# Brief Reports

## Pressure-induced metallization of ZnSe

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(Received 17 June 1994; revised manuscript received 15 August 1994)

High-pressure studies of the resistivity $R$ of the direct-gap insulator ZnSe were carried out using diamond-anvil cells. The pressure dependence $R(P)$ at 300 K in the pressure range of 0–20 GPa revealed a drastic drop in the resistance at $P = 13.5$ GPa and upon decompression recovery of the insulating state at 10.5 GPa. From the temperature dependence of the resistance at $P > 13.5$ GPa it has been concluded that (i) narrow-gap semiconducting and metallic phases coexist in the range 13.5–15 GPa, and (ii) a pure metallic state, characterized by a positive temperature slope and small resistivity value, exists at $P > 17$ GPa. The results are discussed in terms of previous optical data and band-structure calculations.

## INTRODUCTION

Structural and electronic properties of ZnSe and other analogous chalcogenides have been the subject of high-pressure studies for the last three decades. Zinc selenide, a direct-gap semiconductor with its zinc-blende structure and a wide band gap ($E_g = 2.7$ eV) exhibits interesting behavior under pressure. As early as 1961, Samara and Drickamer[1] invoked a phase transition to explain their observed drastic drop in the resistivity at $P = 16.5$ GPa. Later, Tiong et al.[2] using modern pressure calibration points reported the same phenomenon at 13 GPa. Smith and Martin[3] showed that at 13.5 GPa ZnSe undergoes a crystallographic phase transition from a fourfold coordination zinc-blende structure to a sixfold coordination rocksalt-type structure (fcc). The deduced lattice parameter of the high-pressure phase was 5.08 Å corresponding to a volume decrease of 28% relative to the zinc-blende structure at 12 GPa. Recent studies by Köfferlein[4] confirmed this structural transition but assigned a lattice parameter of 5.308 Å to the NaCl structure corresponding to a volume decrease of 15% at the transition.

High-pressure optical studies by Ves et al.[5] within the zinc-blende structure regime showed that the direct energy gap $E_g \sim 2.7$ eV at ambient $P$, corresponding to the $\Gamma_{15}^v \rightarrow \Gamma_1^c$ transition, *increases* monotonically and reaches a value of 3.4 eV at 12 GPa. This corresponds to a gap increase of 25% as the interatomic spacing is reduced in the measured pressure range. At 13.5 GPa the sample became opaque abruptly over the full range of photon energies ($\hbar\omega \geq 1.5$ eV) accessible to their experimental setup.

There is a consensus today that the sharp drop in $R(P)$ concurs with the onset of the structural phase transition at 13.5 GPa. It has been inferred that ZnSe in the high-pressure rocksalt-type structure is *metallic* both from the large abrupt change in $R$ at the transition ($\Delta R \sim 10^6$ $\Omega$) and the saturation of $R(P)$ beyond the structural transition.[1] Yet no experimental evidence has ever been presented to substantiate this conclusion. On the contrary, two experimental groups[5,6] speculated and a theoretical study by Andreoni and Maschke[7] implied, that a transition into a new *semiconductor* phase occurs albeit with a reduced $E_g$ (1.1 eV). This result has not been confirmed experimentally. In this study we provide *experimental* evidence for the occurrence of a metallic state in the high-pressure rocksalt-type phase of ZnSe.

## EXPERIMENT

The definitive way to establish whether the high-pressure phase is metallic is to study the temperature dependence of the resistance. Resistance measurements under variable pressure and temperature conditions were carried out using the *Tel-Aviv University* miniature diamond-anvil cell.[8] The powder sample, obtained from a high purity ZnSe ingot, was inserted without any pressure medium into a 400-$\mu$m-diam 30-$\mu$m-thick cavity drilled in a $Ta_{0.9}W_{0.1}$ metal gasket coated with insulating $Al_2O_3$. Pressure was calibrated with the ruby-fluorescence method[9] and the pressure distribution was obtained by scanning the fluorescence of the various ruby chips within the sample. The pressure gradient was less than 0.5 GPa as deduced from the pressure distribution.

Electrodes were 10-$\mu$m-thick gold wires in the quasi-four-probe configuration with distances of 50 $\mu$m between the contacts. Temperature-dependent studies of the resistance, $R(T)$, have been performed in a He storage dewar by using a conventional *dip-stick* arrangement. Temperatures were measured by using a miniature Si-diode thermometer in close proximity to the anvils. Measurements were carried out on two samples.

## RESULTS

The pressure dependence of the resistance at room temperature is shown in Fig. 1. At $\sim$13.5 GPa one clearly observes the sudden drop in the resistance, the transition coinciding with the onset of the rocksalt structure.

Upon decompression, following a hysteresis cycle, the insulating zinc-blende structure phase is recovered at 10.5 GPa. These results are similar to recent studies of Tiong et al.,[2] where a split-sphere pressure cell was used for generating pressures to 15 GPa.

The $R(T)$ curves for various pressure values above 13.5 GPa are shown in Fig. 2 where the new rocksalt-type structure constitutes the majority phase. For a semiconductor one expects $R_{sm}(T) \sim \exp(E_g/kT)$, namely a *negative* $R(T)$ slope. For metallic behavior $R_m(T) \sim T$, and a *positive* $R(T)$ slope is expected. The curves in Fig. 2 depict the transition from a *mixed* state (multiphase coexistence in the range 13.5–16 GPa) into a pure metallic phase at $P > 17$ GPa. The temperature dependence of $R(T)$ for the mixed state may be attributed to the sum of two contributions:

$$R(T) = fR_{sm}(T) + (1-f)R_m(T) , \qquad (1)$$

where $f$ is the fraction of semiconducting phase. The precipitous drop in resistivity at the structural transition suggests that at the onset of the high-pressure phase of ZnSe any semiconducting contribution must have a narrow gap.
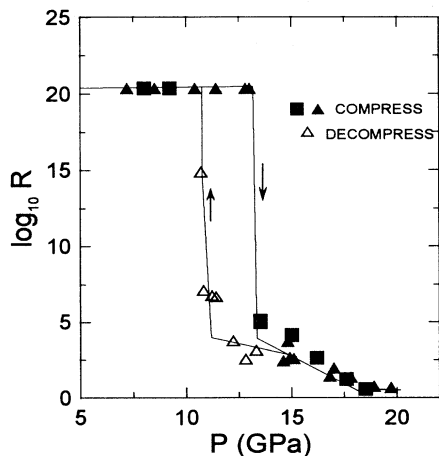


FIG. 1. The pressure dependence of the resistance in ohms measured at 300 K. The solid line is to guide the eye. The arrows indicate the direction of compression and decompression. Symbols ▲■ correspond to data obtained from two different samples.
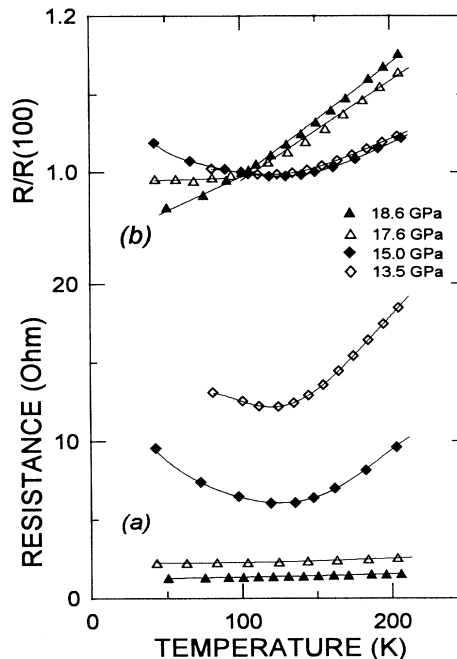


FIG. 2. Temperature dependence of the resistance for various pressures above the phase transition. (a) Absolute values of $R(T)$ for $13.5 < P < 18.6$ GPa. (b) $R(T)$ normalized at 100 K. The minimum in $R(T)$ for 13.5 and 15.0 GPa is attributed to the coexistence of metallic and semiconducting regions both having phases with the rocksalt-type structure. The solid line is to guide the eye.

A linear relation,

$$R = R_0(1 + \alpha T) \qquad (2)$$

has been fitted to the $R(T)$ data for $P \geq 17.6$ GPa and $T \geq 100$ K. The fitted results of the temperature coefficient $\alpha$, estimated resistivity ($\rho$) at 300 K and selected representative values of three metals are tabulated in Table I.

## DISCUSSION AND CONCLUSIONS

At $P > 15$ GPa, $\sim$2 GPa higher than the onset of the rocksalt structure of ZnSe, $R(T)$ shows a definite positive temperature slope. In addition, the estimated value of $\rho$ at 300 K corresponds to that of a typical metal. Therefore the present measurements show unequivocally that the high-pressure phase of ZnSe at $P > 15$ GPa is metal-

TABLE I. Fitted values of the temperature coefficient $\alpha$, the resistivity of the high-pressure phase of ZnSe and of other metals at ambient pressure. The errors in the last figure are shown in parentheses.

| Metal | Pressure | $\alpha$ ($10^{-3}$ K) | $\rho$ ($\mu\Omega$ cm) |
|-------|----------|------------------------|-------------------------|
| ZnSe  | 17.6 GPa | 1.01(5)                | 16(8)                   |
| ZnSe  | 18.6 GPa | 1.68(5)                | 12(8)                   |
| Cu    | 0.1 MPa  | 3.93                   | 1.7                     |
| Au    | 0.1 MPa  | 8.3                    | 2.4                     |
| Sb    | 0.1 MPa  | 3.6                    | 42                      |

lic. In the range 13–15 GPa both semiconducting and metallic phases coexist and $R(T)$ has a weighted contribution from these two phases. The semiconducting state in this pressure range is characterized by an energy gap which is considerably smaller than that of the low-pressure zinc-blend phase, as deduced from the precipitous change in $R$ at 13.5 GPa, (see Fig. 1). Therefore at $\sim 13.5$ GPa where the rocksalt structure first appears, we suggest that a new semiconducting phase is formed which exists in a pressure range of about 13.5–17 GPa, beyond which there is metallization due to gap closure. The short pressure range of existence ($\sim 3$ GPa) and the drastic reduction of $R$ in Fig. 1 are suggestive of a new narrow-gap semiconducting state.

The existence of a semiconducting phase of ZnSe with the rocksalt structure has previously been proposed by Andreoni and Maschke.[7] Their self-consistent pseudopotential study of the pressure-induced structural transition predicted the formation of a new semiconducting state with a rocksalt structure and an indirect gap $E_g = 1.1$ eV. However, our results suggest that the energy gap is considerably smaller than that of the theoretical prediction. The study in Ref. 7 also showed that the electron density around Se (and hence the valence band) is independent of the lattice parameter, both in sixfold and fourfold coordination. Thus, it may be inferred that the pressure-induced changes of the Zn conduction bands are responsible for the collapse of the $sp^3$ character of the zinc-blende structure and the eventual metallization of the high-pressure rocksalt phase.

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