High-Pressure Optical Studies on Sulfur to 121 GPa: Optical Evidence for Metallization

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The pressure dependence of the optical absorption edge to 78 GPa and the reflectivity to 121 GPa were measured in sulfur from 0.5 to 3.5 eV in a diamond anvil cell. Our optical results show no evidence of metallic behavior below 95 GPa. A discontinuous change in absorption was observed at 23 GPa. The absorption edge is about 1 eV at 50 GPa, the pressure at which poor metalliclike behavior of sulfur was suggested earlier based on the measurement of the temperature dependence of the electrical resistance. At 95 GPa the reflectivity has a sudden increase and reaches 62% in the infrared range at the sample-diamond interface at 121 GPa. We attribute this to pressure-induced metallization.

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A number of insulating elements and compounds have been transformed into metals at high pressure and at room temperature. Recent reports include Xe [1,2], O_2 [3], CsI [4,5], BaTe [6], and semiconductors [7]. Sulfur is an insulator at normal conditions with an optical absorption edge at 2.89 eV [8]. The first indication of a possible metallic form of sulfur came from shock experiments to about 23 GPa by David and Hamann [9]. The measurement of the pressure dependence of the absorption edge to about 20 GPa by Slykhouse and Drickamer [8] combined with compressibility data [10] suggested that sulfur should become a metal at a pressure between 40 and 50 GPa. The first experimental approach to and above this pressure range was made by Dunn and Bundy [11,12] in their electrical resistance measurements. They gave convincing evidence of semiconducting behavior (dR/dT is negative) for sulfur starting at pressure above $\sim$33 GPa and temperature above 294 K, and of possible metallic behavior (dR/dT is positive) at 50 GPa and above 300 K. However, they also indicated that from the experimental results and the physical analysis sulfur "is not very metallic at least to 50 GPa" [12]. The resistivity at 50 GPa is still relatively high, approximately 10^4 times larger than that for a good metal. Upon decompression from 50 GPa and a few hundred degrees centigrade to room pressure and temperature, sulfur was again an insulator. X-ray studies showed the recovered sample to be roughly crystalline, but the structure of the recovered sample has not been determined [11]. Peanasky, Jurgensen, and Drickamer [13] measured the energy gap of sulfur to a pressure of 30 GPa and indicated that the optical transition is indirect. Recently, Häfner *et al.* [14] reported phase transitions in sulfur in a pressure range from 10 to 15 GPa by Raman studies. According to the studies, these phase transitions are dependent on the temperature in the sample. In review of the previous experimental results on sulfur under compression, there are at least three important and interesting questions remaining unanswered regarding the high-pressure behavior of sulfur. (1) Why does the resistivity of sulfur remain so high at 50 GPa? (2) What is the mechanism of pressure-induced metallization in sulfur? (3) What are the crystalline structures of sulfur under pressure? Also closely related to these questions is the possibility of pressure-induced molecular dissociation in sulfur and its relation to the metallization. The structural phase transition from molecular to monatomic iodine and the metalliclike reflectivity have been reported in iodine at around 21 GPa [15–17]. Certainly, high-pressure optical and x-ray studies will help in answering these questions with regard to sulfur.

In this paper we present optical absorption and reflection (near-infrared and visible ranges) studies on sulfur to 78 and 121 GPa, respectively, using a diamond anvil cell (DAC). This is the first experimental investigation of sulfur reported in the megabar pressure range. For the optical transmission measurements type-Ia diamonds with 200-μm-diam central flats were used. The initial sample chamber was $\sim$75 μm in diameter and $\sim$30 μm in thickness. For the optical reflectivity measurements type-Ia diamonds with $\sim$75-μm-diam central flats and 7° bevels were employed for generating pressure above 100 GPa. In this case the initial sample chamber was 30–40 μm in diameter and $\sim$35 μm in thickness. Note that type-I diamond is a good optical window in the spectral range from about 0.5 to 3.5 eV. For both absorption and reflection measurements high-purity (99.9995%) orthorhombic sulfur powders were used. In both measurements samples were filled into the sample chambers without using other pressure-transmitting media. The pressure was determined by the pressure-shifted ruby *R*-line luminescence [18] from one ruby crystal, $\sim$5 μm in size, inside the sample chamber. The ruby was excited by the 488-nm line of an Ar^+ laser at an output power of about 200 mW.

Both the transmission and reflection spectra were measured over the same spectral range from 350 to 2500 nm, corresponding to photon energies from $\sim$3.5 to $\sim$0.5 eV, using an optical-scanning-microscopic system similar to that described by Syassen and Sonnenschein [19].

In dealing with the transmission data, we corrected the transmission data to the transmission spectrum (I_0) of the unfilled sample chamber to obtain the optical density (OD), $\log_{10}(I_0/I)$, as a function of photon energy. We chose an energy which corresponds to OD$=$2 at each pressure and defined this energy as an upper bound of energy gap (E_g^u), because the optical absorption is characteristic of an indirect transition [13]. The energy gap so defined is less than 0.1 eV below the energy corresponding to the absorption maxima in this experiment. Our absorption data shown below do not appear with a good quality above 30 GPa. As Knittle and Jeanloz [20] have demonstrated, the shape of the optical-density curves, obtained for polycrystalline samples with no pressure medium, changes substantially at high pressures, making evaluation of the absorption edge more difficult. This phenomenon is present in our results as well. It is an intrinsic shortcoming of this procedure. Although we do not believe the results will change dramatically, it would be useful in the future to carry out measurements on a single crystal in a quasihydrostatic medium such as neon or argon.

In analyzing the reflection spectra, we used the corrected reflectivity data R_d, which means the absolute near-normal incidence reflectivity of the sample at the sample-diamond interface. The correction has been made by taking room-pressure absorption (although very weak) and the possible energy dependence of the optical constants of diamond into account. The method has been shown in detail in Ref. [3].

The transmission spectra could be recorded up to ~78 GPa. Above this pressure, the transmitted signals became too weak to be detected on our optical system. Figure 1 shows the absorption spectra for sulfur at the selected pressures up to 70.1 GPa. The same scale was used for each curve on the plots. The absorption edge shifts toward lower energy with increasing pressure. Meanwhile, the absorption background also increases, probably as a result of increased grain-boundary scattering. Between 22.5 and 32.4 GPa, a shape change of the absorption curve was recorded (see Fig. 1). Figure 2(a) shows the pressure dependence of the upper bound of energy gaps derived from the absorption spectra at a level of OD=2. It is clearly seen that the two sets of data from two sample loadings are in good agreement. The absorption edge (the maximum in absorption) of sulfur at $P=0$ was determined by this experiment to be 3.0 ± 0.1 eV. According to the previous results of Peanasky, Jurgensen, and Drickamer, the energy gap of sulfur at $P=0$ is around 2.75 eV [13]. Below 25 GPa the data points can be fitted by a linear relation with a slope $dE_g^u/dP = -74$ meV/GPa. This is in agreement with the results from other authors [8]. This linear relation between E_g^u and P ends at ~25 GPa where E_g^u is ~1 eV. Above 25 GPa, the data points can be fitted by another linear relation with a slope of $dE_g^u/dP = -15$ meV/GPa. While we would prefer to plot the energy gap versus density for the purpose of extrapolation, the required equation of state is not available. The fitted results are listed below.

$$E_g^u\,(\mathrm{eV}) = 2.9 - 7.4\times 10^{-2} P\,(\mathrm{GPa}) \quad \text{for } P < 25\ \mathrm{GPa}\,, \tag{1}$$

$$E_g^u\,(\mathrm{eV}) = 1.7 - 1.5\times 10^{-2} P\,(\mathrm{GPa}) \quad \text{for } P > 30\ \mathrm{GPa}\,. \tag{2}$$

Even though the experimental errors are substantial and the determination of the energy gap is also dependent on the method used, we found an upshift of E_g^u by a value of ~0.2 eV and a change in slope between 25 and 30 GPa for both of the data sets. From Fig. 1 it can be seen that the sample is still transparent for incident photons with energies ~0.9 eV or less at $P=52.2$ GPa. This is also proved by observing the Fabry-Pérot fringes in the infrared range (IR) of the reflection spectra. According to our data to 78 GPa, the highest pressure reached in the transmission measurements, and a linear extrapolation, the upper bound of the energy gap will finally close in the

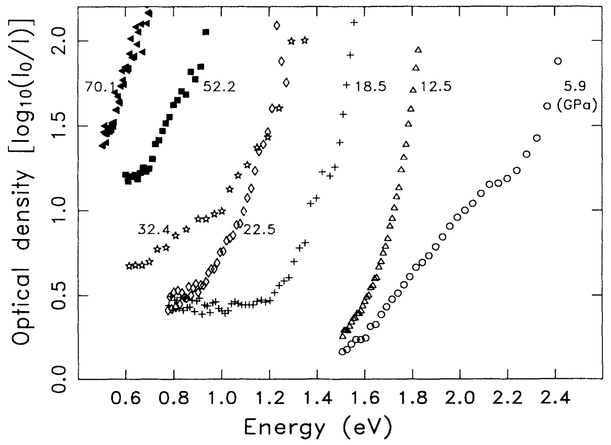

FIG. 1. Absorption spectra (optical density versus energy) for sulfur at different pressures. Pressure is shown in gigapascals.

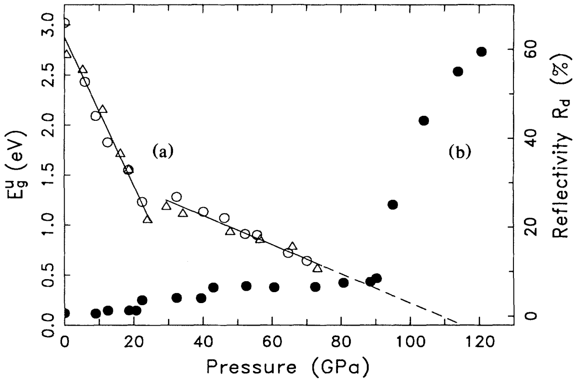

FIG. 2. (a) Pressure dependence of the upper bound of the energy gap defined at OD=2 in sulfur as measured for two sample runs (represented by open circles and triangles, respectively) to 70.1 GPa (scaled on left-hand side). The solid lines represent the fitted curves to the experimental data. The extrapolated line (dashed) reaches zero at about 118 GPa. (b) The reflectivity of the sulfur-diamond interface at a fixed energy of 1 eV as a function of pressure (solid circles) (scaled on right-hand side). The data points shown are from compression only.

neighborhood of 118 GPa. We shall see in the following that our reflection data indicate metallic behavior starting at a pressure about 23 GPa below this extrapolated pressure for closure of the band gap.

Figure 3 shows the absolute reflectivity from the sulfur-diamond interface in the spectral region 0.5–3.0 eV at various pressures up to 121 GPa, the highest pressure reached in the experiment. Figure 2(b) shows the reflectivity as a function of pressure at the fixed energy of 1 eV. In the following discussion we will not attempt a detailed analysis of the reflection spectra because (1) the reflection spectra are basically featureless, and (2) somewhat speculative assumptions about the dielectric response and its pressure dependence at photon energies outside the present experimental range have to be made for both the sample and the diamond. Instead, we limit ourselves mainly to a discussion of the phase transitions viewed by the optical responses and the mechanism of the metallization.

Figure 3 shows that the reflectivity is very low, ~1%, throughout the spectral range below 23 GPa. A small increase of the reflectivity level to ~4% was observed in the IR range starting at 23 GPa. In the pressure range 23–88 GPa, the reflectivity has only gone up by 3%–4%. No evidence of a free-electron-like behavior in the reflection spectrum was found throughout this pressure range and the photon energy range above 0.5 eV. The reflection spectra exhibit Fabry-Pérot fringes on the low-energy side over this pressure range, which indicates that the sample is transparent for low-energy photons. The small increase of reflectivity from ~1% at $P=0$ to ~8% at $P=90$ GPa may be explained as a pressure-induced increase of oscillation strength of the interband transition and the photon absorptions which, in turn, change the optical constants of the sample, and a possible phase transformation above 23 GPa. A high-pressure phase transition in sulfur has been reported by x-ray [14] and Raman studies [14], respectively, in a pressure region from 15 to 30 GPa. However, the structure of the high-pressure phase is unknown.

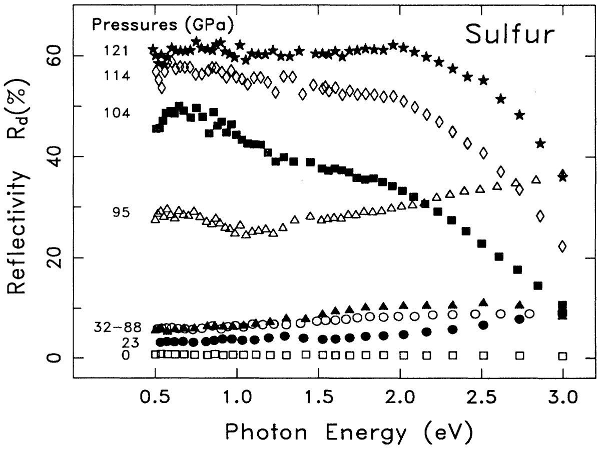

FIG. 3. The reflection spectra from the sulfur-diamond interface at various pressures up to 121 GPa. For each curve the same scale is used and the corresponding pressure is shown at the left side in gigapascals. Note that an abrupt change starts at 95 GPa.

A dramatic increase of reflectivity takes place when the pressure is increased from 88 to 95 GPa. The reflectivity at 1 eV is about 30% at $P=95$ GPa. Note that from the absorption data and a linear extrapolation [see Fig. 2(a)] the absorption edge would be about 0.3 eV at 95 GPa. Above 95 GPa, the reflectivity continues to increase as pressure is increased. At the highest pressure reached, $P=121$ GPa, the reflectivity below 2 eV is approximately constant with a value of about 62%. From visual observation under the microscope, we see that the appearance of the sample has become even *shinier* than the metallic gasket. For these curves above 100 GPa, the high reflection level in the visible range could be a result of pressure-induced extensive interband transition in sulfur. Carefully examining the reflection spectra above 100 GPa (see Fig. 3), one can find that the region of high-level reflection moves sightly toward the high-energy side with increasing pressure. This situation is different from that with oxygen where it appears that the band gap of the diamonds is decreasing and leading to absorption at high energies (Ref. [3]). The reflection spectra above 100 GPa show free-electron-like behavior with intensive intraband transitions at the infrared spectral region, which indicates that the sample is in the metallic phase. The high level of reflection around 2 eV makes the reflection spectra look somehow different from Drude-like behavior. The reflection spectrum at 95 GPa is peculiar because of its high level at visible and near-UV ranges. The effects of a pressure gradient across the sample during a possible phase transition (which will be discussed next) around this pressure may contribute to this peculiarity.

Because of the absence of a theoretical calculation on the electronic band structure of sulfur and the structureless feature of our transmission and reflection spectra, we are not able to show the changing process of the band structure and the type of the band gaps which are described by Eqs. (1) and (2), and we do not know the crystalline structures of sulfur at high pressures. However, in consideration of the earlier experimental results from electrical [11,12], Raman [14], and x-ray (also see Ref. [14]) studies, we explain our optical results in the following way. Below ~23 GPa, sulfur is in its original form with an absorption edge that is linearly dependent on pressure. Between 23 and 30 GPa, sulfur undergoes a phase transformation which is evidenced by an upshift of the absorption edge and a slope change of the E_g^u-P curve. Between 88 and 95 GPa, an abrupt and large change of reflection spectra suggests that sulfur undergoes a first-order phase transition. Our linearly extrapolated absorption data from 75 GPa indicate that the energy gap would be about 0.3 eV at 95 GPa and close to zero at 118 GPa if no transformation occurred. Therefore, the metallization in sulfur that takes place at about 95 GPa is probably caused by a mechanism of first-order phase transition. Mott has suggested that all band overlap processes involve first-order transitions [21], but this seems to be more likely if the reflectivity change is abrupt and large.

The Dunn and Bundy results which showed possible poor metallic behavior in electrical conductivity but with a high resistivity remaining in sulfur at 50 GPa may be explained in three ways: (1) Sulfur has a band overlap at 50 GPa. It is very likely that this band overlap involves an indirect gap, which, when closed, leads to a low carrier density and, hence, a small plasma edge, which could not be observable in our studies. (2) Sulfur is heavily plastically deformed in the resistivity studies with the result that the band gap is heavily populated with defect states, a situation which could lead to apparent poor metalliclike behavior, such as what occurs in silicon with very heavy densities of impurities [22]. For the same reason as in the first case, the sample could be optically transparent for some photons and show no metallic evidence in the reflection spectra, at least above 0.5 eV. (3) As a result of heavy plastic deformation, sulfur probably is very fine grained with a high dislocation density. The dislocation cores and grain boundaries may become metallic at a pressure substantially less than that for the good crystalline material in between. If the composite of the ordered and disordered regions has a volume fraction of metallic disordered material of 10^{-4} at 50 GPa, then the electrical resistivity of the interconnected network would be 10^{-4} times that of a good metal and the plasma edge would be at energies substantially below 0.5 eV [23].

We offer the following conclusions. (i) Below 23 GPa, the upper bound of the energy gap is linearly dependent on pressure with a slope of $dE_g^u/dP = -74$ meV/GPa. (ii) Between 23 and 30 GPa, there is an upshift of the upper bound of the energy gap by a value of 0.2 eV. Above 30 GPa the E_g^u-P curve can be fitted by a linear relation with a slope of $dE_g^u/dP = -15$ meV/GPa. These changes suggest a phase transformation between 23 and 30 GPa. (iii) Below 88 GPa, the reflectivity is low, typically between 1% and 7%. No evidence of free-electron-like behavior is seen on the reflection spectra in the range from 0.5 to 3.5 eV. The small rise in reflectivity is probably due to the increasing difference of the refractive index of the sulfur and of the diamond. (iv) An increase of pressure from 88 to 95 GPa results in an abrupt increase of the reflectivity. The reflection spectra at and above 95 GPa indicate free-electron-like behavior. (v) High-pressure x-ray-diffraction experiments are needed to determine the crystalline structure, the possibility of molecular dissociation of sulfur in its metallic phase, and the equation of state. (vi) Electrical resistivity studies on the single-crystal form of sulfur under quasihydrostatic conditions are needed to clarify the resistivity results around 50 GPa.

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