

Phase transitions in CdTe to 5 GPa

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Angle-dispersive powder-diffraction techniques using an image-plate area detector have been used to study the high-pressure phases of CdTe to 5 GPa. The recently discovered cinnabar phase between the zinc-blende and NaCl phases is found to be stable on both pressure increase and decrease. No pressure range of single-phase cinnabar has been found on pressure increase, but a single phase is obtained on pressure decrease, between 3.6 and 2.7 GPa. The cinnabar phase has an average bulk modulus of 32(1) GPa and is significantly more compressible than the zinc-blende and NaCl phases. All three phases are site ordered. Each atom in the cinnabar structure has two nearest-neighbor distances of ~ 2.74 Å (a bonds) and two of ~ 2.94 Å (b bonds), and the structure is thus close to fourfold coordinated. The next-nearest-neighbor distances are two of ~ 3.5 Å (c bonds). The a bonds are very similar in length to the nearest-neighbor distance in the zinc-blende phase, and the b bonds increase with pressure towards the nearest-neighbor distance in the NaCl phase. The c -bond distance and the interbond angles also become closer to the geometry of the NaCl structure with increasing pressure, but there are still large discontinuities in bond lengths and angles at the cinnabar-to-NaCl transition.

I. INTRODUCTION

The high-pressure behavior of CdTe has attracted continuing interest for over 30 years. A phase transition at about 3.5 GPa was first found in optical studies,¹ and then confirmed in electrical measurements which revealed a further transition at ~ 10 GPa.² Density measurements³ showed the transition at 3.5 GPa was to a solid phase, with a volume decrease ($\Delta V/V_0$) of about 10%; the authors speculated that the high-pressure phase had the NaCl structure. Subsequent diffraction studies confirmed this,⁴⁻⁶ giving a more accurate estimate of 16% for the volume decrease at the zinc-blende-NaCl transition,^{6,7} and the transition at ~ 10 GPa was found to be to the β -tin structure.^{5,6} More recent diffraction work has reproduced these results and revealed yet another transition, to an orthorhombic structure with space group $Pmm2$, above 12 GPa.⁸

We have embarked on a diffraction study of CdTe, to compare its structural pressure dependence and site ordering with the behavior found recently in the iso-electronic compound InSb.⁹ Using angle-dispersive techniques and synchrotron radiation, we have shown¹⁰ that CdTe has *two* transitions over a narrow pressure range at ~ 3.5 GPa—first zinc-blende-to-cinnabar and then cinnabar-to-NaCl. The cinnabar structure has not, to our knowledge, previously been reported outside the mercury chalcogenides. In fact, Cline and Stephens⁷ found evidence of an intermediate phase in their direct-compression measurements, but only on pressure decrease, between 3.5 and 2.7 GPa. They speculated that the phase was cinnabar, but neither they nor, later, Borg and Smith⁶ could find any evidence for it in diffraction studies. Recent studies of HgTe and $Hg_{0.8}Cd_{0.2}Te$ (Ref. 11) suggested that the cinnabar structure would be unstable above $\sim 73\%$ Cd.

In our refinements of the cinnabar phase,¹⁰ we ob-

tained a crystal structure significantly different from HgS cinnabar.¹² In particular, the CdTe structure is close to fourfold coordinated, whereas the coordination of HgS is twofold. We were able to detect the weak (003) reflection, which arises from the difference in scattering between the Cd and Te atoms, and thus show the structure to be site ordered. These previous refinements were carried out on a powder pattern from a mixture of the zinc-blende and cinnabar phases, because we were unable to obtain single-phase cinnabar on pressure increase. The results of Cline and Stephens⁷ suggest that this can be achieved on pressure decrease and we have now carried out a detailed study on pressure increase and decrease over the range up to 5 GPa. In this paper we report the results, including the compressibility and structural pressure dependence of the cinnabar phase.

II. EXPERIMENTAL DETAILS

Diffraction data were collected on station 9.1 at the Synchrotron Radiation Source, Daresbury, using angle-dispersive diffraction techniques and an image-plate area detector. To enhance the difference in scattering power of the Cd and Te atoms, the incident wavelength was set at 0.4650(1) Å, 59 eV from the measured position of the Cd K edge. The incident monochromatic beam was collimated by a platinum pinhole to a diameter of 75 μm . The two-dimensional powder patterns collected on the image plates were read on a Molecular Dynamics 400A PhosphorImager and then integrated to give conventional one-dimensional diffraction profiles. Details of our experimental setup and pattern integration program have been reported previously.¹³⁻¹⁵

The CdTe sample was a finely ground powder prepared from starting material of 99.99+ % purity supplied by the Aldrich Chemical Company. Merrill-Bassett diamond-anvil cells, having full conical apertures of 40° half angle, were used, with diamond-anvil cutlets of di-

ameter 600 or 800 μm . Samples were loaded into 175- μm holes in tungsten gaskets with a 4:1 mixture of methanol:ethanol as the pressure-transmitting medium. The pressure was measured before and after each exposure using the ruby-fluorescence technique,¹⁶ which gives a precision of 0.05 GPa. Taking into account small pressure drifts which sometimes occurred during exposures, we estimate the standard deviation on our pressure measurements to be 0.1 GPa. The structural results described were obtained from Rietveld refinement¹⁷ of the integrated profiles using the program MPROF.¹⁸

III. RESULTS AND DISCUSSION

On pressure increase, the cinnabar phase was first detected at 3.53 GPa, slightly higher in pressure than in our first study (3.4 GPa).¹⁰ At 3.74 GPa, the proportion of the cinnabar phase was sufficiently increased to carry out a two-phase refinement of the crystal structure; the integrated powder profile and the fit are shown in Fig. 1. The refined lattice parameters are $a = 6.324(2)$ \AA for the zinc-blende phase, and $a = 4.282(2)$ \AA , $c = 10.219(3)$ \AA for the cinnabar phase. The volume decrease ($\Delta V/V_0$) at the transition is then 13.4(1)%, where V_0 is the volume per formula unit in the zinc-blende phase at ambient pressure (17.01 \AA^3).

A further increase in pressure to 3.80 GPa resulted in an almost complete transition to the NaCl phase, as shown by the integrated profile in Fig. 2. Although the cinnabar and NaCl phases are closely related, and very little cinnabar remains, it was possible to obtain lattice parameters for both phases from this profile. The refined values are $a = 4.279(1)$ \AA , $c = 10.205(18)$ \AA for the cinnabar phase, and $a = 5.932(1)$ \AA for the NaCl phase. The volume decrease at this second transition is thus 2.6(2)%.

The profile in Fig. 2 also contains very weak peaks from a residual zinc-blende component, as marked. In a

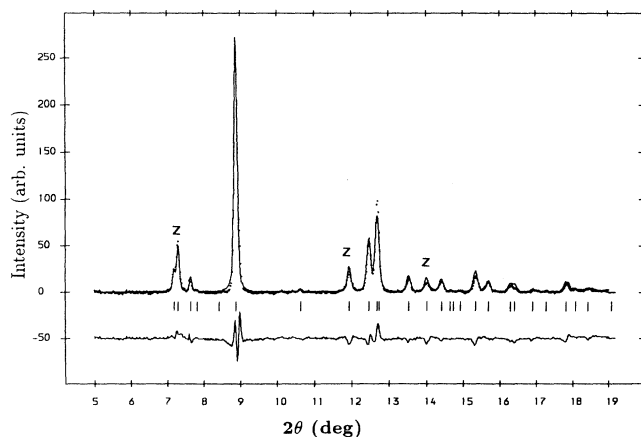


FIG. 1. The fit to the mixed zinc-blende-cinnabar profile collected at 3.74 GPa. The tick marks show the positions of all the reflections allowed by symmetry. The difference between the observed and calculated profiles is displayed below the tick marks. The (111), (220), and (311) reflections from the zinc-blende phase are marked z.

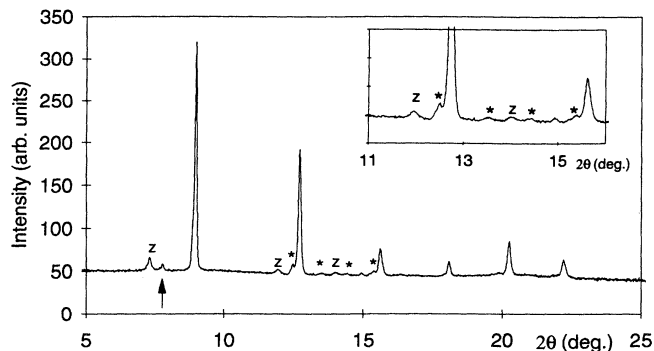


FIG. 2. The integrated profile of a pattern recorded from a mixture of zinc-blende, cinnabar, and NaCl phases at 3.80 GPa. The peaks marked z correspond to the same zinc-blende reflections marked in Fig. 1. Asterisks mark the positions of the cinnabar reflections, which are enlarged in the inset, while the arrow indicates the position of the (111) difference reflection in the NaCl phase.

second sample, this residual component was detectable at 3.95 GPa—beyond the full completion of the cinnabar-to-NaCl transformation. The V/V_0 values obtained from this pattern give the highest pressure point plotted for zinc blende in Fig. 3, and the corresponding point for NaCl. The open symbols in Fig. 3 show all the V/V_0 values obtained from both samples on pressure increase up to 5 GPa in the zinc-blende, cinnabar, and NaCl phases, and the region of coexistence of zinc blende and cinnabar is bounded by the two dashed vertical lines.

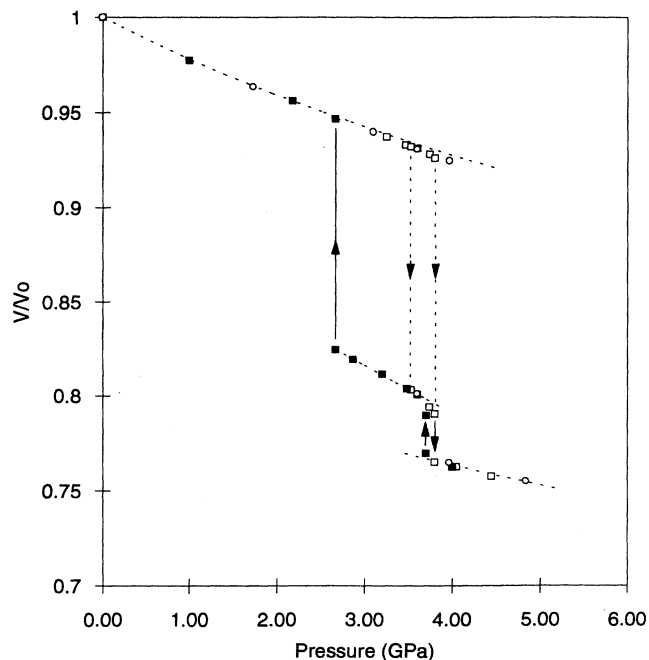


FIG. 3. V/V_0 as a function of pressure for two samples of CdTe on pressure increase (\circ and \square) and one of them on pressure decrease (\blacksquare). The dotted curves are first-order Murnaghan equations of state as discussed in the text; those for the zinc-blende and NaCl phases are reproduced from Ref. 19.

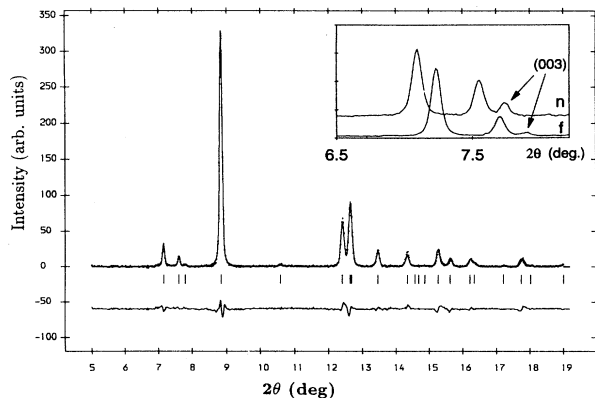


FIG. 4. The fit to the single-phase cinnabar profile collected at 3.48 GPa. The tick marks show the positions of all the reflections allowed by symmetry. The difference between the observed and calculated profiles is displayed below the tick marks. The inset shows the weak (003) difference reflection recorded at 26.175 keV, far (*f*) from the Cd *K* edge, and at 26.656 keV, near (*n*) the Cd *K* edge (at 26.715 keV), as in the main profile.

After reaching 5 GPa, the pressure was slowly reduced on both samples. The reverse transition from NaCl to cinnabar was found at 3.70 GPa, possibly indicating a small hysteresis as shown in Fig. 3. A further reduction in pressure to 3.48 GPa for one sample, and 3.60 GPa for the other, resulted in patterns that contained peaks from *only* the cinnabar phase, as shown for the first sample in Fig. 4. Further patterns were collected from this sample at 3.20 and 2.87 GPa, and then the reverse cinnabar-to-zinc-blende transition was observed at 2.67 GPa. There is thus a difference of ~ 0.8 GPa between this pressure and the first appearance of the cinnabar phase on pressure increase. The volume increase ($\Delta V/V_0$) between NaCl extrapolated to 3.50 GPa and the fully transformed cinnabar phase at that pressure is 3.4(2)%, followed by an increase of 2.0(2)% as the pressure falls through the cinnabar phase (to 2.67 GPa), and then a 12.2(1)% increase at the transition to the zinc-blende phase.

Cline and Stephens⁷ obtained remarkably similar results in their direct volume measurements on pressure decrease. They found a relatively abrupt volume increase of 4.3% from the NaCl phase, starting at 3.6 GPa; then a gradual increase of 1.2% through the intermediate phase; and finally another abrupt increase of 12.9%, which is completed at 2.65 GPa in the zinc-blende phase. It seems beyond reasonable doubt that this is the same sequence of changes as we have now seen, and that their intermediate phase was cinnabar.

Values of V/V_0 obtained on pressure increase and decrease lie on common curves in all three phases, as shown in Fig. 3. The dashed curves through the zinc-blende and NaCl data are first-order Murnaghan equations of state calculated from an initial bulk modulus B_0 of 42(2) GPa and first derivative B' of 6.4(6) for the zinc-blende phase, and $B_0=69(5)$ GPa, $B'=5.1(6)$ for the NaCl phase, as determined by Strössner *et al.*¹⁹ The agreement can be seen to be good, except that our zinc-blende data require

a smaller value of B' : A best fit to our data gives $B_0=43.7(1.0)$ GPa and $B'=3.8(6)$. There are insufficient data to obtain new values of B_0 and B' in the NaCl phase. Our data for the cinnabar phase give an average bulk modulus of 32(1) GPa, corresponding to the straight line shown in Fig. 3. The highest pressure points for this phase lie below the line; this may be an artifact of the refinements of the mixed cinnabar-NaCl patterns, in which cinnabar is the minority phase and has many reflections overlapped with those from the NaCl component. This feature and the small pressure range prevent the refinement of a reliable value for B' . But the average compressibility is well determined, and is clearly much larger than for either the zinc-blende or NaCl phases. (Consequently, the volume changes between the cinnabar and other two phases are significantly pressure dependent.) The cinnabar phases of HgTe and HgS are also known to have anomalously small bulk moduli.²⁰ This probably reflects the fact that the cinnabar structure can respond to pressure by changes in interbond angles and reduction of the distance between the -Cd-Te-Cd-spirals (see below), as well as by direct compression of nearest-neighbor distances. By contrast, only the last of these is possible in the zinc-blende and NaCl structures.

The results shown in Fig. 3 were all obtained from refinements in which the atomic coordinates and thermal parameters, an overall scale factor for each phase, and peak-width parameters were all varied, as well as the lattice parameters used to derive V/V_0 values. Before carrying out these refinements, a careful check was made that the observed reflections conform to the cinnabar space group $P3_121$. As required, the only systematic absences found were (00*l*) reflections with $l \neq 3n$. But these absences are also consistent with the lower symmetry $P3_1$ (or, equivalently, $P3_2$). Test refinements in $P3_1$ showed a very small change of ~ 0.01 in the difference in *z* coordinate between the Cd and Te atoms, while their *y* coordinates both remained zero within error. We concluded that any departure from $P3_121$ is too small to determine with confidence, and all further refinements were carried out in $P3_121$. As before, the Cd atoms were placed on the 3(*a*) at (*u*,0,1/3), and the Te atoms on the 3(*b*) sites at (*v*,0,5/6).

Refinement of the mixed zinc-blende-cinnabar pattern shown in Fig. 1, recorded on pressure increase at 3.75 GPa, gave $u=0.643(2)$ and $v=0.566(2)$, close to the values obtained at 3.6 GPa in our first study.¹⁰ A typical fit to a *single*-phase pattern obtained on pressure decrease is presented in Fig. 4, using the data recorded at 3.48 GPa. The refined values for the *u* and *v* coordinates, and the *c/a* ratio, from the single-phase patterns are shown in Fig. 5, together with the results from the mixed-phase pattern at 3.75 GPa. There is no evidence of strong preferred orientation effects; but a preferred orientation parameter has been included in all the refinements, and this shifts the values of *u* and *v* by about one estimated standard deviation. There are some small but significant and systematic variations of peakwidth, such that reflections with $l > h, k$ are sharper than those with $l \leq h, k$. This indicates that the average crystallite is longer along the crystallographic *c* axis than perpendicular to it, as we

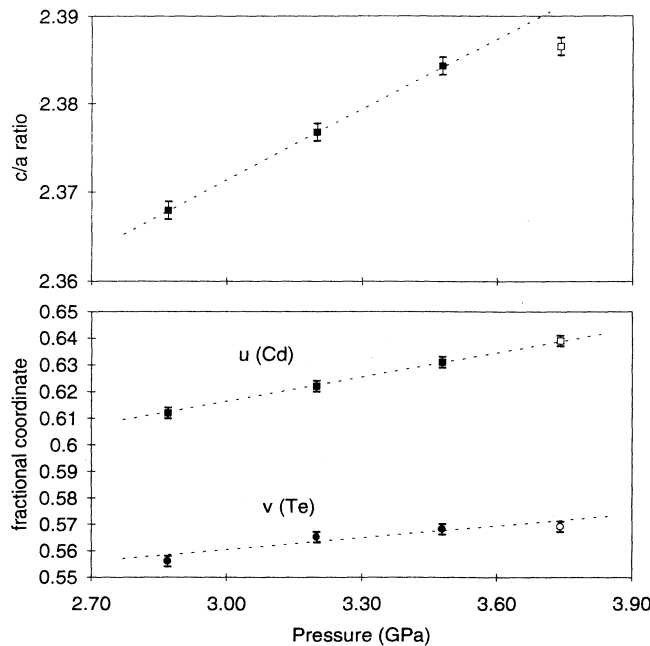


FIG. 5. The pressure dependence of the c/a ratio, and the u and v atomic coordinates for the cinnabar phase of CdTe. The points shown as \circ and \square were obtained from the mixed-phase profile observed on pressure increase (see Fig. 1), while points shown as \bullet and \blacksquare were obtained from the single-phase cinnabar profiles observed on pressure decrease. The dotted lines are guides for the eye.

have also found in HgTe.²¹

The c/a ratio at 3.75 GPa on pressure increase can be seen to deviate from the trend of the values obtained on pressure decrease (Fig. 5). In case this could be an artifact of the two-phase refinement, we fitted to the cinnabar reflections alone, but the same c/a values was obtained. Further work is needed to establish whether this is a reproducible feature of CdTe. However, we note that

we have found other evidence of unit-cell distortion in mixed-phase environments—in InSb for example.²²

The (003) reflection is enlarged in the inset of Fig. 4, which also includes the corresponding part of a profile recorded with an x-ray energy much further (540 eV) from the Cd K edge. The evident change in the relative intensity of (003) shows directly that it arises from the difference in scattering between Cd and Te, and hence that the structure is site ordered. [The arrow in Fig. 2 marks the (111) reflection of the NaCl phase. This reflection also arises from Cd-Te difference scattering, and hence the NaCl phase is shown to be site ordered too.] The site assignment was also examined further with the present single-phase refinements. As before,¹⁰ if the Cd and Te atoms are interchanged and then the site occupancies are refined (keeping the scale factor constant), the values obtained are equivalent to the atoms interchanging back again. And refinements carried out with the atoms interchanged and the occupancies fixed at 100% give a significantly poorer fit to the data, as illustrated in Fig. 6. We thus conclude that the original site assignment is correct.

Table I compares the structural results obtained from the single-phase refinements of CdTe with the corresponding values for HgTe in its cinnabar phase at 3.6 GPa (Ref. 21) and for HgS cinnabar at ambient pressure.¹² The cinnabar structure can be interpreted as a distorted NaCl structure, and the final column gives values for ideal (cubic) NaCl referred to the hexagonal unit cell of cinnabar. As shown, the cinnabar structure becomes identical with NaCl when $c/a = 2.449$ ($\sqrt{6}$) and $u = v = \frac{2}{3}$. The six equal nearest-neighbor distances in NaCl become two short distances (a bonds), two longer ones (b bonds) and two yet longer ones (c bonds) in cinnabar. These distances are given for CdTe, HgTe, and HgS in Table I. In the prototype cinnabar structure of HgS, the b and c bonds are similar in length, and much longer than the a bonds. Hence the structure is regarded as twofold coordinated. The a bonds link the Hg and S

TABLE I. The refined lattice parameters, c/a ratio, and u and v atomic coordinates of CdTe obtained from refinements of the three single-phase cinnabar patterns collected on pressure decrease. The calculated values for the nearest-neighbor (a bond and b bond), and next-nearest-neighbor (c bond) distances, and the intrachain bond angles are also given. The corresponding structural results for the cinnabar phase of HgTe at 3.6 GPa, and for HgS at atmospheric pressure (AP), are given for comparison. The final column gives the structural parameters of the NaCl phase expressed in terms of the cinnabar structure.

MX	CdTe			HgTe	HgS	NaCl
Pressure	2.87 GPa	3.20 GPa	3.48 GPa	(Ref. 21) 3.6 GPa	(Ref. 12) AP	
a (Å)	4.338(1)	4.319(1)	4.301(1)	4.383(1)	4.146	
c (Å)	10.273(1)	10.265(2)	10.255(2)	10.022(1)	9.497	
c/a	2.368(2)	2.378(2)	2.384(2)	2.287(2)	2.292	2.449
u	0.612(2)	0.622(2)	0.631(2)	0.641(1)	0.720(3)	0.667
v	0.556(2)	0.565(2)	0.568(2)	0.562(1)	0.480(10)	0.667
a bonds (Å)	2.741(4)	2.749(4)	2.745(3)	2.732(4)	2.36(5)	all equal
b bonds (Å)	2.929(5)	2.937(5)	2.948(4)	2.995(4)	3.10(5)	
c bonds (Å)	3.567(5)	3.493(5)	3.441(5)	3.460(5)	3.30(5)	
$M-X-M$ (°)	110.2(2)	107.7(2)	106.1(2)	104.2(2)	105.2(2.0)	90
$X-M-X$ (°)	159.9(3)	162.7(2)	164.7(2)	165.6(2)	172.4(1.7)	180

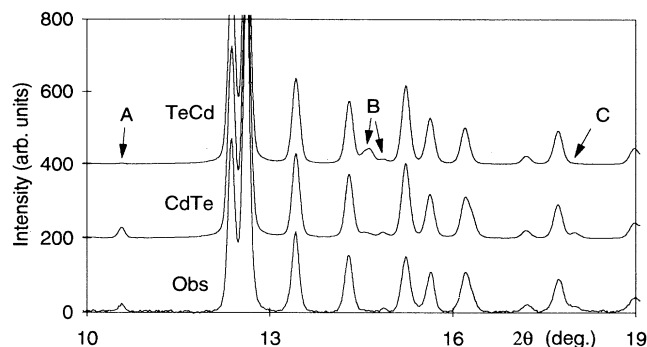


FIG. 6. The observed integrated profile of the cinnabar-phase pattern collected at 3.48 GPa, with calculated profiles from (i) the best-fitting cinnabar structure with the Cd atoms on the 3(*a*) sites and Te atoms on the 3(*b*) sites (labeled CdTe), and (ii) the best-fitting cinnabar structure with the Te atoms on the 3(*a*) sites and Cd atoms on the 3(*b*) sites (labeled TeCd). The major discrepancies between the TeCd profile and the observed data (labeled Obs) are marked A, B, and C.

atoms into spirals along the *c* axis, and the *b* and *c* bonds form relatively weak links between adjacent spirals. Within the spirals, the S-Hg-S angle is close to 180° and the Hg-S-Hg angle is close to 105°, as expected for Hg and S in twofold covalent bonding.¹² Values for these angles are given in Table I. It can be seen that, as already shown,¹⁰ the CdTe structure is significantly different from HgS and is close to fourfold coordinated—the *a* and *b* bonds are similar in length. Our recent study²¹ shows that the same is true for HgTe in its cinnabar phase (Table I).

Figure 5 indicates that the structure of CdTe moves closer to that of cubic NaCl with increasing pressure—that is, as the transition to the NaCl phase is approached. This is shown more directly by the pressure dependence of the *a*-, *b*-, and *c*-bond distances, and the in-spiral bond angles (from the single-phase refinements) presented in Fig. 7. The figure includes also the nearest-neighbor distances in the zinc-blende and NaCl phases over the pressure ranges adjacent to that of the cinnabar phase. (Because of the phase coexistence on pressure increase, values are available for the zinc-blende phase at pressures above as well as below the range of the cinnabar measurements.)

The short *a* bonds can be seen to behave very similarly to the zinc-blende bond length, in both magnitude and (small) variation with pressure. The longer *b* bonds increase in length with increasing pressure, towards the nearest-neighbor distance in the NaCl structure. And the long *c* bonds, and the two in-spiral bond angles, all change rather rapidly with pressure towards the values required for the NaCl structure. However, the transition occurs well before any aspect of the structure has become NaCl-like, and the discontinuities in structural geometry at the transition can be seen to be large. It will be of considerable interest to compare this behavior with the mercury chalcogenides, and further work is in progress on HgTe following the recent refinement of its cinnabar structure.²¹

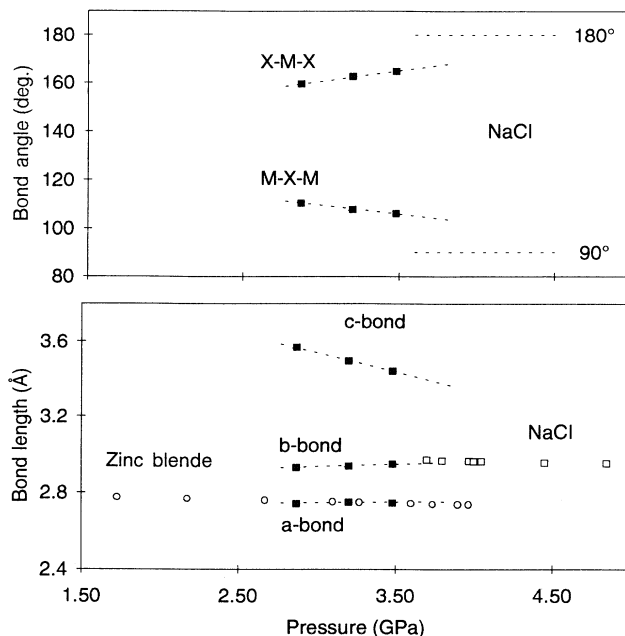


FIG. 7. The pressure dependence of the *X-M-X* and *M-X-M* chain angles, and the nearest-neighbor (*a* bond, *b* bond) and next-nearest-neighbor (*c* bond) distances in the cinnabar phase of CdTe. The dotted lines through the cinnabar points (denoted ■ and obtained on pressure decrease) are guides for the eye. The nearest-neighbor bond lengths in the zinc-blende (○) and NaCl phases (□) are given for comparison with the *a* bonds and *b* bonds, while the *X-M-X* and *M-X-M* bond angles in the NaCl phase are shown for comparison with the values in the cinnabar phase.

In summary, our main conclusions are as follows.

- (1) CdTe has a cinnabar phase between the zinc-blende and NaCl phases. The cinnabar phase is stable on both pressure increase and pressure decrease, but no pressure range of single-phase cinnabar was found on pressure increase. There is a single-phase region on pressure decrease, between 3.6 and 2.7 GPa.
- (2) The cinnabar phase has an average bulk modulus of 32(1) GPa and is significantly more compressible than the zinc-blende and NaCl phases.
- (3) The zinc-blende, cinnabar, and NaCl phases are all site ordered.
- (4) The cinnabar structure is close to fourfold coordinated, with two nearest-neighbor distances of ~ 2.74 Å (*a* bonds) and two of ~ 2.94 Å (*b* bonds). The *a* bonds are very similar in length to the Cd-Te distance in the zinc-blende phase, and the *b* bonds increase with pressure towards the Cd-Te distance in the NaCl phase.
- (5) The next-nearest-neighbor distances and the inter-bond angles exhibit a marked pressure dependence, and become closer to the geometry of the NaCl structure with increasing pressure. But there are still large discontinuities in bond lengths and angles at the cinnabar-to-NaCl transition.
- (6) The structure is very similar to that of HgTe in its cinnabar phase, and different from that of HgS cinnabar. Until recently, the cinnabar phase has been thought to

be unique to the mercury chalcogenides,²³ which were all assumed to have the same twofold-coordinated structure as HgS. The structure has been interpreted as an intermediate step in which the sp^3 bonding of the zinc-blende structure first changes to sp bonding (in twofold coordination) before completing the change to NaCl.^{24,25} The discovery of a cinnabar phase in CdTe, with a structure closer to fourfold coordinated, indicates that a broader interpretation may be required. Also, the magnitudes of the nearest-neighbor distances, in relation to those in the zinc-blende and NaCl phases, suggest a geometrical aspect to the role of the cinnabar phase in the zinc-blende-to-NaCl transition.

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- ²⁵The words "to sp bonding (in twofold coordination) before completing the change" were inadvertently omitted from a similar statement in the penultimate paragraph of Ref. 10.