Metallization of CsI

Robin Reichlin, Marvin Ross, Sue Martin, and Kenneth A. Goettel[a]

Lawrence Livermore National Laboratory, University of California, Livermore, California 94550

(Received 17 December 1985; revised manuscript received 21 April 1986)

The infrared reflectivity of CsI has been measured in a diamond-anvil cell up to a pressure of 1.7 Mbar. An analysis of the data indicates that the metallization pressure lies in the range of 1.1 ± 0.1 Mbar.

PACS numbers: 71.30.+h, 62.50.+p, 78.30.Gt

The insulator-to-metal transition in CsI is currently the subject of intense interest.[1-7] CsI has the smallest band gap of the alkali halides and is thus likely to metallize at a lower pressure than other materials in this group. Theoretical estimates of the transition pressure range from 0.65[8] to 1 Mbar.[9] In a recent paper Vohra *et al.*[6] claimed to have observed metallic CsI at 0.65 Mbar. They reported "this metallization pressure is based on the visual observation of the onset of reflection of the dark red (wavelength) at 0.65 Mbar." Subsequently, Williams and Jeanloz[10] carried out infrared absorption measurements and found that the band gap had not closed at 0.65 Mbar but in fact decreased continuously to a value of 0.55 eV measured at their peak pressure of 0.93 Mbar. An extrapolation of their data leads to a metallization pressure above 1 Mbar.

In an attempt to clarify the insulator-to-metal transition in CsI experimentally, we have undertaken a series of infrared reflectivity measurements over the pressure range 0.9 to 1.7 Mbar. The results presented in this paper lead to an estimated transition pressure of 1.1 ± 0.1 Mbar. These are the first infrared measurements reported in the megabar pressure range.

In the two experiments reported here, a single grain of CsI powder (99.999% purity) was loaded into the sample chamber of a "megabar" diamond-anvil cell.[11] The anvils used were beveled with a central flat of 80 μm, 5° bevel angle, and 500 μm total culet diameter in one sample and 50 μm, 5°, and 300 μm in the second (marked by an asterisk in Fig. 1). Sample chambers were formed by preindenting 250-μm-thick T-301 stainless-steel gaskets to a thickness of approximately 20 μm, and drilling a 60-μm-hole in the center of the area corresponding to the central flat. A small amount of <2-μm-diam ruby powder was placed on the central flat of the cylinder diamond for pressure calibration.[12] Final volume ratios of ruby to CsI were less than 1% in both experiments.

The single-beam infrared-reflectivity measurements were made by use of an experimental technique similar to that of Syassen and Sonnenschein.[13] Measurements were made in the energy range 0.5 to 1.5 eV using a tungsten-halogen source and a $\frac{1}{2}$-m scanning spectrometer with 600-groove/mm grating and 500-μm slits. Chopped signals were detected using a two-stage thermoelectrically cooled PbS detector. The data were integrated with a 1-sec time constant using a PAR 5206 lock-in amplifier. The highest pressure spectrum was collected with a 30-sec integration time. Reflectivities were measured on a 25-μm-diam sample area in both experiments and great care was taken to reposition the incoming beam in the exact same sample area at each pressure. Pressures were measured in as many locations as possible throughout the sample chamber to determine pressure variations within the sampling area. In the one sample which contained enough ruby to measure pressure gradients, pressure variations within the sampling area at peak pressures of 1.0 and 1.26 Mbar, were -0.08 and -0.15 Mbar, respectively.

Reflectivity was measured at the diamond-sample interface and was normalized to the reflectivity at the diamond-air interface over the same spectral region. The reference spectra at the diamond-air interface were collected immediately before and after each sample spectrum to minimize the effects of variations in

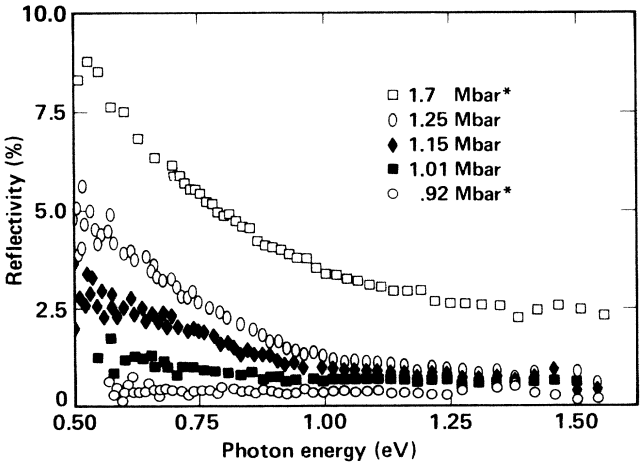

FIG. 1. High-pressure infrared-reflectivity spectra of CsI at the diamond-sample interface as a function of photon energy. An asterisk indicates spectra from run #1; unmarked are from run #2.

source intensity. The CsI spectra were corrected for reflections at the diamond-air interface and for absorption in the diamonds.

The results of two experiments are illustrated in Fig. 1. Reflectivity (%) of CsI is plotted as a function of photon energy over the range 0.5 to 1.55 eV. Spectra are shown at pressures ranging from 0.92 to 1.7 Mbar. These measurements are of the reflectivity at the sample-diamond interface. Below 0.92 Mbar reflectivities are well below 0.5% and are near the limit of detectability of the optical system at low energies. At pressures above 0.92 Mbar, precise measurements can be made over most of the spectral region of interest, although at the lowest and highest energies where source output and detector sensitivity are lowest, resolution is not as good. This is the reason for the larger scatter of the data in these spectral regions. In the highest-pressure spectrum longer integration times have resulted in less scatter at lower energies.

At average pressures above 115 GPa it became increasingly difficult to measure pressures in the sampling area because of very low concentrations of <2-μm-size ruby particles, and absorption by CsI of argon-laser lines used to excite ruby fluorescence. In the spectrum shown at 1.25 Mbar it was not possible to determine an average pressure over the sample area, but only to measure a pressure on the edge of this area. The pressure for the spectrum at 1.7 Mbar was measured at the center of the CsI sample.

We also measured reflectivities between 1.5 and 3.5 eV at 1.15 Mbar to see if there was any structure in the visible spectrum. The reflectivities ($<3\%$) in this region are very low and the samples remained black in reflected light up to the highest pressures studied.

Figure 2 is a plot of all the high-pressure optical data for CsI and includes our reflectivities at the lowest photon energy ($\omega = 0.5$ eV) and the derivative of the reflectivity $\partial R/\partial\omega$ at this energy. These are the reflectivities measured at the sample-diamond interface. The results show that 0.93 Mbar must be a lower bound to metallization. Band-structure calculations have demonstrated that metallization will occur as the result of an overlap of the Γ_{15} $5p$-like state of the filled valence band with the Γ_{12} $5d$-like state of the empty conduction band.[8,9] Thus, while the increase of reflectivity at 0.9 Mbar is clearly inconsistent with the reported metallization at 0.65 Mbar[6] it cannot be assumed that this is the pressure of metallization. We expect interband absorption to occur prior to the onset of closure and to be responsible for the toe in the reflectivity curve. A more sensitive probe of the low-energy reflectivity curve than R itself is provided by the derivative of the reflectivity ($\partial R/\partial\omega$) at 0.5 eV. At low pressure the derivatives are near zero and the reflectivity curves are flat and unstructured as they appear in Fig. 1 at 0.92 and 1.0 Mbar. We believe that it is physically reasonable to identify the sharp increase in the derivative between 1.0 and 1.2 Mbar with metallization. Such a conclusion appears justified since it is well known that in the infrared region metals with large electrical conductivity are good reflectors and have reflectivities which increase with decreasing photon frequency.

A proper analysis of reflectivity data should be carried out in terms of the optical constants. However, in the present case such a study is complicated by the fact that these measurements have been made at the diamond-sample interface and they cover too narrow a

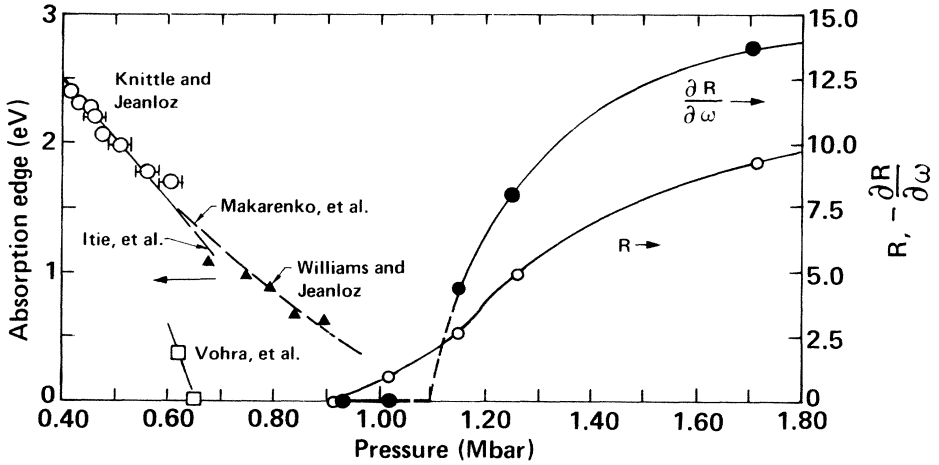

FIG. 2. A summary of the high-pressure optical properties of CsI. The reflectivities, R (open circles, in %), and their derivatives with respect to photon energy, $\partial R/\partial\omega$ (filled circles, in %/eV), are those at the sample-diamond interface measured at $\omega = 0.5$ eV. The dashed lines between 1.0 and 1.15 Mbar are an extrapolation of the high- and low-pressure values of $\partial R/\partial\omega$. We identify the intersection at 1.1 Mbar as metallization. We estimate the error in R to be $\pm 1\%$ and in $\partial R/\partial\omega$ to be $\pm 5\%$.

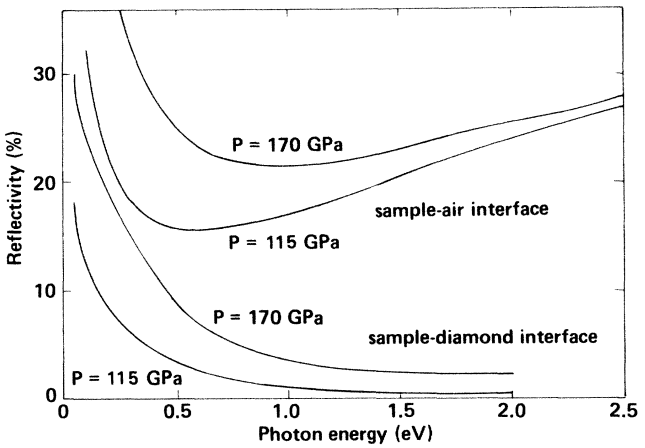

FIG. 3. Optical reflectivity of CsI. The lower curves correspond to the sample-diamond interface and were obtained by fitting to the data in Fig. 1. The upper curves correspond to the air-sample interface.

range of photon energies to allow a reliable Kramers-Kronig analysis or a unique fit to the optical constants. For example, the reflectivity of the sample in the diamond anvil is related to the index of refraction n and the extinction coefficient k by

$$R = [(n - n_d)^2 + k^2]/[(n + n_d)^2 + k^2],$$

where n_d is the index of refraction of the diamond taken here to be 2.4. The value of k_d is small and may be neglected. We have determined n and k by fitting polynomial functions of photon energy to the reflectivity data at 1.7 and 1.15 Mbar. To remove some of the ambiguity we assumed that CsI is metallic and in the spirit of the Hagen-Rubens law that in the low-frequency limit these constants are each proportional to $(1/\omega)^{1/2}$. After some trials a good fit to the reflectivity data was obtained. Other models gave similar results. The fitted reflectivity is plotted in Fig. 3 and labeled as the "sample-diamond interface" curves. The upper curves represent the sample-air interface flectivity and were calculated by use of the fitted values of n's and k's with $n_d = 1$. These curves exhibit the increase in reflectivity with increasing frequency that is characteristic of interband transitions at high pressure. However, the calculated optical conductivities do not exhibit Drude conductivity at low photon energies. This does not mean such a contribution is absent but only that fits to the reflectivity above 0.5 eV are not sensitive to this feature. We find that below this energy the values of the optical constants can be adjusted arbitrarily to create a Drude curve, while retaining the excellent fit to the reflectivity above 0.5 eV. In short, any extrapolation of the low-frequency reflectivity curve which requires some assumption as to the functional dependence of R naturally biases the final conclusion regarding the existence of metal or insulator. In this regard the value of $\partial R/\partial\omega$ at 0.5 eV provides a less ambiguous estimate of the low-energy behavior. The rapid rise in this derivative indicates that below 0.5 eV R is increasing as in the case of a metal.

To summarize, the present results are consistent with an extrapolation of the data of Williams and Jeanloz and lead to a pressure of 1.1 ± 0.1 Mbar as the best estimate for the metallization of CsI.

We wish to thank Karl Syassen, Ken-itchi Takemura, and Roland Sonnenschein for sharing their design and expertise for measuring reflectivities in the diamond cell. We would like to thank Neil Ashcroft, Neil Holmes, Harry Radousky, B. Bonner, and H. Graboske for helpful discussions and C. Boro and E. Arnold for technical contributions. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory, under Contract No. W-7405-ENG-48.

[a]Also at Department of Geological Sciences, Brown University, Providence, R.I. 02912

[1]K. Asaumi and Y. Kondo, Solid State Commun. **40**, 715 (1981).

[2]E. Knittle and R. Jeanloz, Science **223**, 53 (1984).

[3]I. N. Makarenko, A. F. Goncharov, and S. M. Stishov, Phys. Rev. B **29**, 6018 (1984).

[4]J. P. Itie, A. Polian, and J. M. Besson, Phys. Rev. B **30**, 2309 (1984).

[5]K. Asaumi, Phys. Rev. B **29**, 1118 (1984).

[6]Y. K. Vohra, S. T. Weir, K. E. Brister, and A. L. Ruoff, Phys. Rev. Lett. **55**, 977 (1985).

[7]A. N. Zisman, I. V. Aleksandrov, and S. M. Stishov, Phys. Rev. B **32**, 484 (1985).

[8]S. Satpathy, N. E. Christiansen, and O. Jepsen, Phys. Rev. B **32**, 6793 (1985).

[9]J. Aidun, M. S. T. Bukowinski, and M. Ross, Phys. Rev. B **29**, 2611 (1984).

[10]Q. Williams and R. Jeanloz, Phys. Rev. Lett. **56**, 163 (1986).

[11]H. K. Mao and P. M. Bell, *Carnegie Institution of Washington Year Book* (Carnegie Institution of Washington, Washington, D.C., 1975), p. 300.

[12]H. K. Mao, P. M. Bell, J. Shaner, and D. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[13]K. Syassen and R. Sonnenschein, Rev. Sci. Instrum. **53**, 644 (1982).