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Cinnabar phase in ZnSe at high pressure

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We have performed an energy-dispersive x-ray-diffraction experiment on $ZnSe_{1-x}Te_x$ alloys under high pressure with $x=0$, 0.05, 0.1, and 0.2. In the downstroke a hexagonal phase appears. We suggest that this phase is cinnabar, whose stability range decreases as the Te content is reduced. The analysis of the whole series of compositions enables us to establish its lattice parameters in ZnSe ($a=3.785$ Å and $c=8.844$ Å at 10.5 GPa). The extinction of some diffraction peaks also suggests that the internal parameters u and v are close to 0.5, indicating that the cinnabar phase in ZnSe is similar to that observed in GaAs and ZnTe.

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From a physical point of view, the structure of A^NB^{8-N} compounds can be considered as a consequence of the competition between the energy gain obtained by the formation of sp^3 bonds and the gain in Madelung energy due to a larger coordination number (CN). In zinc chalcogenides the ambient-pressure structure is either zinc blende or wurtzite, which are both tetrahedrally bonded and consequently fourfold coordinated (CN 4). When pressure is applied the covalent energy increases less rapidly in magnitude than the Madelung term, and semiconductors tend to augment their coordination number. ZnO transforms[1,2] from wurtzite to rocksalt (CN 6) at 9 GPa. ZnS in its zinc-blende form transforms towards the rocksalt structure at 15 GPa.[1,3–5] ZnSe transforms[1,6–7] from zinc blende to rocksalt at 13.5 GPa. The behavior of ZnTe is richer.[1] A combined extended x-ray-absorption fine structure (EXAFS) and energy-dispersive x-ray diffraction (EDXRD) experiment proposed the transformation from zinc blende to cinnabar at 9.5 GPa.[8,9] Cinnabar is the name given to the α form of HgS, stable in ambient conditions, with space group $P3_121$ and whose atoms occupy Wyckoff positions $3(a)$ $(u,0,1/3)$ and $3(b)$ $(v,0,5/6)$. In fact, different values of u and v describe very different structures, with CN ranging from 2 (HgS at ambient pressure[10,11]) to 4 (HgTe and CdTe at high pressure[12,13]) and 6 (rocksalt, given by $c/a=\sqrt{6}$ and $u=v=2/3$). Cinnabar structure appears then[9] as an intermediate structure between the fourfold- and sixfold-coordinated phases in heavy II-VI compounds and even in one III-V compound, GaAs (Ref. 14). Using angle-dispersive x-ray-diffraction (ADXRD), the authors in Refs. 15 and 16 confirmed the existence of a cinnabar phase in ZnTe, with internal coordinates $u(\mathrm{Zn})=0.540$ and $v(\mathrm{Te})=0.504$. A rigorous search was made in ZnS (Ref. 4) along the 300-K isotherm, between 11.4 and 14.5 GPa, to look for an indication of the cinnabar phase, with negative results. In Ref. 1 it is stated that no cinnabar structure was ever observed in ZnSe on either pressure increase or decrease. On the opposite, on the basis of optical measurements, the authors in Ref. 17 claim the existence of a new phase between the zinc-blende and rocksalt phases, which is observed in the upstroke, but they do not give any structural characterization.

In parallel with the experimental research, a number of theoretical investigations on the stability of the cinnabar structure have been performed.[18–22] The presence of localized cation d electrons in the valence band makes the computations for II–VI semiconductors rather demanding.[18,21] The calculations result in similar total energies for the tested structures, so the establishment of the high-pressure systematic is very difficult. In addition, the presence of energy barriers can hinder some phase transitions. The authors in Refs. 19–21, using a pseudopotential method, found that the cinnabar phase is unstable in ZnS and ZnSe. Their calculations[19] yield a lower energy for the SC16 (simple cubic with a 16-atom base) phase with respect to the cinnabar phase and suggest that SC16 would be the thermodynamically stable phase of ZnSe between 9.2 and 16.4 GPa. On the opposite, a pseudopotential calculation carried out in Ref. 18 found that the cinnabar phase in ZnSe is stable from 10.3 to 13.4 GPa. They suggest that, as the stability of the cinnabar phase depends on total energy variations of the order of the precision achieved in the calculations, it may be metastable and should be searched for in the downstroke.

In this paper we present evidence of the existence of the cinnabar structure in ZnSe. Our conclusions are derived from EDXRD experiments carried out on the $ZnSe_{1-x}Te_x$ alloy and pure ZnSe under high pressure.

EDXRD experiments were performed at the DW11 wiggler station of DCI in LURE (Laboratoire pour l'Utilisation du Rayonnement Électromagnétique, Orsay, France). The polychromatic x-ray beam was collimated down to 80

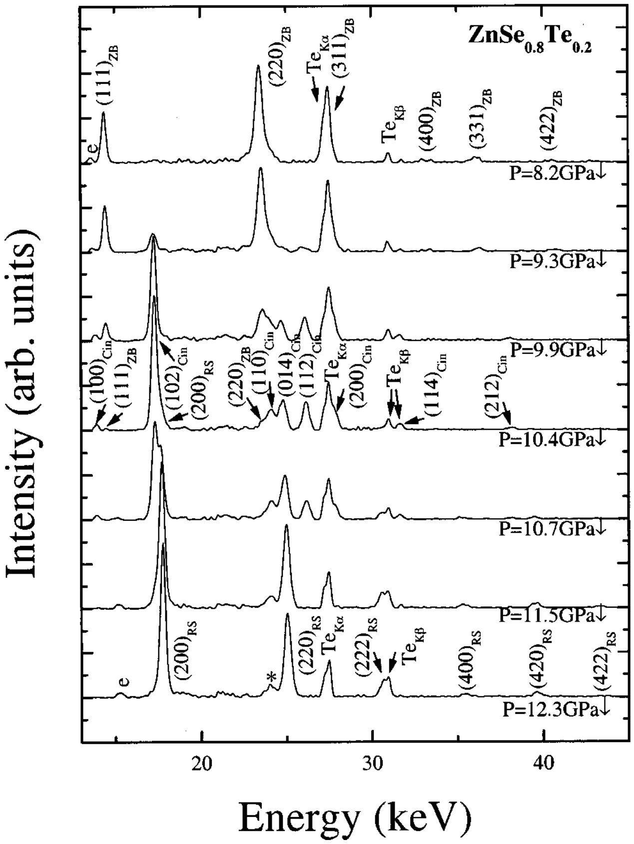

FIG. 1. Downstroke EDXRD spectra of $ZnSe_{0.8}Te_{0.2}$. Here *e* means escape peak. The peak marked $*$ is due to the gasket. ↓ means downstroke.

$\times 80\,\mu m^2$, and the diffraction angle was fixed at $2\theta = 15.5°$. The collimated diffracted beam was detected with a Ge solid-state detector. The samples studied correspond to nominal Te concentrations given by $x=0$, 0.05, 0.10, and 0.20. The samples were grown using a vapor phase transport method and then reduced to powder. All the spectra were taken at room temperature. We used a diamond anvil cell to generate pressure. A 16:3:1 methanol/ethanol/water mixture was used as pressure transmitting medium. This mixture transits to a glass phase at a pressure[23] of 14.5 GPa and should remain hydrostatic at lower pressures. The pressure was measured using the linear ruby fluorescence scale.

All the studied samples show similar behavior under high pressure. In the upstroke the samples undergo the well-known zinc-blende–rocksalt phase transformation. In spite of a careful search, no evidence of a new phase has been found in the upstroke, contrary to the results of Ref. 17. In the downstroke, however, a new high-pressure phase appears. The existence of this phase is more clearly appreciated in the spectra corresponding to the sample with the highest Te content, $ZnSe_{0.8}Te_{0.2}$ (Fig. 1). The analysis of the EDXRD pattern indicates that the new phase has hexagonal symmetry, with $a = 3.829$ Å and $c = 8.996$ Å at 10.4 GPa. In Fig. 1 we present the indexing of the new phase. By comparison with ZnTe (see Table I), we propose that the new phase observed has the cinnabar structure. Indeed, direct indexing of diffraction peaks gives $c' = c/2 = 4.498$ Å. We have doubled the unit cell size, arguing that diffraction peaks like (003), which depend on the difference of scattering power between the anion and cation, are missing due to the similar atomic number of Zn and Se. In fact, (*hkl*) peaks with $h+k+l = 2\times(2n+1)$ in zinc blende and $h+k+l = 2n+1$ in rocksalt are absent for the same reason. The cinnabar phase is not strictly isolated in any of the obtained spectra. In $ZnSe_{0.8}Te_{0.2}$ at 10.4 GPa (Fig. 1) there are slight, but observable, remains of the high-pressure rocksalt phase. At 9.9 GPa the zinc-blende phase clearly appears. In the composition range studied, the cinnabar range of existence diminishes as the Te content is reduced (Table I), but study of the series of compositions have let us follow the presence of the cinnabar structure in the downstroke. We should stress that, although the most characteristic diffraction peaks coming from the cinnabar structure, (102) and (112), are clearly observable in ZnSe (Fig. 2), without an analysis of the whole series of compositions it would have been very difficult to establish its lattice parameters.

TABLE I. Stability range of the cinnabar phase, its cell parameters, the c/a ratio, and the change in specific volume at the zinc-blende–cinnabar and cinnabar-rocksalt phase transitions. ↑ means upstroke and ↓ downstroke.

	Pressure range (GPa)	a at 10.5 GPa (Å)	c at 10.5 GPa (Å)	c/a at 10.5 GPa	$\Delta V/V$ ZB→Cin	$\Delta V/V$ Cin→RS
ZnSe	10.1–10.9↓	3.785	8.844	2.34	9.8%	6.3%
	10.2–13.4[a]			2.26[a]	9.2%[a]	7.7%[a]
$ZnSe_{0.95}Te_{0.05}$	9.9–12.6↓	3.823	8.833	2.31	9.3%	7.2%
$ZnSe_{0.90}Te_{0.10}$	10–13.4↓	3.824	8.889	2.32	9.2%	6.9%
$ZnSe_{0.80}Te_{0.20}$	9.3–11.5↓	3.825	8.998	2.35	9.5%	5.5%
ZnTe	8.9–11.0↑[a]	4.105[b,c]	9.397[b,c]	2.29[b,c]		
	9.5–12.0↑[d]	4.066[d,e]	9.25[d,e]	2.27[d,e]	13%[d]	

[a] Theoretical. See Ref. 18.
[b] Experimental. See Ref 16.
[c] At 8.9 GPa.
[d] Experimental. See Ref. 8.
[e] At 11.7 GPa.

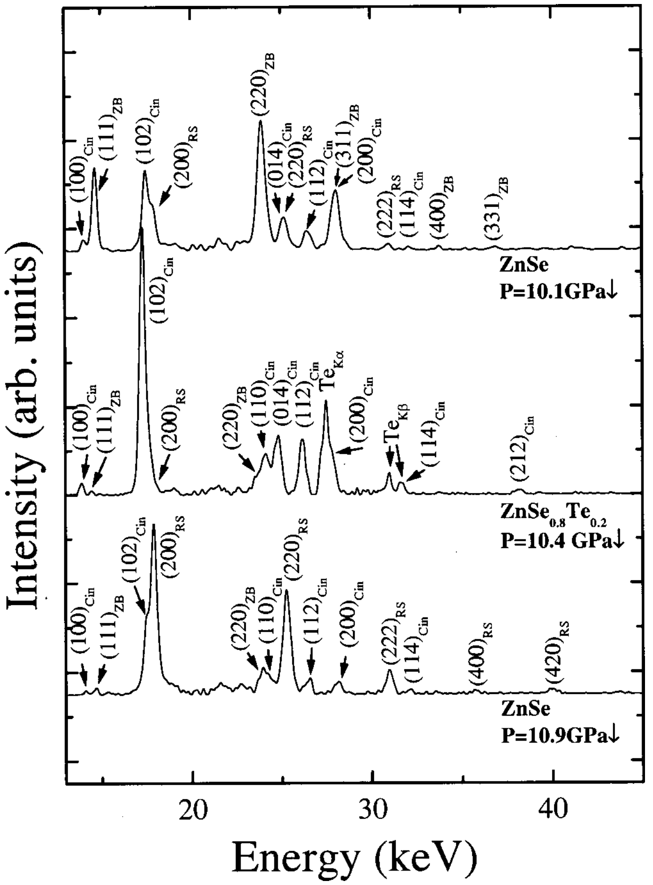

FIG. 2. Comparison of the downstroke EDXRD spectra of $ZnSe_{0.8}Te_{0.2}$ and ZnSe. Here *e* means escape peak. The peak marked $*$ is due to the gasket. ↓ means downstroke.

In Fig. 3 we show the pressure dependence of the volume in ZnSe. In the zinc-blende phase it can be described with a Murnaghan equation of state, resulting in an isothermal bulk modulus of $B_0(\mathrm{ZB}) = 58 \pm 3$ GPa, with its pressure derivative given by $B'(\mathrm{ZB}) = 5.5 \pm 0.5$. The errors given in the B_0 and B' values are statistic. In the pressure range studied the rocksalt dependence of volume with pressure is almost linear, so it is very difficult to obtain B_0 and B' simultaneously. With $B'(\mathrm{RS})$ fixed to 5.5 the Murnaghan fit yields $B_0(\mathrm{RS}) = 54 \pm 2$ GPa.

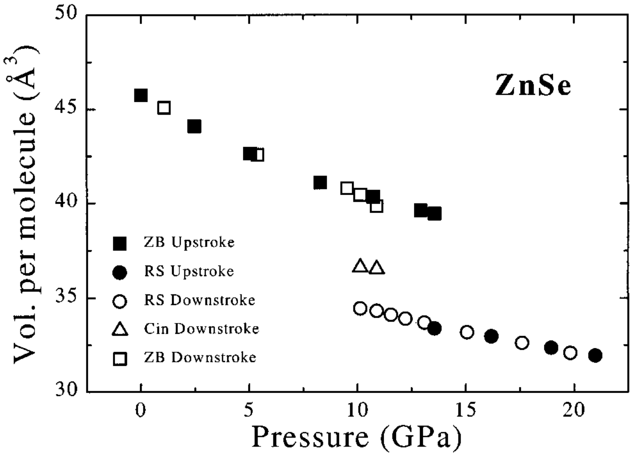

FIG. 3. Equation of state of ZnSe.

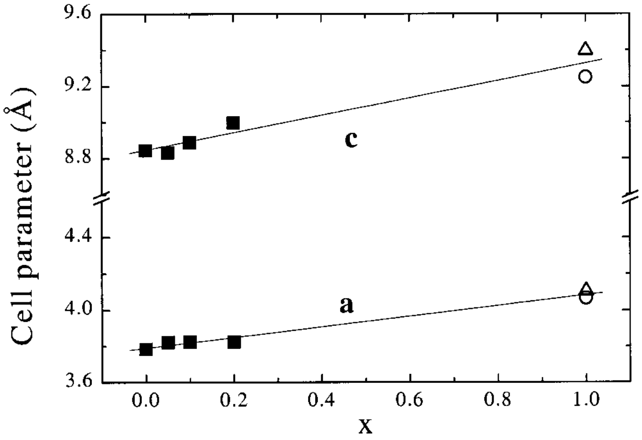

FIG. 4. Variation of the cinnabar cell parameters with composition (x). Solid squares correspond to a pressure of 10.5 GPa. Hollow triangles and circles represent, respectively, data at 8.9 GPa from Ref. 16 and at 11.7 GPa from Ref. 8.

The volume collapse at the zinc-blende–cinnabar and cinnabar-rocksalt phase transitions in ZnSe is 9.8% and 6.3%, respectively (see Table I). Our results agree with the pseudopotential calculation carried out in Ref. 18, which gives 9.2% and 7.7%. The experimental c/a ratio falls in the interval 2.31–2.35 in all the studied samples, whereas the pseudopotential method results in a c/a ratio of 2.26. As in ZnTe and CdTe, the pseudopotential method slightly underestimates the c/a ratio.

The composition dependence of the lattice parameter in the zinc-blende and rocksalt phases is strictly linear. In Fig. 4 we have represented the cinnabar a and c axes for the different compositions studied. Solid squares correspond to a pressure of 10.5 GPa. Hollow triangles and circles represent data at 8.9 GPa (Ref. 16) and 11.7 GPa (Ref. 8). Within experimental precision, the evolution of the a and c axes in cinnabar is also linear with composition.

The reflection intensities in an EDXRD experiment are distorted by the complex diffusion background, different absorption of the experimental system at different energies, the presence of supplementary peaks (as fluorescence peaks), grain statistics, and, in the present case, phase mixtures. A Rietveld refinement of an EDXRD spectrum is then very questionable. Nevertheless, with the aim of extracting qualitative information about the unit cell structure, we have employed the program FULLPROF (Ref. 24) to simulate the diffraction pattern corresponding to the cinnabar structure. We used two strategies to determine the internal parameters. In the first approach we introduced in the simulation the internal parameters resulting from the pseudopotential calculation carried out in Ref. 18, $u = v = 0.5$. We obtained qualitative agreement with the experimental diffraction intensities. In the second approach we supposed that the evolution of first-neighbor distances in ZnSe throughout the phase transitions is similar to the sequence observed in HgTe (Ref. 12) and CdTe (Ref. 13), where on the one hand the first-neighbor distances in the zinc-blende and cinnabar phases are nearly equal just before the phase transition, and on the other hand the first neighbor distance in the high-pressure phase and the next-neighbor distance in the cinnabar phase are almost identical. From the first- and next-neighbor distances in cinnabar we calculated the internal parameters, obtaining $u=0.63$ and $v=0.55$. The introduction of these parameters in the diffraction pattern simulation did not yield intensities which agree with the experimental spectra. In particular, the (202) reflection resulted in being as intense as the (112) one, but it is not observed experimentally. We conclude that the ZnSe cinnabar structure may be close to the GaAs and ZnTe one,[14–16] where the internal parameters are near 0.5 and as a consequence the coordination may be close to fourfold.

In this paper we have shown that there is evidence of a new high-pressure phase in ZnSe, which is observable in the downstroke. Analysis of the EDXRD spectra corresponding to $ZnSe_{1-x}Te_x$ has let us establish its lattice parameters and suggest that the observed phase is cinnabar.

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