1}], AND FREE CARRIER CONCENTRATION OVER EFFECTIVE MASS RATIOS, n_0/m^*, [10^{20} cm^{-3}], OF SELENIUM-RICH PLATINUM DICHALCOGENIDES

	ω_P'	n_0/m^*
$PtS_{0.8}Se_{1.2}$	120[a]	0.02
$PtS_{0.6}Se_{1.4}$	177[a]	0.05
$PtS_{0.5}Se_{1.5}$	420	0.3
$PtS_{0.4}Se_{1.6}$	670	0.7
$PtS_{0.3}Se_{1.7}$	780	1.0
$PtS_{0.2}Se_{1.8}$	940	1.4
$PtS_{0.1}Se_{1.9}$	1150	2.2
$PtSe_2$	1400	3.3
$PtSe_{1.75}Te_{0.25}$	1900	6.3
$PtSe_{1.5}Te_{0.5}$	2650	12.7
$PtSe_{1.25}Te_{0.75}$	3200	19.2
$PtSe_{1.0}Te_{1.0}$	≳4000	≳31.2

[a] Plasmon like Ω_- frequencies (*16*).

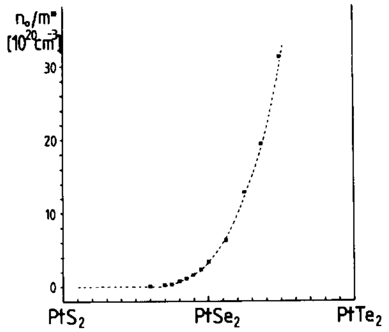

FIG. 5. Free carrier concentrations over effective mass ratios, n_0/m^*, of mixed platinum dichalcogenides.

From Eq. (1) it is seen that from the plasma resonance frequency (ω_P') a determination of the free carrier concentration over the effective mass ratio, n_0/m^*, is possible, if the high-frequency dielectric constant ε_∞ is known. Approximate values (which are certainly too low) of ε_∞ were calculated from R_∞: PtS_2 : $\varepsilon_\infty \gtrsim 10$, $PtSe_2$: $\varepsilon_\infty \gtrsim 15$, for $PtTe_2$ we arbitrary set $\varepsilon_\infty = 20$. In the mixed crystals we assumed a linear x dependence of ε_∞.

Using these values we calculated the n_0/m^* ratios given in Table II and Fig. 5. The plasma resonance frequencies ω_P' and the n_0/m^* ratios increase sharply from $PtS_{0.6}Se_{1.4}$ to higher selenium and tellurium contents indicating that this composition is indeed critical for the free carrier concentration and, therefore, for (p,d)-band overlap. (The plasma resonance frequencies of the tellurium richest alloys are >4000 cm^{-1} and could not determined from our experiments.)

Kramers-Kronig analyses of infrared reflection spectra further allows the determination of the transverse optical (TO) and longitudinal optical (LO) phonon frequencies from the maxima of the $Im(\hat{\varepsilon})$ and $Im(-1/\hat{\varepsilon})$ curves, respectively (*18*). This approach was directly used for PtS_2. The values given for $PtSe_2$ were extrapolated from the corresponding ω_{TO} and ω_{LO} fre-

TABLE III

OPTICAL PHONON FREQUENCIES [cm^{-1}] OF MIXED PLATINUM DICHALCOGENIDES $PtS_{2-x}Se_x$ (KRAMERS-KRONIG ANALYSES)

	Ω_-	ω_{TO}	ω_{LO}	ω_{TO}	ω_{LO}	Ω_+
PtS_2				320[a]	336[a]	
				325	336	
$PtS_{1.6}Se_{0.4}$		227	229	323	331	
$PtS_{1.2}Se_{0.8}$		228	231	318	326	
$PtS_{1.0}Se_{1.0}$		228	231	310	326	
$PtS_{0.8}Se_{1.2}$	120	226	232	300[b]	330	
$PtS_{0.6}Se_{1.4}$	177	226	233	297,317[c]	331	
$PtS_{0.5}Se_{1.5}$	193	227	233	317	335	420
$PtS_{0.4}Se_{1.6}$	198	226		Not resolved		670
$PtSe_2$		226[d]	233[d]			1400

[a] Reference (*3*).

[b] Very flat maximum of $Im(\hat{\varepsilon})$.

[c] Splitted modes.

[d] Extrapolated values.

quencies of the sulfur-rich alloys $PtS_{2-x}Se_x$, because the strong plasmon–LO–phonon coupling in the more-metallic compounds allows only the determination of the coupled $\Omega_\pm$ modes (*16*). The obtained optical phonon frequencies are given in Table III.

Uchida and Tanaka compared the optical phonon frequencies of a number of layered transition metal dichalcogenides (*19*). From a plot of ω_{TO} vs the characteristic frequency $\Omega_0 = (e^2/\mu r_0^3)^{1/2}$ a separation of MoS_2- and CdI_2-type dichalcogenides was extracted. But the corresponding data for PtS_2 and $PtSe_2$ found here are close to the line connecting MoS_2-type compounds, i.e., it seems that primarily the ionicities and the high-frequency dielectric constants (the polarizabilities), and not the specific crystal structures, determine the optical phonon frequencies of the layered transition metal dichalcogenides.

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