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PRECURSOR EFFECTS OF THE RHOMBOHEDRAL-TO-CUBIC PHASE TRANSITION IN INDIUM SELENIDE

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We report on the observation of precursor effects of the rhombohedral-to-cubic phase transition in Indium Selenide (InSe) with several experimental techniques. The pressure at which these precursor defects are first observed depends on the sensitivity of the experimental technique. In transport measurements, which are very sensitive to low defect concentrations, precursor effects are observed 5 to 6 GPa below the phase transition pressure whereas in X-ray diffraction measurements precursor effects are only observed 2 GPa below the phase transition pressure. We report optical absorption measurements, in which the precursor effects are shown by the growth and propagation of dark linear defects appearing 3 GPa below the phase transition pressure. On the base of a simple model of the stress field around edge dislocations, we attribute the darkening of the InSe samples to local phase transitions to a high-pressure modification along linear dislocations. These results agree with room-pressure and high-pressure Raman spectra of samples compressed up to 7–8 GPa, which show new phonon lines not corresponding to the low-pressure phase.

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INTRODUCTION

Indium Selenide is a layered semiconductor of the III–VI family and, like GaSe and GaS, presents an anisotropic structure with strong covalent bonds inside the layers and much weaker van der Waals type bonding between the layers. This bonding anisotropy leads to the existence of polytypes with different stacking sequences and to the observation of mixtures of polytypes separated by stacking faults. These characteristics promote the formation of high densities of both native and extrinsic defects which are mainly composed of screw and edge

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dislocations [1]. InSe overcomes a phase transition from the semi-conducting rhombohedral to the metallic rocksalt phase around 10 GPa at room temperature [2] and a high-pressure phase transition to a monoclinic InS-type structure has been reported at high temperatures [3].

In this work, we show that the phase transition in InSe at room temperature is preceded by precursor effects that can be measured at different pressures (well below the phase transition pressure) depending on the sensitivity of the experimental technique. These precursor effects likely correspond to local transformations of the sample into a modification of the high-pressure phase.

EXPERIMENTAL PROCEDURE

γ-InSe single crystals used in our experiments were cleaved from the ingot which was grown by the Bridgman method from a $In_{1.05}Se_{0.95}$ melt. Dislocation densities present in the material are expected to be lower than $10^{10}\,cm^{-2}$ [1]. For transport measurements under pressure, 100-μm thick samples with 2–4 mm^2 in size were placed in a Bridgman-type cell with pyrophyllite gaskets and NaCl as a pressure-transmitting medium. Silver leads through the gaskets were used to have electric access to both the sample and the manganine pressure sensor [5]. For optical measurements under pressure, samples of 1 to 30-μm thick and $100 \times 100\,\mu m^2$ in size were placed inside a diamond anvil cell (DAC) with a 4:1 methanol-ethanol mixture as a pressure-transmitting medium and a ruby chip for pressure calibration [6]. For Raman scattering and X-ray diffraction measurements at ambient pressure, several samples (0.5 mm thick and $3 \times 3\,mm^2$ in size) were compressed in a Paris-Edinburgh cell at pressures ranging from 6 to 10 GPa, using NaCl as a pressure transmitting medium.

RESULTS AND DISCUSSION

Transport measurements performed in InSe under pressure report an intrinsic reversible decrease of the free carrier concentration in InSe up to 3 GPa and an irreversible decrease of the resistivity above 4 GPa, *i.e.*, 6 GPa below the phase transition pressure to the metallic rocksalt phase [5]. Besides, a decrease of the resistivity has been observed in GaSe at 20 GPa, 5 GPa below the phase transition pressure [9]. The reversible increase of the resistivity in *n*-InSe by three orders of magnitude before the appearance of irreversible changes indicates that transport measurements are very sensitive to small concentrations of defects. As the high-pressure rocksalt phase of InSe and GaSe is metallic, it is reasonable to relate the irreversible decrease of the resistivity to precursor effects of the high-pressure phase transition due to the appearance of some kind of structural instability, as noted by previous authors [5].

In optical measurements of InSe under pressure, dark linear defects (DLD) appear and propagate through the crystal as pressure increases above 7 GPa resulting in a complete blackening of the sample at 9 GPa as shown in Figure 1. Some DLD end at the border of the sample while others do not end at the border because of the crossing of defects which form angles of 60° and 120° that show the hexagonal symmetry of the crystal. The darkening of some III–VI layered samples before the phase transition pressure, as measured by X-ray diffraction measurements, has been already observed in InSe above 6.5 GPa [4] and in GaSe above 13.6–15 GPa [7, 8], however no discussion has been devoted to the appearance or the nature of these precursor defects.

In order to understand the formation of DLD we have analyzed the role of dislocations in phase transitions. The reason for this procedure is that dislocations are regions with a gradi-

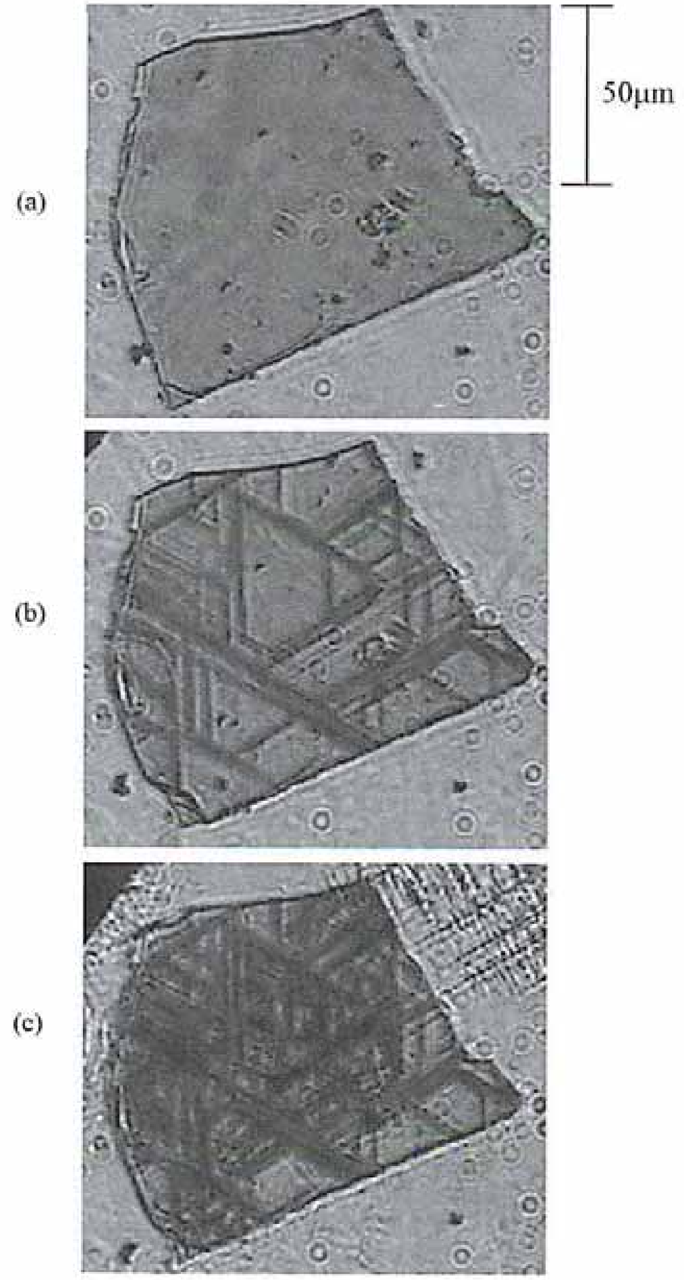

FIGURE 1 Photographs of a 1-μm thick InSe sample at different pressures below the rhombohedral-to-rocksalt phase transition. The appearance of the sample around 1 GPa (a) changes once the precursor defects appear due to local phase transitions around dislocations above 7 GPa (b). The local phase transition propagates through the whole crystal with increasing pressure as can be observed in the sample at 8 GPa (c).

ent of internal stress that: (1) attract structural defects and interstitial atoms, (2) allow the relaxation of tensions inside the solid, thus controlling the deformation processes, and (3) allow the match between different structural phases in a crystal [10]. Usually, dislocations already present at ambient pressure become stable and fixed at high pressures; however, the stress accumulated in dislocations could be delivered by the shift of the layers producing stacking faults along the direction perpendicular to the layers and leading to the crossing of dislocations of different layers. Therefore, the propagation of a dislocation ought to end at the border of the sample unless the crossing with other dislocations prevent it, thus leading to the observation of angles revealing the symmetry of the crystal. In this sense, we think that the location of DLD along dislocations in InSe would explain why DLD with little extension end at the crossing with other defects and form angles of 60° or 120°, and why DLD with bigger extension continue its propagation along the crystal till the border of the sample. Following the above reasoning, the observation of DLD suggests that a phase transition to an opaque phase has occurred along the edge dislocations. This hypothesis is coherent with the presence of a stress field around edge dislocations that leads to an extra compression above the gliding plane and to an extra tension below the gliding plane. The effective pressures of tension and compression around the edge dislocation are given by [10]

$$P = \frac{1}{3\pi}\frac{(1+v)}{(1-v)}G\frac{b\,y}{x^2+y^2} \tag{1}$$

where b is the Burgers' vector modulus, G is the shear modulus and v is the Poisson's coefficient. In order to avoid the singularity at $x = y = 0$ and to fulfil the condition that $P > 0$ at $y > 0$ and $P < 0$ at $y < 0$, we have added a term ε^2 in the denominator of Eq. (1) and neglected the effect in the x axis because direction y is that of the perpendicular plane to the direction of the propagation of the dislocation. In such case, we obtain the following pressure profile around an edge dislocation

$$P = \frac{1}{3\pi}\frac{(1+v)}{(1-v)}G\frac{b\,y}{\varepsilon^2+y^2} \tag{2}$$

Assuming that ε has a value similar to that of the Burgers' vector modulus b, we obtain a maximum and minimum pressure around the dislocation of $P \approx \pm G/10$ at $y = \pm\varepsilon$. In a layered crystal like InSe we assume that the axis of the edge dislocation is contained in the layer plane (perpendicular to the c axis). Then the value of the shear modulus is $G = C_{13} = C_{23} = 32 \pm 2$ GPa [11] and we obtain that the maximum overpressure around an edge dislocation is around 3.2 ± 0.2 GPa. This result suggests that local transitions of the material (along dislocations) to the rocksalt phase should occur about 3 GPa below the phase transition pressure; *i.e.*, around 7 GPa in InSe in agreement with the observation of DLD above this pressure. The present mechanism occurs due to the presence of edge dislocations in the as-grown material and is relatively independent of the dislocation density of the starting material. In this sense, after the transition occurs in a dislocation at high pressure, relaxation of tensions around such dislocation lead to the formation of more dislocations. On the other hand, no contribution to the local phase transition is expected from the screw dislocations because elastic distortion around these defects contains no tensile or compressive components.

The occurrence local phase transitions above 7 GPa in InSe is also supported by high-pressure Raman, X-ray diffraction and XANES measurements. Figure 2 shows room-pressure X-ray diffraction measurements in InSe samples pressurized up to different pressures. The presence of precursor defects may be inferred from the high degree of disorder revealed by the widening of the 003 × n diffraction peaks in samples pressurized to 110 T (8.5 GPa) and 130 T (9.5 GPa) as compared with those of the sample pressurized to 90 T (7.5 GPa). Figure 3 shows the Raman spectrum taken at room pressure in a sample before and after

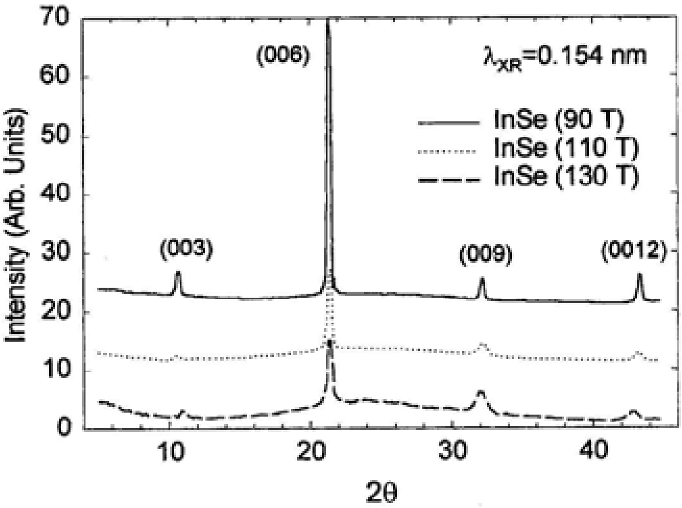

FIGURE 2 Room-pressure X-ray diffraction spectra of InSe samples after compression at 90 T (solid line), 110 T (dotted line), and 130 T (dashed line). The 003 × *n* diffraction peaks are broader in the samples compressed to 110 and 130 T than in the sample compressed to 90 T.

compression up to 7.5 GPa. A new phonon line D, which does not correspond to the initial phase, appears between the A_1 and the E modes of lower energy. This mode was also observed by Ulrich *et al.* [4] and attributed to a local vibrational mode associated with precursor defects of the high-pressure phase transition. This mode agrees in frequency with the most intense phonon mode in the InSe sample transited to the monoclinic InS-type structure at pressures above 4 GPa after heating above 250 °C [3]. As the InS-type structure of InSe has been reported to be quenched at ambient pressure and the defect mode observed by Ulrich *et al.* and us appears above 7 GPa and remained at ambient pressure on downstroke,

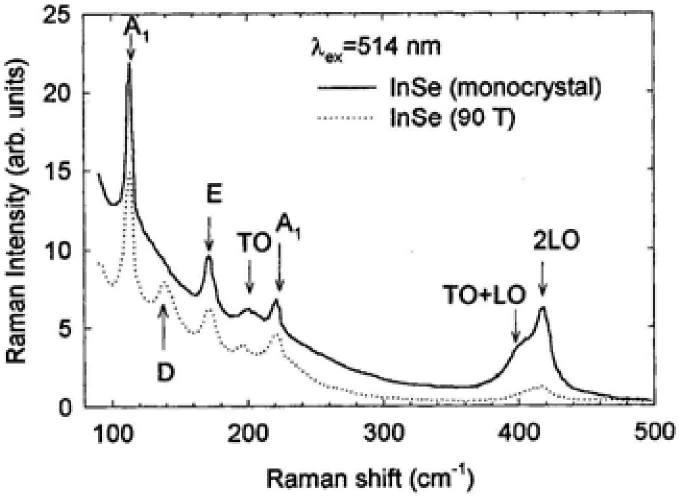

FIGURE 3 Room-pressure Raman spectrum of a sample of InSe before (solid line) and after pressurisation at 90 T (dotted line). A new peak D at 140 cm^{-1}, not corresponding to the rhombohedral phase, is observed in the pressurised sample.

we think that new Raman mode could be related to the DLD. These dark regions could be of monoclinic InS-type structure, which is an intermediate phase between the rhombohedral and the cubic rocksalt phase of InSe and has an atomic coordination number closer to the NaCl structure. In this sense, recent high-pressure XANES measurements in InSe indicate that at 7 GPa the proportion of the material with long range order corresponding to a sixfold coordination is 12% [12].

In summary, the rhombohedral-to-cubic phase transition in InSe at room temperature is preceded by precursor effects whose presence can be measured at different pressures depending on the sensitivity of the experimental technique. We attribute the irreversible increase of the resistivity above 4 GPa to formation of defects due to local transitions from fourfold to sixfold coordination. We attribute the appearing of DLD and a new mode in the Raman spectrum above 7 GPa to the appearance of a long range order phase with sixfold symmetry due to the phase transitions of extended regions along edge dislocations. These transitions are likely to a phase which is a distortion of the rocksalt phase similar to that of the monoclinic InS-type structure.

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