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“Hidden” High-to-Low Cristobalite Type Transition in HgSe and HgTe at High Pressure

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A transition from the zinc blende (ZB) phase to a distorted-ZB structure has been found in both HgSe and HgTe. This is a structure type not previously reported in any of the II-VI or III-V systems. The transition occurs ~1 GPa above the pressure at which the ZB phase becomes unstable against the cinnabar phase, and is thus observable only because of the sluggishness of the ZB to cinnabar transformation. The atomic coordinates of the distorted-ZB structure are remarkably similar to those of the cations in the low-cristobalite phases of $AlPO_4$ and $GaPO_4$. [S0031-9007(96)00885-X]

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HgSe and HgTe both have the tetrahedrally-coordinated zinc blende (ZB) structure at ambient pressure, and transform to the cinnabar structure under applied pressure [1,2]. This transformation involves a substantial structural rearrangement and a 9% increase in density, and is quite sluggish in both systems at room temperature [3]—requiring several hours at pressures some 0.5 GPa above the onset of the transition to reach apparent completion [1,3]. The pressures at which the transitions are reported to start have increased as more hydrostatic techniques have been used: from 0.75 [1,2] to ~1.0 GPa [4] in HgSe, and from 1.4 to ~1.9 GPa [5] in HgTe. This is probably another manifestation of the inherently sluggish and reconstructive nature of the transition. (A similar effect has been reported for the diamond to β-tin transition in Si [6].)

While making a more detailed study of the ZB to cinnabar transition in HgSe, we have found that good hydrostatic conditions also substantially increase the range of coexistence of the ZB and cinnabar phases, allowing the discovery of a previously unobserved phase that appears reproducibly in all mixed ZB/cinnabar samples at ~2.1 GPa, before the transformation to the cinnabar phase is complete. The same behavior has since been found in HgTe. The new phase has a distorted-tetrahedral, orthorhombic structure, with space group $C222_1$. No such structure has been reported previously for any of the II-VI or III-V systems. However, the atomic coordinates are remarkably similar to those of the cations in the low-cristobalite phase of $AlPO_4$ and $GaPO_4$ [7]. Since the cation coordinates in the (idealized) high-cristobalite phases are as in ZB [8], the ZB to $C222_1$ transition in HgSe and HgTe is of the high-to-low cristobalite type. This reveals an interesting and unexpected link to the structures of SiO_2 and its analogs. Another unusual aspect of the $C222_1$ phase is that it is observable only because of the sluggish nature of the lower-pressure transition from ZB to cinnabar: the ZB to $C222_1$ transition may thus be termed a “hidden” transition.

Diffraction data were collected at room temperature on station 9.1 at the Synchrotron Radiation Source, Daresbury, using angle-dispersive diffraction techniques and an image-plate area detector. The incident wavelength was 0.4654 Å. The sample of HgTe was the same as that used in Ref. [9], while the HgSe was a fine powder of 99.999% purity obtained from the Aldrich Chemical Company. Samples were loaded into Merrill-Bassett diamond-anvil pressure cells with 4:1 methanol:ethanol as a pressure transmitting medium and chips of ruby for pressure measurement [10]. After structure solution, the final structural parameters, including lattice parameters, were obtained from Rietveld refinement [11] of the full integrated profiles using the program MPROF [12]. Details of our beam-line setup, experimental procedures, and data analysis techniques have been reported previously [13].

The first and most detailed of the studies reported in this Letter have been carried out on HgSe. On pressure increase, the cinnabar phase of HgSe was first observed at 1.15(5) GPa. This is at the upper end of the range of previously reported pressures for the onset of the transition (see above), in accord with the hydrostatic conditions of the present study. On further compression, the proportion of the cinnabar phase increases only gradually. Figure 1(a) shows a pattern obtained at 2.00 GPa: The strongest reflections are still those of the ZB phase (as indexed)—as said, the sluggishness of the transition is much increased by the hydrostatic conditions. At the slightly higher pressure of 2.15 GPa [Fig. 1(b)], the cinnabar reflections have grown further at the expense of ZB and some extra reflections have appeared, as marked by arrows in the inset. These extra reflections become stronger with a further small increase in pressure to 2.25 GPa [Fig. 1(c)]—they are now visible in the full profile (as marked) as well as in the inset—and the ZB phase has almost all transformed. Above 2.25 GPa, the reflections from the new phase decrease in intensity, and above ~3.4 GPa the sample becomes single-phase cinnabar. On pressure decrease, the new phase is not observed at all; the cinnabar phase transforms directly back to the ZB phase at ~0.4 GPa. (This pressure of ~0.4 GPa is the same as was reported for the reverse transition in early studies [1], which would have been as “hydrostatic” on pressure decrease as the present study.)

It was found that the proportions of the ZB, new, and cinnabar phases could be varied by changing the rate of

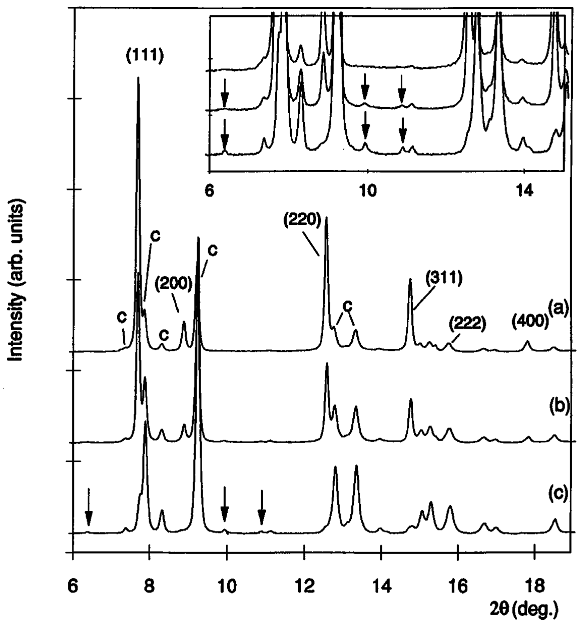

FIG. 1. Integrated powder-diffraction profiles from HgSe at (a) 2.00 GPa, (b) 2.15 GPa, and (c) 2.25 GPa. In profile (a), the reflections from the zinc blende phase are indexed, and those from the cinnabar phase are labeled “C” (up to $2\theta \sim 14°$). The inset shows the range up to $\sim 15°$ on an expanded intensity scale for the same three profiles. Arrows in the inset and in profile (c) mark reflections from the new phase.

increase of pressure. In particular, the amount of the new phase in the sample can be maximized by increasing pressure quite quickly to 2.25 GPa, and then maintaining this pressure for 2–3 days. This is illustrated in Fig. 2. Profile (a) was recorded soon after a sample reached 2.25 GPa. There is much more ZB than in Fig. 1(c), and the extra reflections of the new phase are just visible [their positions are marked by Δ below profile (f)]. Profiles (b) to (e) were recorded at intervals over the following 42 hours, and show the ZB reflections (indexed) decreasing in intensity, while the new-phase reflections grow and the cinnabar peaks (labeled “C”) remain constant. Profile (f) was recorded 34 h after (e), and shows no further change. There is thus a transition directly from ZB to the new phase, starting at 2.10(5) GPa. This phase is stable indefinitely up to 2.25(5) GPa, above which it transforms (sluggishly) to the cinnabar phase.

Closer examination of the profiles in Fig. 2 reveals that it is not only the intensities of the ZB peaks that change as a function of time, but also their apparent *positions*. This is most evident for the ZB (111) and (400) reflections, which are enlarged in the insets; they appear to shift to higher and lower 2θ values, respectively, with time. However, it is only the ZB peaks that exhibit this behavior; neither the extra peaks that arise from the new phase (those marked Δ in Fig. 2) nor the peaks from the cinnabar phase show any change in position with time. It seems clear that the apparent shift in ZB peak positions arises as a result of intensity transfer to new-phase peaks that have slightly different 2θ values. These peaks are marked with arrows below profile (f)—some in the main figure and some in the insets. They will no longer index to the ZB structure, and we conclude that this sample is a mixture of the new and cinnabar phases only: The ZB phase has all transformed.

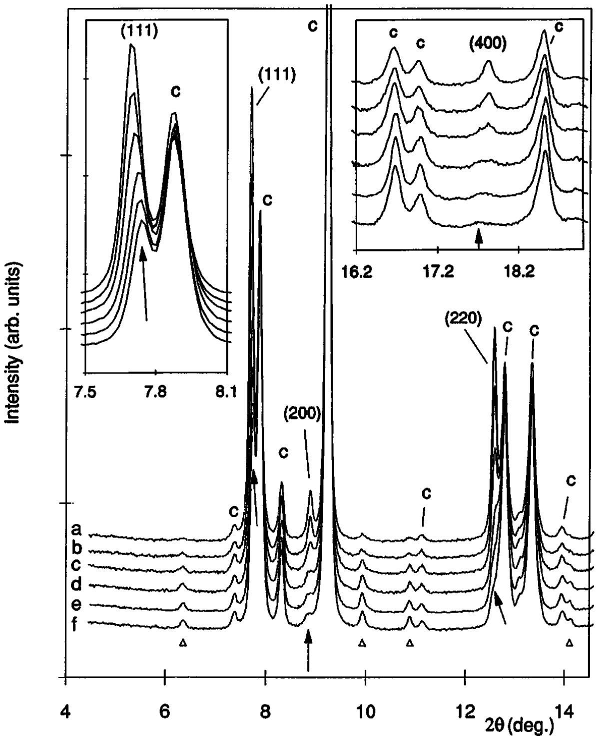

FIG. 2. Integrated powder-diffraction profiles from HgSe (a) on reaching a pressure of 2.25 GPa, and then 9, 20, 30, 42, and 76 h later in (b) to (f), respectively. The insets show the low-angle strong reflections on an expanded 2θ scale, and a higher-angle region around the zinc blende (400) reflection, for the same six profiles. The zinc blende reflections are indexed in profile (a), and the main cinnabar reflections are labeled “C.” The Δ symbols mark the extra reflections of the new phase, and the arrows mark new-phase reflections derived from the zinc blende reflections.

It can be seen that the arrowed reflections in Fig. 2(f) are very similar to the original ZB reflections in their relative intensities as well as their 2θ values. This suggests a close structural relationship between the two phases. Further support for this conclusion comes from the observation that a slight pressure reduction leads to a complete transformation of the new phase back to ZB. The lack of significant hysteresis is in marked contrast to the transition between ZB and the cinnabar phase, which involves a substantial structural rearrangement.

Ab initio indexing, using the program DICVOL [14], revealed that the positions of all 8 reflections marked in Fig. 2(f) could be accounted for by a C-face centered orthorhombic unit cell with approximate lattice parameters of $a = 5.98$ Å, $b = 5.89$ Å, and $c = 6.05$ Å. For a physically reasonable density, this unit cell must contain 8 atoms, the same as the ZB phase. From extrapolation, the lattice parameter of the ZB phase at 2.25 GPa is 5.997(5) Å. The volume decrease at the ZB to new-phase transition is therefore only $\sim 1.2\%$. This is considerably smaller than the volume change at the ZB to cinnabar transition [9.9(1)% at 1.80 GPa], and very much smaller than the volume change accompanying phase transitions on pressure increase from the ZB or diamond phases of other binary and elemental semiconductors, which are typically in the range $\sim 20\%$ [15].

Because the new phase can be observed only as a minority component in two-phase patterns, a definitive determination of the space group of the new structure is difficult. However, only $C222_1$ was found both to be consistent with the observed systematic absences *and* to allow an atomic arrangement at all similar to the ZB structure. With the Hg atoms on the 4(a) sites of $C222_1$ at $(x, 0, 0)$ and the Se atoms on the 4(b) sites at $(0, y, 1/4)$, the ZB structure is obtained when the lattice parameters are all equal $(a = b = c)$, $x = 0.25$, and $y = 0.25$. A more detailed account of the derivation of the space group, the structure solution, and tests of the uniqueness of the solution will be published separately [16].

The best fit to the mixed-phase profile at 2.25 GPa is shown in Fig. 3, in which the 8 reflections identified in Fig. 2(f) are indexed on the $C222_1$ unit cell (some in the inset). The refined lattice parameters for the $C222_1$ phase are $a = 5.992(1)$ Å, $b = 5.879(1)$ Å, and $c = 6.045(2)$ Å, with atomic coordinates $x(\mathrm{Hg}) = 0.302(1)$ and $y(\mathrm{Se}) = 0.207(2)$, and, for the cinnabar phase, $a = 4.174(1)$ Å, $c = 9.626(1)$ Å, and atomic coordinates $u(\mathrm{Hg}) = 0.666(1)$ and $v(\mathrm{Se}) = 0.540(1)$. To check the site ordering of this structure, trial refinements were also made with (i) a site-disordered model, with each site 50:50 occupied by Hg and Se, and (ii) a model in which the positions of the Hg and Se atoms were interchanged. Both gave significantly poorer fits to the data. The (002) reflection would be absent in a site-disordered structure, and is plainly present in recorded profiles [see also Fig. 2(f)]. The fit to the (201) reflection shown in the inset of Fig. 3 is with the site assignment as refined above. If Hg and Se are interchanged, most of the intensity appears instead in the (021) reflection—as shown in the second inset—and this clearly does not fit the data. The lattice parameters and atomic coordinates quoted above for the cinnabar phase in the mixed-phase refinement are the same within error as those given by a single-phase cinnabar sample at the same pressure [0.666(1) and 0.539(1)]—obtained on pressure decrease. This indicates that the $C222_1$ structure accounts well for all the noncinnabar features in the mixed-phase profile, including any that are overlapped by the cinnabar reflections [16].

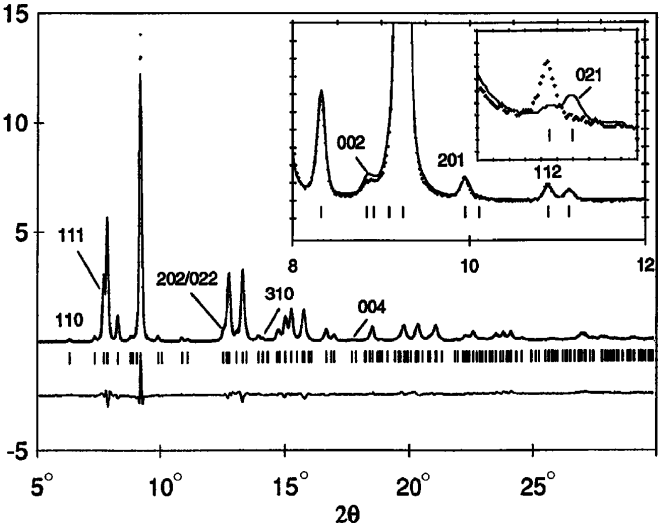

FIG. 3. Two-phase Rietveld fit to the HgSe profile in Fig. 2(f). The visible nonoverlapped $C222_1$ reflections are indexed; other reflections are from the cinnabar phase. The tick marks show the positions of all reflections allowed by symmetry in both phases. The difference between the observed (dots) and calculated (solid line) profiles is displayed below the tick marks. The region from $2\theta = 8°$ to $12°$ is enlarged in the inset; the second inset shows the best fit to the (201) and (021) reflections with the Hg and Se sites interchanged. Intensity scales are arbitrary.

In the light of these results for HgSe, we reexamined the ZB to cinnabar transition in HgTe, and found very similar behavior, except that the $C222_1$ phase appears at a slightly higher pressure. $C222_1$ reflections are first detectable at 2.25 GPa, and the rate of transformation from ZB is greatest at 2.40 GPa. Above that pressure, $C222_1$ transforms to cinnabar and has not been detected in any sample above ~ 3.6 GPa. Refinements of a mixed-phase profile at 2.55 GPa give $a = 6.295(2)$ Å, $b = 6.241(2)$ Å, and $c = 6.364(2)$ Å for the $C222_1$ component, with $x(\mathrm{Hg}) = 0.315(1)$ and $y(\mathrm{Te}) = 0.205(2)$. The distortion of the unit cell (from cubic) is less than in HgSe; also, the difference in scattering between Hg and Te is less than between Hg and Se. For these reasons, it is difficult to detect the (002) reflection or discriminate between the two different fits to (201)/(021) discussed for HgSe, and the site assignment cannot be conclusively tested. However, there is no reason or evidence to expect it to differ from that of HgSe.

The $C222_1$ structure of HgSe is fourfold coordinated, but each atom has two nearest neighbors at 2.580(8) Å, and the other two at 2.653(7) Å; the Se-Hg-Se angles range from 94° to 125°; and the Hg-Se-Hg angles range from 96° to 125°. Thus, though the structural arrangement is very much like that of ZB, the distortions from perfect tetrahedral coordination are considerable. (The distortions are similar in HgTe.) This is the first report of a distorted tetrahedral structure in any of the II-VI or II-V systems. Some structures of this type *are* known in silicon and germanium, namely, the BC8, R8, and ST12 phases obtained on pressure release [17,18]. Though their structures are quite different from $C222_1$, it is interesting to compare the magnitudes of their distortions. In BC8 silicon, the nearest-neighbor (nn) bond lengths are 2.306 and 2.392 Å, with bond angles of 99.2° and 117.9°—and the distortions of R8 silicon are very similar. In ST12 germanium, the nn bond lengths are 2.479, 2.486, and 2.489 Å, and the bond angles vary from 88.1° to 135.0°. These distortions are close to those observed in the $C222_1$ phase of HgSe (and HgTe), particularly for BC8 (and R8) silicon. However, as said, C222$_1$ is another quite different structure.

There is a closer and more remarkable structural relationship with the low-cristobalite phases of AlPO$_4$ and GaPO$_4$. These have the same space group as the C222$_1$ phases of HgSe and HgTe, and have similarly nearly cubic unit cells [7]. Moreover, the fractional coordinates $x(\mathrm{Al}) = 0.306$ and $y(\mathrm{P}) = 0.198$ in AlPO$_4$, and $x(\mathrm{Ga}) = 0.327$ and $y(\mathrm{P}) = 0.183$ in GaPO$_4$ [7] are strikingly similar to those found (above) for HgSe and HgTe. In the same way, the ambient-pressure ZB phase of HgSe and HgTe has the same spatial arrangement of atoms as the cations in the (idealized) high-cristobalite phase of AlPO$_4$ and GaPO$_4$ [8]. The ZB to C222$_1$ transition in HgSe and HgTe is thus analogous to a high-to-low cristobalite transition—a somewhat surprising and unexpected result. However, a relationship of this kind between a tetrahedrally coordinated semiconductor and a SiO$_2$ polymorph *has* been noted previously [19]. The spatial arrangement of the Si atoms in the keatite polymorph of SiO$_2$ [20] is almost identical to the ST12 polymorph of Ge [17]: both have the same space group, P4$_3$2$_1$2, with Si on the 4(a) and 8(b) sites at $(0.410, 0.410, 0)$ and $(0.326, 0.120, 0.248)$, respectively, in keatite [20], and the Ge atoms on the same sites at $(0.4088, 0.4088, 0)$ and $(0.3270, 0.1216, 0.2514)$ in ST12-Ge [17]. However, a relationship of this kind has never previously been reported for any of the II-VI or III-V systems. The new results for HgSe and HgTe suggest that the structures of SiO$_2$ and its polymorphs may provide a fruitful source of structural models for other high-pressure or metastable phase of the tetrahedrally coordinated semiconductors.

A crucial aspect of the ZB to C222$_1$ transitions in HgSe and HgTe is that they would not be observed but for the sluggishness of the ZB to cinnabar transitions. In this sense, we describe the ZB to C222$_1$ transitions as “hidden.” We note that they have all the characteristics of equilibrium transitions: they occur at definite, reproducible pressures; they give rise to a phase that is stable indefinitely over a definable range of pressure; and the structural change is reversible, with very little hysteresis. It is probable that the true equilibrium phase is cinnabar, but this need *not* be the case. We know of no other example of such transitions on pressure increase in the II-VI, III-V, or group IV semiconductors. But the possibility opens up the prospect of an interesting new class of high-pressure structures and phase transitions, and it may well prove fruitful to conduct experiments at low temperature where the sluggishness of reconstructive transitions will generally be enhanced.

In conclusion, we have found that the ZB phase of HgSe and HgTe transforms to a distorted-tetrahedral structure with C222$_1$ symmetry—not previously known in any of the II-VI or III-V semiconductors—at a pressure $\sim$1 GPa above that at which ZB becomes unstable against the cinnabar phase. The C222$_1$ phase can be observed only because of the sluggishness of the transition to cinnabar in these systems. The structural change is remarkably like that undergone by the cations at the high-to-low cristobalite transition in AlPO$_4$ and GaPO$_4$. This, and a similar relationship between ST12 germanium and the keatite polymorph of SiO$_2$, suggest that other SiO$_2$-type structures may be found in the elemental and binary semiconductors.

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