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Pressure-induced metallization of BaSe

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The pressure-induced metallization of BaSe has been observed using both electrical-resistivity and optical-reflectivity measurements. Measurements of the electrical resistivity of BaSe up to a pressure of 65.2 GPa show a leveling off of the resistivity at about 52 GPa, indicating the metallization of BaSe. Optical-reflectivity spectra taken of the BaSe-sample-diamond interface up to 72.2 GPa show a significant rise in the low-energy (0.5 eV) reflectivity at pressures above 61 GPa. We interpret this rise in reflectivity to be associated with the plasma edge of BaSe in its metallic state. The resistivity and reflectivity data are compared with each other as well as with published high-pressure optical-absorption data.

High-pressure insulator-to-metal transitions are currently of great interest because of advances in the generation of ultrahigh static pressures with the diamond anvil cell. Two of the most valuable tools that have been developed for use with the diamond anvil cell to observe sample metallization are electrical-resistivity measurements and optical-reflectivity measurements. The study of BaSe reported here is the first to combine both tools, resistivity and reflectivity, to confirm sample metallization and to pinpoint the metallization pressure.

The barium chalcogenides (BaTe, BaSe, BaS, BaO) have been extensively studied during the past few years.¹⁻⁶ BaTe (Ref. 1) was found to undergo a structural phase transition from the sodium chloride structure (*B1*) to the cesium chloride structure (*B2*) at 4.8 GPa. High-pressure x-ray studies of BaSe (Ref. 2) and BaS (Ref. 3) reported *B1*-to-*B2* transitions at 6.0 and 6.5 GPa, respectively. The BaSe *B2* phase is stable⁴ to at least 60 GPa, and the BaS *B2* phase is stable⁵ to at least 89 GPa. Recently, we reported⁵ BaO to undergo a phase transition from the *B1* to the hexagonal NiAs structure at 10.0 GPa, and to undergo a phase transition from the NiAs to the PH₄I structure (a distorted *B2* structure) at 15.0 GPa. The BaO sample remained in this PH₄I state up to the maximum pressure of 60.5 GPa.

Insulator-to-metal transitions in these compounds have been studied as well. Electrical-resistivity measurements¹ indicate that BaTe metallizes by band overlap at 20 GPa. For BaSe, Ruoff and Gryzybowski,⁴ on the basis of optical-absorption and electrical-resistivity measurements to about 30 GPa, predicted BaSe to metallize at about 40 GPa. BaS and BaO are believed to have much higher metallization pressures. High-pressure optical-absorption

data on BaS by us indicate a metallization pressure in the region of 80 GPa (Ref. 7). The fact that BaO remains transparent and colorless at 60.5 GPa (Ref. 5) suggests that the BaO metallization pressure is well over 1 Mbar.

The sample used in this study was hydrogen-treated BaSe powder (> 99.5% purity). In both the resistivity and reflectivity experiments, diamonds with flats 300 μm in diameter were used in the diamond anvil cell. For the resistivity experiment, a pattern of electrical probes was fabricated on one of the diamond flats. The probes were made by using the optical lithography equipment at the National Research and Resource Facility for Submicron Structures (NRRFSS) at Cornell University, Ithaca, NY, to first mask off parts of the 300- μm diamond flat with a layer of photoresist. A layer of zirconium 3000 \AA thick was then sputtered onto the diamond, bonding to the parts of the diamond not masked by the photoresist. Finally, the photoresist was washed away with acetone, yielding a diamond with a pattern of four electrical probes with "fingers" 5 μm wide extending in toward the center of the diamond flat where the sample is located during the high-pressure experiment (see Ref. 1 for a description of a similar resistivity experiment). An insulating high-pressure gasket was made by taking a preindented and predrilled (75- μm hole) stainless-steel gasket and plasma-spraying a 100- μm layer of Al₂O₃ onto one side of it, which was then ground down to approximately 30 μm . The gasket was placed in the diamond anvil cell with the Al₂O₃-coated side facing the diamond with the probes, and the BaSe sample plus a ruby chip for pressure calibration⁸ was then loaded into the sample hole of the gasket. The sample resistivity was measured using the four-probe van der Pauw⁹ method.

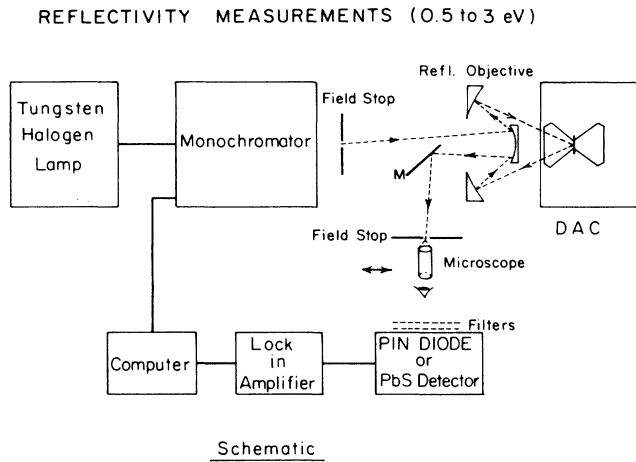


FIG. 1. Diagram of the optical-reflectivity apparatus. The two field stops were set to illuminate and collect light from a 60- μm diameter sample region of the diamond anvil cell (DAC).

For the reflectivity experiment a stainless steel gasket with a 75- μm sample hole was loaded with BaSe plus a ruby chip. The setup diagrammed in Fig. 1 was used to take reflectivity spectra in the 0.5- to 1.6-eV (0.8- to 2.6- μm) range (Ref. 10). A 100-W quartz-tungsten-halogen lamp and a 0.25-m monochromator with 1000- μm slits were used. The chopper was run at 40 Hz and the data collected with a cooled PbS detector and a lock-in amplifier operating with a 3-sec time constant. The sample-diamond reflectivity spectra were normalized against diamond-air reflectivity spectra taken immediately afterwards in order to correct the sample-diamond spectra for variations in the source intensity and the detector sensitivity throughout the spectral range. The sample-diamond reflectivity spectra were also corrected for the small amount of optical absorption by diamond in the 2.0- to 2.5- μm wavelength region.

The result of the resistivity experiment is shown in Fig. 2. van der Pauw's⁹ equation for the resistivity requires the sample thickness t . The sample thickness after unloading was measured with a microscope. The sample thickness at high pressure was then calculated from this zero-pressure sample thickness, the equation of state of BaSe (Ref. 4), and the sample areas before and after unloading. The resistivity drops precipitously by orders of magnitude between 30 and 50 GPa before leveling off in the region of 50–54 GPa. There is then no appreciable change in the resistivity up to the maximum pressure of 65.2 GPa. The absolute values of the resistivity data points may be affected by a small systematic error resulting from the fact that the probes are not attached to the sample to insure a two-dimensional current flow as required by van der Pauw's theorem. Nonetheless, random errors appear to be very small and the leveling off of the resistivity around 50–54 GPa is a strong indication of the metallization of the sample.

The infrared reflectivity spectra of the sample-diamond interface at various pressures are shown in Fig. 3. Below 58.8 GPa the spectra are very low in level throughout the

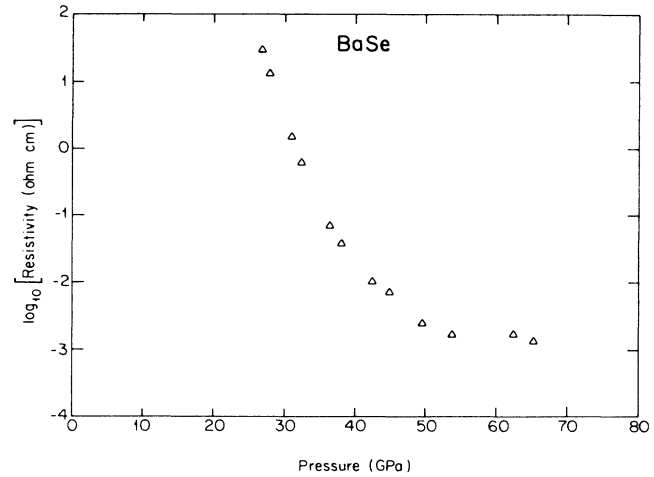


FIG. 2. Plot of BaSe resistivity vs pressure. The resistivities were determined with the 4-lead van der Pauw method.

spectral range observed, the reflectivity levels being less than 1.0%. At 61.2 GPa, however, there is a marked rise in the reflectivity in the 0.5- to 0.6-eV region. As the pressure is increased, the rise becomes more prominent and extends to higher energies. We interpret this significant rise in the infrared reflectivity as being associated with the plasma edge of the metallic state of BaSe.

A determination of the plasma frequency, though, is difficult because of the lack of reflectivity data below 0.5 eV. As pointed out by Reichlin, Ross, Martin, and Goettel¹¹ fits of the Drude curve are not very sensitive to the smooth features of the reflectivity curve above 0.5 eV. In fact, it is difficult to comment on the accuracy of the Drude model in this case because of the lack of distinctive features in the reflectivity above 0.5 eV. In an attempt to provide a

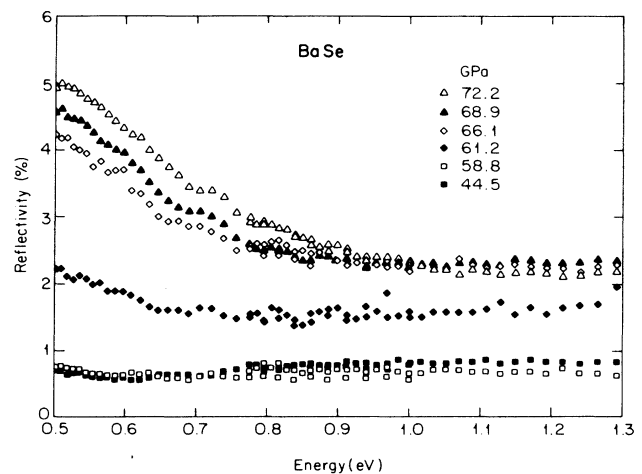


FIG. 3. Plots of the BaSe-diamond interface reflectivity vs energy at various pressures. These curves have been corrected for variations in source intensity and detector sensitivity throughout the spectral range as well as for diamond absorption.

rough estimate of the metallization pressure based on the reflectivity, though, we adopt the method used by Reichlin *et al.*¹¹ for their CsI reflectivity data: The slope of each reflectivity curve at the low-energy limit (0.5 eV) is taken, and the points obtained are plotted versus pressure. A linear extrapolation of these points is made to find the pressure where $dR/dE|_{E=0.5}=0$, that is, the pressure where the plasma edge first appears at 0.5 eV. The values of $dR/dE|_{E=0.5}$ are plotted in Fig. 4. Also plotted in this figure are the optical absorption data of Ruoff and Grzybowski,⁴ as well as the metallization pressure range (52 ± 2 GPa) determined by our resistivity data (vertical dashed lines). It is seen that all three sets of data are in quite good agreement on the approximate metallization pressure. The metallization pressure determined by resistivity is 52 ± 2 GPa; by optical absorption extrapolation, about 46 GPa; and by optical reflectivity extrapolation, about 48 GPa. We believe the 52 ± 2 GPa ($V_m/V_0 = 0.555 \pm 0.005$) metallization pressure determined by resistivity to be the most accurate one because the other two values were obtained by extrapolations of their respective data points. For comparison, the metallization volume predicted by the Goldhammer¹²-Herzfeld¹³ criterion is $V/V_0 = 0.580$ which, using Ruoff and Grzybowski's⁴ equation of state for BaSe, corresponds to a pressure of 42.8 GPa.

It is interesting to note that even at pressures far above the metallization pressure, the region of strong reflectivity is still in the infrared. Reichlin *et al.*¹¹ found CsI to have a similar behavior; the plasma reflectivity rise in CsI was still below 1.5 eV at a pressure of 1.7 Mbar, although the sample metallized at 1.1 Mbar. Apparently, the area of the Fermi surface, or the number of conduction electrons, increases very slowly as a function of pressure for these two pressure-induced band overlap metals.

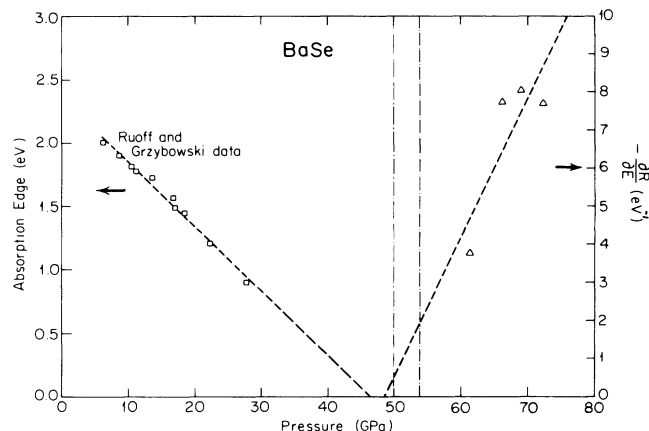


FIG. 4. Comparison of data from reflectivity and resistivity measurements as well as from the optical-absorption data of Ruoff and Grzybowski (Ref. 4). The BaSe pressure vs volume equation of state presented by Ruoff and Grzybowski (Ref. 4) was used to convert their band gap vs volume data points to band gap vs pressure. The vertical dashed lines indicate the metallization pressure range (52 ± 2 GPa) given by the resistivity experiment.

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