

Pressure evolution of the cinnabar phase of HgTe

A. San-Miguel*

*Physique des Milieux Condensés, Centre National de la Recherche Scientifique, Université Pierre et Marie Curie, B77,
4 Place Jussieu, F-75252 Paris CEDEX 05, France*

N. G. Wright, M. I. McMahon, and R. J. Nelmes

Department of Physics and Astronomy, The University of Edinburgh, Mayfield Road, Edinburgh, EH9 3JZ, United Kingdom

(Received 24 August 1994)

The first high-pressure phase of HgTe has been studied by angle-dispersive powder diffraction with an image-plate area detector and synchrotron radiation. The evolution of the full structure of the cinnabar phase has been followed over its pressure domain (from 1.5 to 8.0 GPa). The pressure evolution of atomic positions, angles, and interatomic distances are discussed. In particular, the evolution of the interatomic distances reveals the intermediate role of the cinnabar phase between fourfold and sixfold coordination in a similar way to that observed in CdTe. The Murnaghan and Birch equation of state adjusted to the data gives values of the bulk modulus considerably higher than previously published ones and closer to the average bulk modulus of cinnabar CdTe. Volume changes at the transition are $11 \pm 2\%$ for the zinc blende to cinnabar transition and $3 \pm 1\%$ for the cinnabar to rocksalt transition.

I. INTRODUCTION

Nearly all elements of the group IV and the binary compounds of the III-V and II-VI classes can exhibit phases that present semiconductor or semimetallic character under ambient conditions of temperature and pressure. These phases are fourfold coordinated and are of the diamond, zinc blende, or würtzite structure. For most of these materials a transformation to a metallic state is observed if sufficiently high pressures are applied. This transformation is associated with a change to sixfold coordination. In II-VI materials and the more ionic III-V's, the first metallic phase has the rocksalt structure or at least a local structure close to the rocksalt one. Before reaching the metallic phase some II-VI materials exhibit an intermediate phase (semimetallic or semiconducting) with the cinnabar structure (space group $P3_121$ or $P3_221$). There is even one II-VI compound which adopts the cinnabar structure as a stable phase under ambient condition: HgS,¹ the red natural colorant that gives the name to the structure. The cinnabar structure is also known under ambient conditions as a metastable phase in HgO (Ref. 2) and is also the first high-pressure phase of the other two mercury chalcogenides, HgSe and HgTe.³ In fact for a long time the cinnabar structure has been associated with the presence of mercury in II-VI's.⁴ However very recent studies have shown that this is not the case. This structure is also present in the first high-pressure phase of CdTe,^{5,6} and it has been proposed for the first high-pressure phase of ZnTe.^{7,8} In summary, the cinnabar structure appears before the sixfold-coordination phases in mercury chalcogenides (HgS, HgSe, and HgTe),^{9,10} CdTe,^{5,6} ZnTe (Refs. 7 and 8) and has also been observed in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ (Ref. 11) and in the entire composition domain of the pseudobinary alloy $\text{Zn}_x\text{Hg}_{1-x}\text{Te}$.¹² In the case of HgO, the transition from the stable phase at ambient pressure (an orthorhombic

structure close to the cinnabar structure) to the rocksalt phase has been observed.¹³ Numerous studies on the fourfold to sixfold transformation of the other II-VI materials (CdO, CdS, CdSe, ZnO, ZnS, ZnSe) (Ref. 14) do not report the presence of any intermediate phase between zinc blende and rocksalt. Thus we should associate the cinnabar structure with the heavier II-VI semiconductors and/or semimetals or may be with the presence of Hg or Te atoms.

HgTe is a zero-gap material (semimetal). Under hydrostatic pressure HgTe undergoes several structural phase transitions that have been extensively studied (Table I), namely zinc blende (semimetallic) \rightarrow cinnabar (semiconductor) \rightarrow rocksalt (conductor) \rightarrow body-centered tetragonal proposed as the diatomic equivalent of β -tin (conductor). In addition a further transition to a distorted form of the CsCl structure has been also proposed.¹⁰

The phase diagram of semiconductor materials permits a test of potential and pseudopotential models in phase stability calculations. However the difficulty of these calculations is greatly increased if there is a lack of knowledge of the full structure of the phases involved in the transition and this can be considered the primary explanation as to why the cinnabar structure has never been taken into account in phase stability calculations. It could also be argued that the similarities between the rocksalt and the cinnabar phase may justify omitting the cinnabar phase in such calculations. Indeed, the only well-known cinnabar structures until very recently (α -HgS and HgO) can be considered as a distortion of the rocksalt structure. But the local order of the cinnabar structure is determined by two atomic positional parameters that can give coordination types far from the rocksalt structure. In addition, the atomic position parameters can change with pressure as has been observed in CdTe.⁶ This could explain why total-energy calculations failed to predict the stability domain of the zinc blende

and the rocksalt phases in HgTe, while they could predict a relatively good value for the transition pressure between the rocksalt and the β -tin structure.¹⁵

It is thus clear that in order to describe the evolution of the cinnabar phase, it is not enough to know the equation of state (EOS) and the c/a evolution with pressure. Variation of the coordinates describing the atomic position in the unit cell must also be considered. This evolution has been observed in the cinnabar phase of CdTe, mainly in the downstroke process (rocksalt \rightarrow cinnabar \rightarrow zinc blende), because it was not possible to get a pure cin-

bar phase during the upstroke. An important feature revealed by the evolution of cinnabar CdTe was that the local structure of the cinnabar phase has the signature of the local structures of the zinc blende and of the rocksalt phase. Effectively, in the cinnabar structure the first two shells of atoms around a given one have two atoms each. The first shell exhibit an evolution of distances with pressure in the continuity with the evolution observed in the first shell of the zinc-blende phase, and the second one does the same with respect to the first shell of the rocksalt phase.

Historically, the cinnabar structure was proposed as a high-pressure structure for HgTe by Bridgman in 1940.¹⁶ However, the first determination of HgTe-cinnabar structural parameters had to wait until 1963.³ The determination of the EOS of HgTe cinnabar came in 1982 (Ref. 17) and the real confirmation of the structure including the fractional coordinates for the Hg and Te atoms has only been done very recently.¹⁸ In addition, in this last work an incorrect indexing was found in the diffraction analysis of Ref. 17, that invites a revision of the HgTe-cinnabar EOS.

In this paper we report the evolution with pressure of the full structure of cinnabar HgTe. We analyze the evolution of cell parameters, atomic positions, angles, and interatomic distances. Especially interesting are the similarities with the observed behavior in CdTe. Two EOS are fitted to the data and values of the relative volume variation at the transitions are obtained. These values are then discussed in comparison with previous results.

The experimental values given in this paper constitute the set of structural parameters needed for phase stability calculations between the zinc blende (semimetallic), cinnabar (semiconductor), and the metallic rocksalt phases of HgTe.

II. EXPERIMENTAL PROCEDURE

Merrill-Bassett¹⁹ and Diacell diamond-anvil cells were used as high-pressure generators with diamonds with culets of 600 μm diameter. Fine grained powdered samples were loaded in 200 μm diameter holes drilled in tungsten gaskets. The 4:1 methanol:ethanol mixture was used as pressure transmitting medium and the pressure was measured using the 5th power-law ruby fluorescence scale.²⁰ The ruby chips loaded with the sample showed no enlargement of their fluorescence lines with the increasing pressure, as it is expected for the pressure domain explored. The pressure conditions inside the cell can be considered quasihydrostatic.

Experiments were done on the angle-dispersive powder diffractometer of station 9.1 at the Daresbury Synchrotron Radiation Source. An image-plate area detector was used to collect two-dimensional powder patterns that were read on a Molecular Dynamics 400A Imager Phosphor. Integration of the read image enabled conventional one-dimensional (1D) diffraction profiles to be obtained. Details of the experimental setup and pattern integration procedure have been described elsewhere.²¹⁻²³ All experimental points were obtained during the upstroke process.

TABLE I. Transitions pressures for HgTe (from M.-C. Record, Thesis of the University of Languedoc, 1992).

HgTe	P_T (GPa)	Reference
Zinc blende	1.28	Bridgman (1940) ^a
\rightarrow	1.88	Turusbekow (1979) ^b
Cinnabar	1.4	Jayaramnan (1963) ^c
	1.4	Pitt (1972) ^d
	1.4	Werner (1983) ^e
	1.53	Lacam (1970) ^f
	1.6	Blair and Smith (1961) ^g
	1.6	Morissy (1974) ^h
	1.6	Omel'Chenko (1982) ⁱ
	1.6	Qadri (1990) ^j
Cinnabar	8	Werner (1983) ^e
\rightarrow	8	Qadri (1990) ^j
Rocksalt	8	Onodera (1981) ^k
	8	Huang and Ruoff (1983) ^l
	8.4	Ohtani (1982) ^m
Rocksalt	11.5	Qadri (1990) ^j
\rightarrow	12	Werner (1983) ^e
bct	12	Huang and Ruoff (1983) ^l
	12	Ohtani (1982) ^m

^aRef. 16.

^bT. M. Turusbekov and E. I. Estrin, *Sov. Phys. Solid State* **21**, 558 (1979).

^cA. Jayaraman, W. Klement, Jr., and G. C. Kennedy, *Phys. Rev.* **130**, 2277 (1963).

^dG. D. Pitt, J. H. Mc Cartney, J. Less, and D. A. Wright, *J. Phys. D* **5**, 1330 (1972).

^eRef. 17.

^fA. Lacam, B. A. Lombos, and B. Vodar, *Phys. Earth Planet. Inter.* **3**, 511 (1970).

^gJ. Blair and A. C. Smith, *Phys. Rev. Lett.* **7**, 124 (1961).

^hJ. H. Morissy, G. D. Pitt, and M. K. R. Vyas, *J. Phys. C* **7**, 113 (1974).

ⁱA. V. Omel'Chenko and V. I. Soshnikov, *Izv. Akad. Nauk. SSSR, Neorg. Mater.* **18**(4), 685 (1982).

^jS. B. Qadri, A. W. Webb, E. F. Skelton, N. Moulton, J. Furdyna, and L. Colombo, *High Press. Res.* **4**, 303 (1990).

^kRef. 26.

^lT. Huang and A. L. Ruoff, *Phys. Status Solidi A* **77**, K193 (1983).

^mRef. 9.

III. RESULTS AND DISCUSSION

Three different samples were studied as described above. Pressure was only measured for one of the experiments for which the Murnaghan EOS obtained by fitting the volume variation with pressure was then used to calibrate the pressure of the other two experiments. Details about the procedure followed for the structure refinement of the diffraction data are described in Ref. 18. For the experiment where pressure was measured, Table II gives the crystallographic parameters obtained after refinement.

The relative variation of volume in HgTe cinnabar is shown in Fig. 1. This figure also includes (i) the Murnaghan EOS (Ref. 24) of the zinc-blende phase,²⁵ (ii) the experimental points in the rocksalt phase,^{17,26} (iii) the experimental point of Quadri *et al.*,¹¹ and (iv) the fit to our experimental data and the point of Quadri *et al.* in the cinnabar phase using the two parameter Birch²⁷ EOS or the Murnaghan one (both type of EOS superpose in this pressure domain).

In Table III our values of the bulk-modulus (B_0), its pressure derivative (B'_0), and the reduced volume at zero pressure obtained with the Birch and Murnaghan EOS are compared with previously published values. Both equations fit well the data and their extrapolations to zero pressure are very close to one another. In fact, the Birch and Murnaghan zero-pressure extrapolation of all fitted parameters (zero-pressure volumes, bulk-modulus, and its pressure derivative) are the same within the error bars. It is nevertheless observed that there is a strong correlation between the values of B_0 and B'_0 and within the actual precision of the data, the (B_0, B'_0) pairs are strongly dependent on the EOS that is used to fit the data.

As may be seen in Table III, the values of the bulk modulus and its pressure derivative that we have obtained using any of these EOS are very different from the values of Ref. 17. The indexing error in that work is not the only reason for this difference. An extra virtual point at zero pressure was added to do the Murnaghan fit in Ref. 17. This point was calculated by considering that the volume ratio between hypothetical HgTe cinnabar at zero pressure and HgTe zinc blende at zero pressure, $V(0)/V_0$, should be the same as that between α -HgS (cinnabar) and β -HgS (zinc blende), namely 0.942. The significant difference in the atomic positions between HgTe cinnabar and α -HgS does not justify such a hypothesis. In fact, with our fits, we obtain a volume ratio at zero pressure between hypothetical HgTe cinnabar and

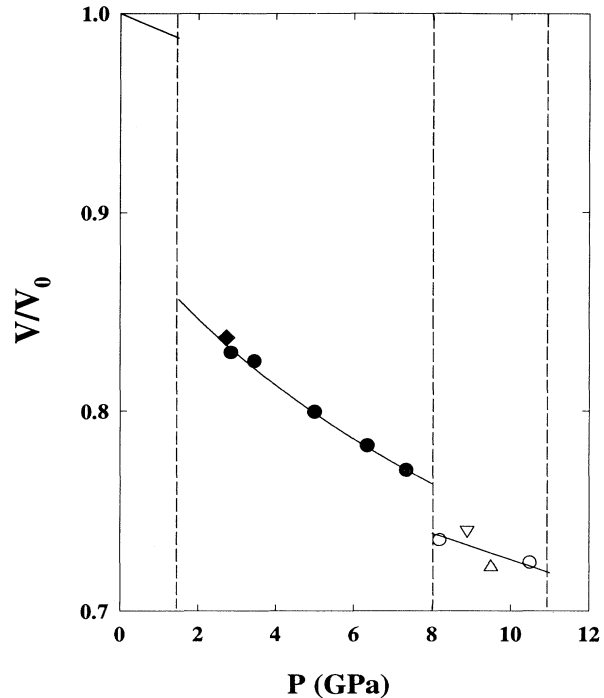


FIG. 1. Relative volume variation as a function of pressure. Vertical lines indicate the phase transitions. The continuous lines in the zinc blende and in the cinnabar phases are the Murnaghan equations of state as discussed in the text. In the rocksalt phase the continuous line is just a linear fit. Symbol notation is filled circles, this work; hollow circles, Ref. 17; triangle up and diamond, Ref. 11; triangle down, Ref. 26.

HgTe zinc blende of 0.89 (or 0.90) ± 0.01 , which corresponds to the fact that HgTe cinnabar is a much less open structure than α -HgS.¹⁸ Our bulk modulus value for cinnabar HgTe ($B_0 = 41 \pm 10$ GPa for the Murnaghan EOS and 32 ± 10 GPa for the Birch EOS) is closer to the average bulk modulus of cinnabar CdTe (Ref. 6) ($B_0 = 32$ GPa). From our EOS, one cannot be tempted to consider cinnabar HgTe as a molecularlike crystal as was done by Werner *et al.* This is also obvious when the structure of cinnabar HgTe is compared with the structure of α -HgS (see Fig. 2 in Ref. 18). In fact the spiral chains of the cinnabar structure are much closer together in HgTe than in α -HgS in which a 1D approximation to the molecular crystal could be considered. As was pointed out we will

TABLE II. Cell parameters (c, a) and fractional coordinates of Hg (u) and Te (v) atoms of the cinnabar phase of HgTe as a function of pressure obtained by Rietveld refinement of our first experiment.

Pressure (GPa)	c (Å)	a (Å)	u	v
2.85	10.033	4.392	0.6375	0.550
3.45	10.022	4.383	0.6395	0.562
5.00	9.953	4.330	0.646	0.557
6.35	9.903	4.295	0.649	0.5595
7.35	9.869	4.268	0.650	0.574

TABLE III. Bulk modulus (B_0), its pressure derivative (B'_0) and the zinc blende to cinnabar atomic volume ratio at ambient pressure for cinnabar and zinc blende HgTe.

Reference	Cinnabar HgTe			Zinc blende HgTe
	This work	Ref. 17	Murnaghan	Ref. 25
EOS	Birch	Murnaghan	Murnaghan	Murnaghan
B_0 (GPa)	32 ± 10	41 ± 10	16	42.3
B'_0	5.5 ± 2	3.3 ± 2	7.3	2.1
$V(0)/V_{0B3}$	0.90 ± 0.01	0.89 ± 0.01	0.942	1

use our Murnaghan fit to calibrate the other two experiments of this paper. The experimental points in the rock-salt phase are just linearly fitted in Fig. 1.

In Fig. 2 the pressure evolution of the c/a ratio for HgTe cinnabar is plotted and compared with other available experimental data. We have included experimental points obtained by energy-dispersive diffraction^{11,17,28} and note the relatively good agreement between all of the results. As was pointed out by Werner *et al.*,¹⁷ the c/a ratio evolves with pressure towards the value that should be found in the rocksalt structure described as a hexagonal one [$c/a = (6)^{1/2}$], but the phase transition towards the rocksalt structure at 8.0 GPa takes place well before this value is attained. The same has been observed in other cinnabar structures that undergo a phase transition towards sixfold-coordinated structures [HgS,¹⁰ CdTe (Ref. 6)].

In Table IV the volume variations at the transition pressures are presented. The bigger value of the bulk modulus obtained for the cinnabar EOS in our study implies an increase of the volume variation at the transition pressures compared with other published data.

Figure 3 shows the pressure evolution of the two fractional coordinates of the cinnabar structure observed in our three experiments. The values of the fractional coordinates of a rocksalt structure described as a cinnabar one are both equal to 0.667 ($\frac{2}{3}$). Both coordinates of HgTe tend to approach this limit value, but the transition takes place before it is reached. We have fitted linearly the evolution with pressure of these parameters

$$\begin{Bmatrix} u \\ v \end{Bmatrix} = \begin{Bmatrix} u_{Pt} \\ v_{Pt} \end{Bmatrix} + m \begin{Bmatrix} u \\ v \end{Bmatrix} P(\text{GPa}),$$

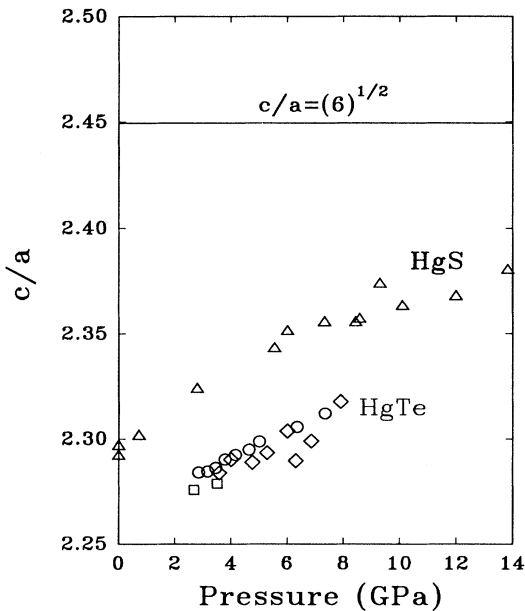


FIG. 2. Pressure evolution of c/a for HgS (Ref. 17, triangles) and HgTe (Circles, this work. Rhombus, Ref. 28. Squares, Ref. 11). The continuous line is c/a in the rocksalt structure.

TABLE IV. Volume changes at the zinc blende to cinnabar phase transition and at the cinnabar to rock-salt phase transition in HgTe.

$\Delta V/V_0$ (%) Zinc blende → Cinnabar	$\Delta V/V_0$ (%) Cinnabar → Rocksalt	Reference
6		Jayaraman (1963) ^a
6.4		Lacam (1970) ^b
8.4		Bridgman (1940) ^c
8.5	2.5	Werner (1983) ^d
11 ± 2	3 ± 1	This work

^aA. Jayaraman, W. Klement, Jr., and G. C. Kennedy, Phys. Rev. **130**, 2277 (1963).

^bA. Lacam, B. A. Lombos, and B. Vodar, Phys. Planet. Inter. **3**, 511 (1970).

^cRef. 16.

^dRef. 17.

^eA. Kalafas, H. C. Gatos, M. C. Lavine, and M. D. Banus, J. Phys. Chem. Solids **23**, 1541 (1962).

^fRef. 5.

with u_{Pt} and v_{Pt} the values of the fractional coordinates at the zinc blende to cinnabar transition pressure. Table V shows the values obtained compared with those of CdTe. We observe that at the beginning of the stability of the cinnabar structure, the Te atoms are in a very similar position in cinnabar HgTe and CdTe. The total displacement of the atoms inside the cell between the two transition pressures (1.5 and 8.0 GPa) is relatively small but not negligible: 6.5% for the Te atoms and 2% for the Hg atoms whereas in CdTe there is a 3.2% variation of the Te atoms and a 4.5% of Cd atoms in a pressure

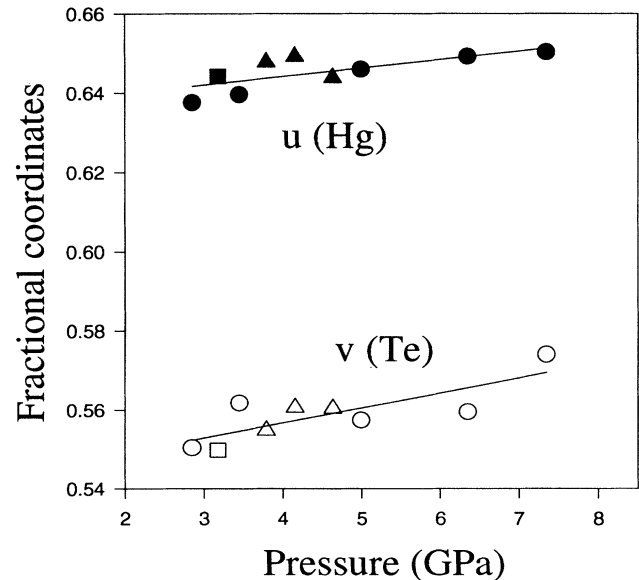


FIG. 3. Pressure dependence of the fractional coordinates $u(\text{Hg})$ and $v(\text{Te})$ of the cinnabar structure for the three experiments. Different symbols hold for different experiments. Continuous lines are the linear fit to the data.

TABLE V. Coefficients of the linear adjustments of the fractional coordinates evolutions with pressure in the cinnabar phase of HgTe and CdTe.

	u_{Pt} (cation)	m_u (10^3 GPa^{-1}) (cation)	v_{Pt} Te	m_v (10^3 GPa^{-1}) Te
HgTe	0.635 ± 0.01	2.0 ± 0.5	0.54 ± 0.01	4 ± 2
CdTe	0.607	31	0.553	20

domain of only 0.9 GPa. This is probably due to the proximity of cinnabar CdTe to the phase transitions (the pure phase was only observed from 2.7 to 3.6 GPa and only in the downstroke) where the mobility of the atoms can increase. In fact the evolution of the Te atoms (v parameter) in HgTe could be interpreted as following three different regimes but more data is needed to confirm this point.

The knowledge of the pressure evolution of the cell parameters and the fractional coordinates permits the pressure evolution of any other structural parameter to be determined. Of special interest are the evolution of the interatomic distances and of the bond angles of the spiral chains that characterize the cinnabar structure. Consider first the evolution of the chain angles. These angles can be directly calculated from the values of the fractional coordinates and the c/a ratio. A rocksalt structure described as cinnabar will have a Te-Hg-Te angle of

$\Theta_{1Rs} = 180^\circ$ and a Hg-Te-Hg angle of $\Theta_{2Rs} = 90^\circ$. In Fig. 4 it is observed that for all measured pressures $\Theta_1 < 180^\circ$ and $\Theta_2 > 90^\circ$ but that with increasing pressures both angles approach Θ_{1Rs} and Θ_{2Rs} .

We have determined the pressure evolution of the three first interatomic distances in cinnabar HgTe and we have plotted them in Fig. 5 in comparison with the first neighbor distances of the neighboring phases (zinc blende with fourfold coordination and rocksalt with sixfold coordination). We observed that the first and second coordination distance of atoms of the cinnabar phase vary continuously with the first coordination shell of the zinc blende and the rocksalt phases, respectively. The same was observed in CdTe,⁶ reinforcing the supposition that the cinnabar phase has a real geometric role between the two cubic phases. It is therefore possible that there is a geometric relationship between the three phases. The extension of this type of study to other cinnabar compounds is needed to clarify this point.

In summary, we have studied the cinnabar phase of HgTe by x-ray diffraction in the angular-dispersive mode. The results can be summarized as follows:

(1) The variation with pressure of anion and cation fractional coordinates in cinnabar HgTe have been measured. HgTe fractional coordinates are very close to those of cinnabar CdTe and tend towards the critical value of 0.667 in both cases but in HgTe at a rate much

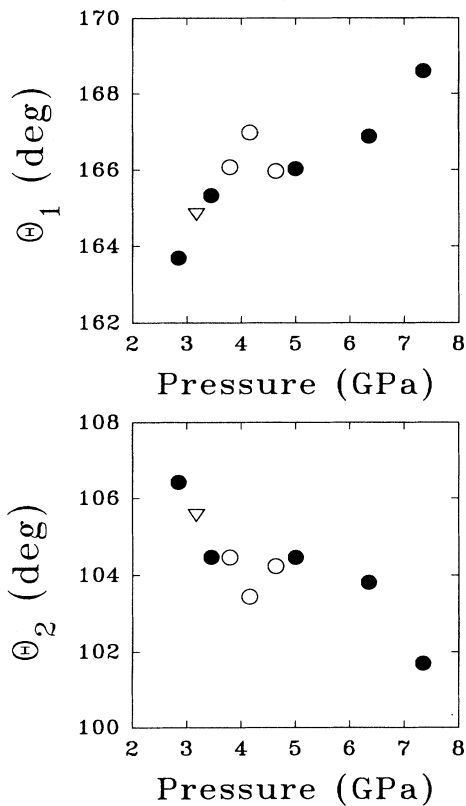


FIG. 4. Evolution with the applied pressure of the angles Te-Hg-Te (Θ_1) and Hg-Te-Hg (Θ_2) in the spiral chains of the cinnabar structure.

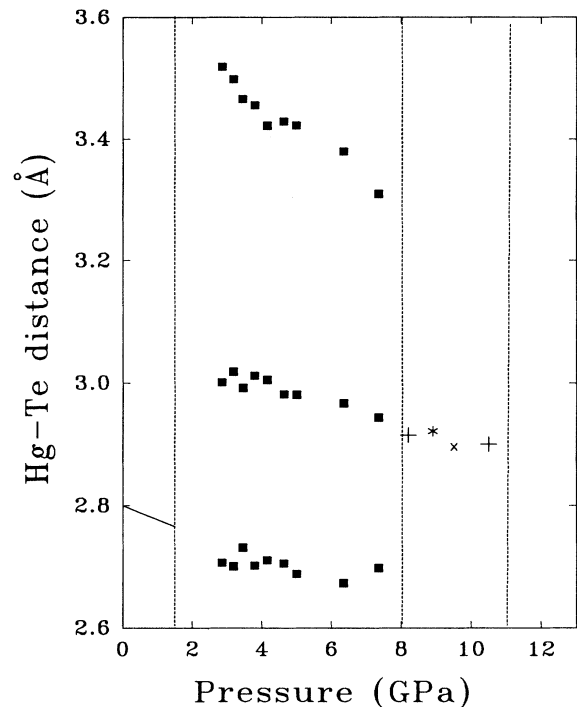


FIG. 5. Pressure evolution of the three first interatomic distances in cinnabar HgTe (squares) between the first-neighbor distances of the neighboring phases. In the zinc blende phase (fourfold-coordinated) the Murnaghan EOS of Miller, Saunders, and Yagurtçu, *Philos. Mag.* **43**, 1447 (1981) is plotted. In the rocksalt phase (sixfold-coordinated) symbols correspond as follows: (+) Ref. 17; (*) Ref. 11; (x) Ref. 26.

smaller than in CdTe (Table V). In both cases the transition to the rocksalt structure takes place well before attaining the critical value. The same is observed for the angles inside the spiral chains.

(2) We have observed the same type of relation between the first-neighbor distances for the zinc blende, cinnabar, and rocksalt phases as in CdTe.

(3) The Murnaghan (Birch) EOS, adjusted to our data, gives a bulk modulus of 41 ± 10 (32 ± 10) GPa which is significantly larger than the previously published value (16 GPa) for a Murnaghan EOS and closer to the average bulk modulus known for cinnabar CdTe (32 GPa). The values of the bulk modulus and its pressure derivative for zinc blende and for the cinnabar phase of HgTe are very similar.

(4) The c/a ratio evolution with pressure is in good agreement with previously reported values.

(5) The volume changes at the transition pressures are $11 \pm 2\%$ at the zinc blende to cinnabar transition and

$3 \pm 1\%$ at the cinnabar to rocksalt transition. These values are slightly higher than those previously published.

ACKNOWLEDGMENTS

We gratefully acknowledge the assistance of J. S. Loveday in many aspects of the experimental work. The samples were grown and supplied by R. Triboulet (Laboratoire de Physique des Solides de Bellevue). One of us (A.S.M.) wants to express his gratitude to Dr. J. P. Itié and Dr. A. Polian for many interesting discussions. Physique des Milieux Condensés is Unité Associée au Centre National de la Recherche Scientifique No. 782. This work was also supported by a grant to one of us (N.R.J.) from the U. K. Science and Engineering Research Council and by facilities made available by Daresbury Laboratory.

*Present address: ESRF, BP220 38046 Grenoble, France.

¹K. L. Aurivillius, *Acta Chem. Scand.* **4**, 1423 (1950).

²R. W. G. Wyckoff, *Crystal Structures* (Krieger, Malabar, 1982).

³A. N. Mariano and E. P. Warekois, *Science* **142**, 672 (1963).

⁴T. Huang and A. L. Ruoff, in *Proceedings of 9th AIRAPT Conference*, edited by C. Homan, P. K. Maccrone, and E. Whalley (North-Holland, New York, 1984), Vol. 22, Pt. 3, p. 37.

⁵R. J. Nelmes, M. I. McMahon, N. G. Wright, and D. R. Allan, *Phys. Rev. B* **48**, 1314 (1993).

⁶M. I. McMahon, R. J. Nelmes, N. G. Wright, and D. R. Allan, *Phys. Rev. B* **48**, 16 246 (1993).

⁷A. Othani, M. Motobayashi, and A. Onodera, *Phys. Lett. A* **75**, 435 (1980).

⁸A. San Miguel, A. Polian, M. Gauthier, and J. P. Itié, *Phys. Rev. B* **48**, 8683 (1993).

⁹A. Ohtani, T. Seike, M. Motobayashi, and A. Onodera, *J. Phys. Chem. Solids* **43**, 627 (1982).

¹⁰T. Huang and A. L. Ruoff, *Phys. Rev. B* **31**, 5976 (1985).

¹¹S. B. Quadri, E. F. Skelton, A. W. Webb, and J. Dinan, *J. Vac. Sci. Technol. A* **4**, 1974 (1986).

¹²A. San Miguel, Ph.D. thesis, Paris VI University, 1993.

¹³A. San Miguel, J. P. Itié, A. Polian, and P. Bordet (unpublished).

¹⁴E. Yu Tonkov, *High Pressure Phase Transformation. A Handbook* (Gordon and Breach, Philadelphia, 1992).

¹⁵Z. W. Lu, David Singh, and Henry Krakauer, *Phys. Rev. B* **39**, 10 154 (1989).

¹⁶P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **74**, 21 (1940).

¹⁷A. Werner, H. D. Hochheimer, K. Strössner, and A. Jayaraman, *Phys. Rev. B* **28**, 3330 (1983).

¹⁸N. G. Wright, M. I. McMahon, R. J. Nelmes, and A. San Miguel, *Phys. Rev. B* **48**, 13 111 (1993).

¹⁹L. Merill and W. A. Basset, *Rev. Sci. Instrum.* **45**, 290 (1974).

²⁰H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, *J. Appl. Phys.* **49**, 3276 (1978).

²¹R. J. Nelmes, P. D. Hatton, M. I. McMahon, R. O. Piltz, J. Crain, R. J. Cernik, and G. Bushnell-Wye, *Rev. Sci. Instrum.* **63**, 1039 (1992).

²²R. O. Piltz, M. I. McMahon, J. Crain, P. D. Hatton, R. J. Nelmes, R. J. Cernik, and G. Bushnell-Wye, *Rev. Sci. Instrum.* **63**, 700 (1992).

²³R. J. Nelmes, M. I. McMahon, P. D. Hatton, R. O. Piltz, J. Crain, R. J. Cernik, and G. Bushnell-Wye, *High Press. Res.* **8**, 677 (1992).

²⁴F. D. Murnaghan, *Proc. Natl. Acad. Sci. U.S.A.* **30**, 244 (1944).

²⁵A. J. Miller, G. A. Saunders, and Y. K. Yogurtçu, *Philos. Mag.* **43**, 1447 (1981).

²⁶A. Onodera, A. Ohtani, M. Motobayashi, T. Seike, O. Shimomura, and O. Fukunaga, *Proceedings of the 8th AIRAPT Conference (Uppsala)*, edited by C. M. Backman, T. Johannisson, and L. Tengner (Arkitektopia, Uppsala, 1982), Vol. 1, p. 321.

²⁷F. Birch, *J. Geophys. Res.* **83**, 1257 (1978).

²⁸A. San Miguel, A. Polian, and J. P. Itié, *Physica B* (to be published).