

High-pressure x-ray diffraction studies on HgTe and HgS to 20 GPa

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HgTe and HgS have been investigated with the use of the high-pressure x-ray diffraction technique to 20 GPa. HgTe undergoes three pressure-induced phase transitions in the (0–20)-GPa range, from zinc blende to cinnabar to rocksalt to β -Sn, at 1.4, 8, and 12 GPa, respectively. HgS does not show any evidence for a transition from the cinnabar structure up to 20 GPa, either in high-pressure x-ray diffraction or in high-pressure Raman studies. The above transition sequence agrees with the pressure-induced sequence for CdTe except for the intrusion of the cinnabar structure. Evaluation of the bulk modulus B_0 and B'_0 from high-pressure x-ray data reveals that the cinnabar phases of HgTe and HgS are very compressible; B_0 and B'_0 are 19.4 ± 0.5 GPa and 11.1 for HgS, and 16.0 ± 0.5 GPa and 7.3 for HgTe. Bulk moduli, volume changes for transitions, and lattice parameters of the high-pressure phases have all been determined from the x-ray data. The observed transition sequence for HgTe appears to be in agreement with the predictions of recent pseudopotential total-energy calculations for phase stability in III-V and II-VI compounds under pressure.

I. INTRODUCTION

The mercury chalcogenides which belong to the group of II-VI compounds exhibit structural and electronic properties somewhat different from the other members of the group. Thus HgS (known as cinnabar) crystallizes in the so-called cinnabar structure, a dihedrally coordinated structure with hexagonal symmetry. HgSe and HgTe crystallize in the zinc-blende structure, but are semimetallic, a deviation from the expected semiconducting behavior. Both HgSe and HgTe are known to undergo a pressure-induced phase transition to the cinnabar structure at modest pressures,^{1–3} accompanied by several orders of magnitude increase in resistivity.^{1–3}

Recently Onodera *et al.*⁴ have investigated HgSe and HgTe by resistance and *in situ* high-pressure x-ray diffraction to 20 GPa and have reported transformation to the rocksalt structure near 16 and 8 GPa, respectively. They have noted another phase transition near 12 GPa in HgTe, but the high-pressure phase was not identified. Resistance measurements show that HgSe and HgTe become metallic after the above transitions. We have investigated HgTe and HgS to 20 GPa by *in situ* high-pressure x-ray diffraction, to bring out the systematics of pressure-induced phase transitions in mercury chalcogenides and their relationship to the other II-VI compounds. We find that the high-pressure phase of HgTe above 12 GPa has the β -Sn structure, and HgTe behaves analogously to CdTe at high pressure. The high-pressure x-ray and high-pressure Raman studies on HgS show no evidence for any phase transitions up to 22 GPa. These results will be presented and discussed in this paper.

II. EXPERIMENTAL

High pressure was generated in a gasketed diamond anvil cell⁵ using a 4:1 methanol-ethanol mixture as a pres-

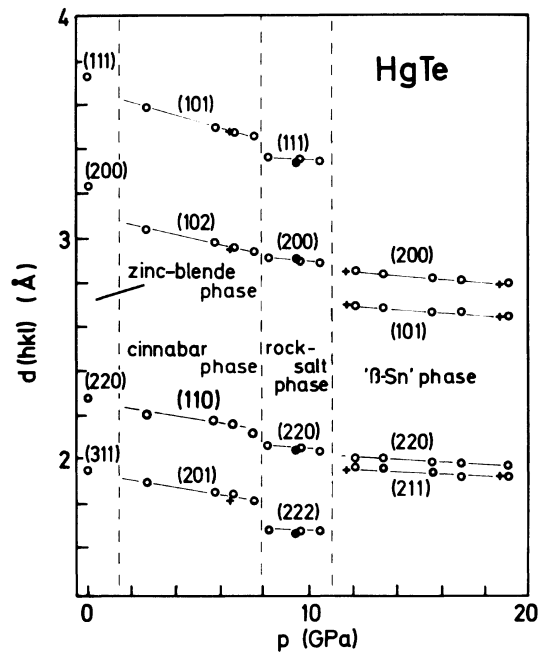


FIG. 1. Pressure dependence of the $d(hkl)$ values of HgTe. The dashed lines indicate the phase transformations. Different symbols are for different runs. The filled circles represent the data from Ref. 4.

sure medium. The pressure generated was determined by the well-known ruby-fluorescence technique.⁶ X-ray diffraction patterns were taken at room temperature in the energy-dispersive mode. Raman spectra of HgS were recorded with a conventional double monochromator, employing backscattering geometry. For excitation the 647.1-nm line of a krypton laser was used.

Red transparent cinnabar HgS crystals were obtained from Professor A. K. Ramdas. These crystals were grown by the chemical-vapor-transport (CVT) technique.⁷ HgTe crystals were made in Bell Laboratories by reacting the elements in sealed thick-walled quartz tubing capable of withstanding the Hg vapor pressure under the conditions of preparation.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the pressure dependence of the $d(hkl)$ values of the observed reflections in HgTe and HgS, respectively. Different symbols signify different runs. The lines connecting the data points represent the $d(hkl)$ calculated by fitting the lattice parameters (a or a and c) from individual measurements at various pressures to a polynomial equation of second degree in P .

In the (0–20)-GPa range HgTe exists in four modifications. The energy-dispersive x-ray patterns obtained in the range 0–0.7 GPa show reflections from the (311), (220), (200), and (111) planes of the zinc-blende structure. At higher pressure the (201), (110), (102), and (101) reflections of the cinnabar structure appear and these can be followed up to 8 GPa. Above 8 GPa, a new x-ray pattern appears and this can be indexed as the (222), (220), (200), and (111) reflections of the rocksalt structure.

At pressures above 11 GPa, the pattern changes again, in agreement with the results obtained by Onodera *et al.*⁴ We have indexed this new pattern on the basis of β -Sn structure with $a = 5.68$ Å and $c = 3.04$ Å at 11.7 GPa and the observed reflections as the (211), (220), (101), and (200) of the β -Sn (white tin) lattice. But for the intrusion of the

cinnabar phase between the zinc blende and rocksalt, HgTe shows the same pressure-induced transition sequence as CdTe,⁸ namely zinc blende to rocksalt to β -Sn, with increasing pressure. This close analogy between CdTe and HgTe suggests similarities, also for the pairs CdSe-HgSe and CdS-HgS, although their zero-pressure structures are different: wurtzite for CdSe and CdS, zinc blende for HgSe, and cinnabar for HgS. It is well known⁹ that CdS and CdSe transform to the rocksalt structure at ~ 2.0 and ~ 2.2 GPa,¹⁰ respectively. Also, a transition from the cinnabar structure to the rocksalt-type structure has been observed in HgSe (Ref. 4) at pressures above 16 GPa. This prompted us to study HgS.

A. HgS

In the cinnabar phase of HgS, the (104), (111), (110), (103), (102), (003), and (101) reflections may be expected in the energy-dispersive x-ray pattern. However, the (104), (111), and (110) reflections cannot be resolved with our technique even at zero pressure, as their d values differ only by 0.04 Å. In addition, a reflection from the Inconel gasket overlaps them and makes the problem even more difficult. On the other hand the (103), (102), (003), and (101) reflections are well separated at zero pressure, but they converge with increasing pressure (see Fig. 2). The cinnabar structure can be viewed as a distorted rocksalt structure and hence there is a correspondence between the reflections from the two structures as shown below.

Cinnabar	→	Rocksalt
(101)	→	(111)
(003)	→	
(102)	→	(200)
(103)	→	(forbidden)
(110)	→	(220)
(111)	→	
(104)	→	

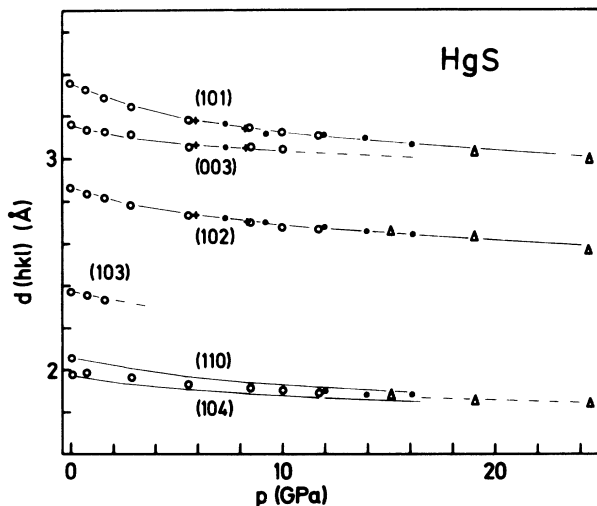


FIG. 2. Pressure dependence of the $d(hkl)$ values of the observed reflections in HgS. Different symbols indicate different runs. The indexing is based on the cinnabar structure.

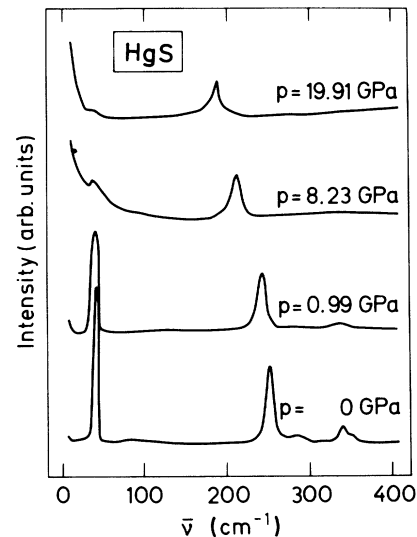


FIG. 3. Raman spectra of HgS at several different pressures.

The (101) and (003) reflections of cinnabar merge with pressure and cannot be separated above 10 GPa. Also the (103) reflection is weak at zero pressure and disappears above 2 GPa. These circumstances make it difficult to conclude whether a cinnabar-to-rocksalt transition occurs in HgS up to 24 GPa, the highest pressure reached in the present study. The fact that the (103) reflection reappears when pressure is released below 2 GPa suggests that its disappearance mentioned above is not due to any preferred orientation. We therefore needed a very sensitive probe to verify the occurrence of a cinnabar-to-rocksalt transition. Hence we resorted to Raman spectroscopy of HgS as a function of pressure. In the event of a cinnabar-to-rocksalt transition, there will be no first-order Raman scattering from the rocksalt phase, for it is symmetry forbidden, and the Raman peaks of the cinnabar phase should disappear.

B. Raman data on HgS

The spectra are shown in Fig. 3. At ambient pressure, peaks at 43, 86, 105, 256, 288, and 345 cm^{-1} are observed. All the Raman-active modes are not seen when the sample is placed within the diamond cell, which is not unusual. The agreement between the observed frequencies and the published data¹¹ is good. With increasing pressure some of the peaks disappear due to increasing absorption of the sample at the laser frequency. In fact, the sample visibly changes color from red to black and becomes opaque above 1.5 GPa. However, the continuity to 20 GPa of the observable Raman peaks clearly indicates that the cinnabar phase still exists up to this pressure. We show in Fig. 4 the pressure dependence of the observed frequencies in HgS to support the above statement. From this we conclude that there is no transition to the rocksalt structure up to 20 GPa.

C. c/a ratio

In Fig. 5, the c/a ratio for HgS and HgTe is plotted against pressure. In determining c/a , all reflections plot-

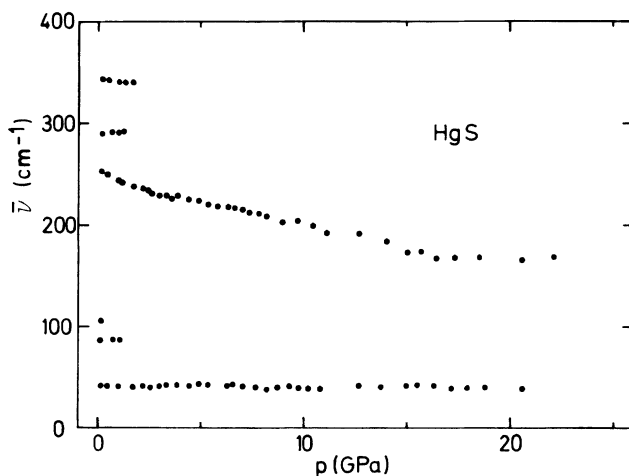


FIG. 4. Pressure dependence of the observed Raman peaks.

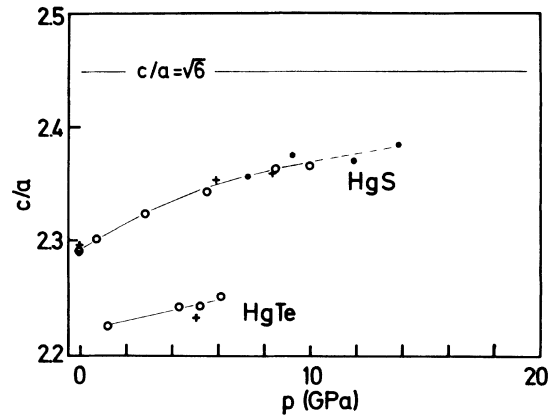


FIG. 5. Pressure dependence of the c/a ratio for HgS and the cinnabar phase of HgTe (note: HgTe exists in the cinnabar structure above 1.4 GPa).

ted in Fig. 1 were used in the case of HgTe, whereas for HgS only the well-separated (101), (003), and (102) reflections were used. The rocksalt structure in the hexagonal representation would have $c/a = \sqrt{6}$. It can be seen from Fig. 5 that c/a for HgS in the cinnabar phase increases first rapidly and then slowly with pressure. Also, at ambient pressure, the ratio for HgS is closer to $\sqrt{6}$ compared to the value for mercury telluride, even near its transition pressure (cinnabar-to-rocksalt phase). We believe that the stability of the cinnabar structure in the case of HgS is connected with its electronic structure.

D. Compressibility

In Figs. 6 and 7, the relative volume V/V_0 is plotted against pressure for HgTe and HgS, respectively. The

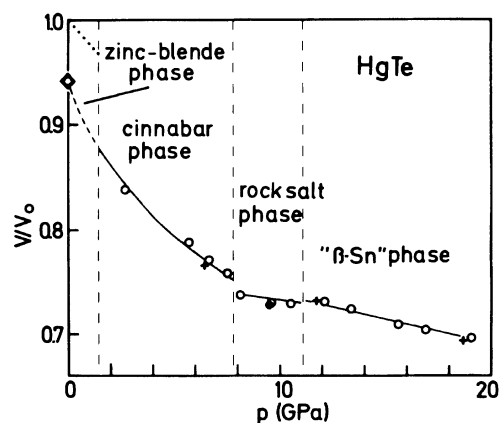


FIG. 6. Pressure-volume data for HgTe. The dashed lines indicate phase transformations. The solid line connecting the data points of the cinnabar phase was obtained from a fit of the data including a volume data point (square at zero pressure) of a hypothetical cinnabar structure of HgTe at zero pressure (for details see text) to the Birch equation of state, with the parameters listed in Table I. The dashed line represents an extrapolation of the pressure-volume behavior of a hypothetical cinnabar structure of HgTe in the pressure range up to 1.4 GPa. The dotted curve represents the data of Ref. 14.

TABLE I. Structural transition pressure, lattice parameter, volume change, bulk modulus B_0 , and $dB_0/dp = B'_0$ data for HgS and HgTe.

Substance	Structure	Pressure range (GPa)	Transition pressure (GPa)	Lattice parameter (Å)	Volume change (%)	Bulk modulus B_0 at $p=0$ GPa (GPa)
HgS	Cinnabar phase	0 to at least 24.0		$a=4.149, c=9.495$ (at zero pressure)		$19.4 \pm 0.5 (B'_0 = 11.1)$
	Zinc-blende phase	0-1.4	1.4 (Ref. 14)	$a=6.453$ (at zero pressure)		
HgTe	Cinnabar phase	1.4-8.0	8.0 \pm 0.3	$a=4.45; c=9.89$ (at $p=2.6$ GPa) $a=4.28; c=9.63$ (at $p=7.6$ GPa)	8.5, ^a 6.0 (Ref. 15) 8.1 (Ref. 18)	42.3 (Ref. 14) ($B'_0 = 2.1$) 16.0 \pm 0.5 ($B'_0 = 7.3$)
	Rocksalt phase	8.0-11.5	11.0 \pm 0.6	$a=5.83$ (at $p=8.2$ GPa) $a=5.80$ (at $p=10.5$ GPa)	2.5	
	β -Sn phase	≥ 11.0		$a=5.68; c=3.04$ (at 11.7 GPa)	No change of volume	

^aThis value is obtained by using the volume data of Ref. 12 of the zinc-blende phase at 1.5 GPa and using the extrapolated volume of the cinnabar phase of 1.5 GPa.

values of $V(P)$ were determined using the data shown in Figs. 1 and 2. For calculating the bulk modulus B_0 and its pressure derivative B'_0 for the cinnabar phase of HgTe, we needed to know the volume of a hypothetical cinnabar phase of HgTe at ambient pressure. We have estimated this using HgS which is known to exist also in the zinc-blende structure (known as cubic metacinnabar^{12,13}). From the lattice parameter of the latter and the parameters for the cinnabar phase we obtain $V_{\text{cin}}/V_{\text{zb}}=0.9419$ for HgS. Using this value the volume change for a hypothetical transition from the zinc-blende to the cinnabar structure in HgTe at zero pressure was evaluated. The B_0 and B'_0 were then obtained by fitting the Birch equation of state to the experimentally determined P - V data of HgTe in the (2-8)-GPa range and the point at zero pressure determined from the above-mentioned procedure (see Fig. 6). We have listed in Table I, B_0 and B'_0 for the cinnabar as well as for the zinc-blende phase of HgTe. For the latter, the values were obtained again from a fit of the Birch equation of state to the P - V data of Fond *et al.*¹⁴ The bulk modulus $B_0=16.0$ GPa and 19.4 GPa, respectively for HgTe and HgS are anomalously low; for instance compared with the B_0 (Ref. 9) of zinc-blende CdTe ($B_0=25.3$ GPa) and wurtzite CdS ($B_0=38.2$ GPa), both of which are low coordination structures. Thus the cinnabar phase appears to be quite compressible and further, the large value for B'_0 indicates that the cinnabar lattice stiffens rapidly with pressure. This high compressibility of the cinnabar phase causes the volume change at the cinnabar-to-rocksalt transition in HgTe to be rather small (2.5%). From the high compressibility one is tempted to draw the conclusion that the cinnabar phase behaves somewhat like a molecular crystal which characteristically exhibits a high initial compression and rapid flattening. Relevant data for the phase transitions are collected in Table I.

IV. FURTHER COMMENTS

Recent pseudopotential total-energy calculations^{17,18} for group-IV (Ref. 17) semiconductors and for III-V (Ref. 18) compounds accurately predict not only their ambient pres-

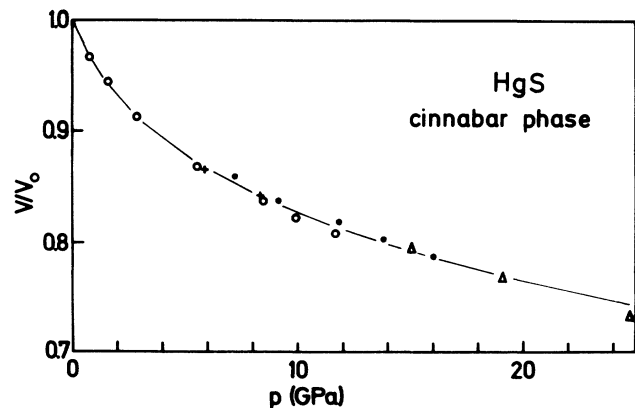


FIG. 7. Pressure-volume data for HgS. The solid line connecting the data points is the calculated V/V_0 using the Birch equation of state, with the parameters listed in Table I.

sure properties but also the relative stability of the possible phases as a function of volume. For the III-V compounds the calculations emphasize that the rocksalt phase consistently has the lower energy relative to the β -Sn phase, and hence the rocksalt transition should precede the β -Sn transition. This means that the pressure-induced transition sequence should be zinc blende to rocksalt to β -Sn for the III-V compounds. We find that this is certainly true also for CdTe, CdSe, HgTe, and possibly also for HgSe, which suggests that the above theoretical prediction holds good for the II-VI compounds.

The band calculations¹⁷ also predict that the rocksalt phases of the III-V compounds should be metallic, and speculate further that the same phase for II-VI compounds should be insulating, CdSe and CdTe having the smallest gap. From the resistivity measurements of Onodera *et al.*,⁴ it appears that the rocksalt phases of both HgSe and HgTe are metallic. Thus there appears to be an apparent discrepancy between the prediction from theory and the experiment. However it is possible that the gap, predicted to be small for rocksalt CdSe and CdTe, becomes even smaller for the rocksalt Hg analogs. It is to be noted here that the zinc-blende forms of HgSe and HgTe are both semimetallic rather than semiconducting.

For HgSe the existence of a β -Sn phase is yet to be proved. We may expect HgS to exhibit these pressure-induced phase transitions at much higher pressures. From the experimental point of view, resistivity measurements on HgS to several hundred kbar pressure would be valuable, for the result would have a bearing on the evolution of the rocksalt phase from the cinnabar, as pressure is increased. From the theoretical point of view it would be

interesting to perform pseudopotential calculations for the mercury chalcogenides, for we now have well-established results for HgTe, with HgSe very likely to be analogous to HgTe.

V. SUMMARY

We have shown that HgTe has the β -Sn structure at pressures above 12 GPa and in the (0–20)-GPa range transforms in the sequence zinc blende to cinnabar to rocksalt to β -Sn with increasing pressure. HgS retains its cinnabar structure up to the highest pressure of this study, namely 20 GPa. The cinnabar phase is found to be very compressible in both HgS and HgTe.

The transition sequence observed above agrees with the results obtained for CdTe. The lower energy of the rocksalt phase relative to β -Sn, for mercury chalcogenides as well as for CdTe and CdSe, is in agreement with the predictions of the pseudopotential total-energy calculations for III-V compounds. However, the rocksalt phases of HgTe and HgSe are metallic which is in apparent contradiction with the suggestion that the rocksalt phases of II-VI compounds would be nonmetallic. Further high-pressure x-ray studies on HgSe, higher-pressure resistance measurements on HgS, and theoretical calculations for Hg chalcogenides would definitely be fruitful.

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