High-pressure infrared spectroscopy: tuning of the low-energy excitations in correlated electron systems

I. Kézsmárki,¹  R. Gaál,²  C.C. Homes,³  B. Sípos,²  H. Berger,²  S. Bordács,¹  G. Mihály,¹  and L. Forró²

¹Department of Physics, Budapest University of Technology and Economics, 1111 Budapest, Hungary
²Ecole Politechnique Federale, Lausanne, CH-1015 Switzerland
³Condensed Matter Physics and Materials Sciences Department, Brookhaven National Laboratory, Upton, NY 11973 USA

(Dated: February 1, 2008)

We have extended the range of the high-pressure optical spectroscopy to the far-infrared region keeping the accuracy of ambient-pressure experiments. The newly-developed method offers a powerful tool for the study of pressure-induced phase transitions and electronic-structural changes in correlated electron systems. The novel-type optical pressure cell, equipped with large free-aperture diamond window, allows the measurement of optical reflectivity down to \( \omega \approx 20 - 30 \text{ cm}^{-1} \) for hydrostatic pressures up to \( p \approx 26 \text{ kbar} \). The efficiency of the technique is demonstrated by the investigation of the 2-dimensional charge-density-wave 1T-TaS₂ whose electronic structure shows high sensitivity to external pressure. The room-temperature semi-metallic phase of 1T-TaS₂ is effectively extended by application of pressure and stabilized as the ground state above \( p = 14 \text{ kbar} \). The corresponding fully incoherent low-energy optical conductivity is almost temperature independent below \( T = 300 \text{ K} \). For intermediate pressures, the onset of the low-temperature insulating phase is reflected by the sudden drop of the reflectivity and by the emergence of sharp phonon resonances.

PACS numbers:

The application of hydrostatic pressure offers a clean and controllable way to fine-tune the electronic and magnetic properties of solids via the change of their bandwidth/dimensionality or by altering the energy scale of the relevant interactions, such as magnetic exchange interactions or the electron-phonon coupling. The possibility to gain spectroscopic information about the electronic structural changes upon pressure-induced phase transitions has recently attracted broad interest. As one of the earliest trials, the possible metallization of solid hydrogen was studied under extremely high pressures \( (p \sim 1500 \text{ kbar}) \) by infrared absorption and reflectivity techniques.¹,² In correlated electron systems, due to the strong competition between neighboring thermodynamic phases, moderate pressures can effectively induce phase transitions. Therefore, hydrostatic pressure has been successfully applied to investigate the phase diagram of correlated electron materials, especially for compounds located in the vicinity of an insulator-metal phase boundary. The pressure-driven collapse of the insulating state has been recently followed by infrared spectroscopy in the colossal magnetoresistance manganite La₁₋ₓCaₓMnO₃,² in Mott insulators such as YNiO₂,² and V₃O₅,² in the band insulator YH₃,² and in the charge-density-wave rare-earth tritellurides.² Besides the phase transition phenomena, strong pressure-induced variation of the electronic structure has been reported for CeSb,² β-Na₃V₅O₈·silane,¹⁰ etc. All of these experiments were performed using diamond anvil cells (DAC) which allowed the generation of hydrostatic pressure up to \( p \approx 260 \text{ kbar} \). The disadvantage of DACs is their pressure-limited small aperture, typically \( \sim 100 \mu \text{m} \) in diameter, which introduces a low-energy cutoff (a few hundred \( \text{cm}^{-1} \)) due to the diffraction effects. Consequently, these investigations were restricted to the mid-infrared and higher energy range, although owing to its high transparency diamond is an ideal optical-window material down to microwave frequencies.²

In strongly correlated electron systems, where usually the low-energy excitations are of interest, spectral information about the far-infrared region is highly desirable. Focusing on materials which show high sensitivity to external pressure, we have developed a conceptually new type of optical pressure cell which extends the low-energy limit of the infrared experiments by more than one decade as it is applicable typically down to \( \omega \approx 20 - 30 \text{ cm}^{-1} \). In our design, this improvement is the result of the large free aperture of the window \( (d = 1.5 \text{ mm}) \) which restricts the maximum applied pressure to \( p \approx 26 \text{ kbar} \) at the same time. On the basis of reflectivity measurements performed on the two dimensional charge-density-wave material 1T-TaS₂, we demonstrate that this type of pressure cell allows the determination of the absolute value of the reflectivity even in the far-infrared region. Furthermore, its precision is comparable to that of standard ambient-condition reflectivity experiments. Our design for the diamond-window based self-clamping type pressure cell is shown in Fig. 1. The light access is achieved through a type IIA diamond window fixed at the lateral part of the metallic body with the beam being perpendicular to the horizontal axis of the cell. In order to determine the absolute value of reflectivity for the diamond-sample interface, \( R_{ds} \), the window has wedged plane surfaces which facilitates the measurement of reference signal. It is also sufficient to eliminate interference fringes coming from multiple reflections. Besides the optical access, an electrical leadthrough is also implemented, which facilitates either the in situ moni-
toring of pressure by a resistive sensor (InSb, amorphous carbon, etc.) or the simultaneous measurement of the sample resistivity during the pressure runs. For low-temperature experiments the pressure cell is attached to the cold finger of a He flow cryostat and the thermalization is ensured by a radiation shield.

As followed in the sketch of Fig. 1b, the intensity reflected back from the vacuum-diamond and diamond-sample interfaces \(I_{vd}\) and \(I_{ds}\), respectively) can be detected separately by a few degree (typically \(\sim 7^\circ\)) rotation of the cell around its vertical axis due to the wedging of the diamond. (A wedging angle of 2° results in \(\sim 10^\circ\) angular deviation between the two reflected beams which, together with the finite beam size and the rotation of the cell, requires an opening angle of \(\sim 28^\circ\) for the conical bore on the diamond holder in our optical arrangement.) The nearly normal incidence is still held for the both positions. Correspondingly, the reflectivity of the sample relative to the diamond can be obtained from the measured intensities:

\[
R_{ds}(\omega) = \frac{R_{vd}(\omega)}{(1 - R_{vd}(\omega))^2} \cdot \frac{I_{ds}(\omega)}{I_{vd}(\omega)}
\]

where \(R_{vd}\) (\(\equiv R_d\)) is the absolute reflectivity of the diamond. The \(R_{vd}(\omega)/(1 - R_{vd}(\omega))^2\) prefactor can be calculated from the well-documented refractive index of diamond, \(\hat{n}_{d}\) \(^{11,12,13,14,15}\). High-quality, such as type IIA, optical diamonds show no significant absorption up to \(\omega \approx 40000 \text{ cm}^{-1}\). On the other hand, the effect of weak absorption introduces only another frequency-dependent factor into Eq. 1 (which can be directly determined from the transmittance of the window) but its influence on \(R_{vd}\) and \(R_{ds}\) can be usually neglected. If \(R_{ds}(\omega)\) is measured over a sufficiently broad range of energy, the complex refractive index of the sample relative to the diamond \(\hat{n}_{ds}(\omega)\) can be obtained by the Kramers-Kronig analysis. Since \(\hat{n}_{d}(\omega)\) is purely real and shows a monotonous increase of about 10% up to \(\omega \approx 40000 \text{ cm}^{-1}\), it is straightforward to calculate the complex dielectric response of the sample relative to the vacuum. This analysis fails only for the multiphonon absorption bands of the diamond located in the range of \(\omega = 1500-2700 \text{ cm}^{-1}\).\(^{13}\) We note at this point that, additional to the absorption of the diamond above \(\omega \approx 40000 \text{ cm}^{-1}\), the high-energy limit of this method is determined by the roughness and/or planarity of the diamond-sample interface \(\delta_{ds}\). Therefore, special care should be taken for the proper matching between the window and the sample in order to eliminate interference and diffraction effects inherently appearing for wavelength shorter than \(\delta_{ds}\).

\[\text{FIG. 1: (Color online) Our home-designed optical pressure cell: steel body equipped with a type IIA diamond window. The upper panel shows the prorata drawing of the cell. The sample is mounted on the inner surface of the diamond window which has } d = 1.5 \text{ mm free aperture. As demonstrated in the lower panel, the angle of wedging between the two surfaces of the window allows for a clean separation of the reflections from the vacuum-diamond and diamond-sample interface and thus facilitates reference measurements (see text for details).}\]

\[\text{FIG. 2: (Color online) Temperature dependence of the resistivity for three selected pressures in } 1T-\text{TaS}_2. \text{ At each pressure infrared reflectivity was measured at temperatures labeled by different symbols: } \circ, \bullet, \oplus \text{ and } \ominus \text{ correspond to points in the pressure-temperature phase diagram which are characterized by the reflectivity spectrum as the room-temperature, low-temperature phase, or as a mixed state, respectively. At } p = 1 \text{ bar/}14 \text{ kbar the corresponding symbols are shown above/below the resistivity curve. For } p = 4 \text{ kbar the reflectivity measurements performed in cooling run are indicated below while those in warming up are shown above the } \rho(T) \text{ curve.}\]
In the following we shall present the high-pressure optical study of the 2-dimensional charge-density-wave (CDW) system $1T$-TaS$_2$ carried out by the above described pressure cell. At ambient pressure and room temperature $1T$-TaS$_2$ is a bad metal or semi-metal characterized by a high and almost temperature independent resistivity ($\rho \approx 10^{-3} \Omega \text{cm}$) and by a fully incoherent low-energy optical conductivity.\textsuperscript{14} With lowering the temperature, the material goes through a first-order phase transition at $T_{lock} = 180$ K which is clearly manifested in the electronic transport as it is accompanied by a jump-like enhancement of the resistivity\textsuperscript{16} and by the opening of a soft gap $\Delta \approx 800$ cm$^{-1}$ in the optical conductivity.\textsuperscript{17} Recent photoemission experiments also reflect that the electronic structural changes are dominantly restricted to the low-energy region.\textsuperscript{18,19,20,21} On the other hand, due to its 2-dimensional CDW ordering and the large electron-phonon coupling\textsuperscript{20,21} the material shows extremely high sensitivity to external pressure.\textsuperscript{15} Therefore, $1T$-TaS$_2$ offers an ideal playground to study the pressure-induced electronic and structural changes by infrared spectroscopy.

Prior to the optical experiments under pressure, we have investigated the pressure-temperature phase diagram of the material by means of dc resistivity. The results are shown in Fig. 2 for three selected pressures $p = 1$ bar, 1 kbar, and 14 kbar. In agreement with early data,\textsuperscript{16} the low-temperature insulating phase is strongly suppressed although the resistivity is almost unchanged in either of the phases. Already at $p = 4$ kbar the transition is shifted to $T_{lock} \approx 150$ K and the hysteresis is significantly broadened\textsuperscript{22} while at $p = 14$ kbar the high-temperature phase is extended to the lowest temperatures. This semi-metallic state exhibit nearly temperature independent charge transport as the resistivity increases only by a factor of $\sim 3$ below $T = 300$ K. We note here that the resistivity in the insulating phase also shows anomalous behavior which may be attributed to Mott-Anderson localization effects together with the opening of the pseudo-gap $\Delta \approx 800$ cm$^{-1}$.

The far-infrared reflectivity of $1T$-TaS$_2$ was investigated below room temperature for various pressures $p = 1$ bar, 1 kbar, 4 kbar, and 14 kbar in the photon energy range of $\omega = 30 - 700$ cm$^{-1}$ as shown in Fig. 3. For verification of the results, besides the $R_{ds}(\omega)$ spectra measured inside of the pressure cell, Fig. 3 also displays spectra evaluated from the ambient pressure absolute reflectivity $R_s(\omega)$ reproduced from Ref. 17. (For these data the complex refractive index $\hat{n}_s$ was obtained by Kramers-Kronig transformation and $R_{ds}$ was calculated with use of the Fresnel equation from $\hat{n}_s$ and $\hat{n}_d$.) The ambient pressure data measured inside and out of the pressure cell show fairly good agreement both at room and low temperature verifying the applicability of our method for the fully quantitative measurement of reflectivity under pressure even in the hardly accessible far-infrared spectral range.

Similarly to the resistivity, the room-temperature reflectivity of the sample does not show significant variation up to $p = 14$ kbar. The reflectivity spectrum in the low-temperature insulating phase is reduced and exhibits sharp phonon resonances for $\omega < 400$ cm$^{-1}$. Its variation with pressure is also negligible for $p = 1$ bar $- 4$ kbar and probably the same remains valid, as long as the insulat-
ing phase is not completely suppressed. On the other, at $p = 14$ kbar when the semi-metallic phase becomes the ground state, the low-temperature reflectivity is reminiscent to that of at room temperature. Although it is somewhat reduced in absolute value the spectral shape is still semi-metallic-like and the phonon modes remain almost completely screened. For comparison, we also plotted the reflectivity measured out of the cell just above $T_{lock} = 180$ K. As expected from the tiny variation of the resistivity at $p = 14$ kbar below room temperature, the two spectra are close to each other over the whole far-infrared range.

The temperature dependence of $R_{ds}(\omega)$ has been studied in more details, especially in the hysteretic region of the transition, for the intermediate pressure $p = 4$ kbar (see Fig. 3b). The spectra follow the tendency of the $R(T)$ curve both in the cooling and warming run as depicted by symbols plotted simultaneously with the resistivity curves. Except for $T = 140$ and 120 K in cooling down, where the coexistence of the two phases was observed in the reflectivity, $R_{ds}(\omega)$ spectra purely showed either the semi-metallic or the insulating character.

In conclusion, we have extended the range of the high-pressure optical spectroscopy to the far-infrared region keeping the accuracy of ambient-pressure experiments. For this purpose we have developed an optical pressure cell equipped with a wedged diamond window of large free aperture by which reflectivity spectra can be measured down to $\omega \approx 20-30$ cm$^{-1}$ for hydrostatic pressures up to $p = 26$ kbar. This technique, which is strongly based on the excellent optical properties of high-quality (type IIA) diamonds, is well-suited to study the systematics of bandwidth-controlled metal-insulator transitions in interacting electron systems via the pressure-induced changes in their low-energy electronic structure. Its applicability was demonstrated by the optical study of the 2-dimensional charge-density-wave $1T$-TaS$_2$. We have pointed out that the room-temperature semi-metallic phase can be effectively extended by external pressure and stabilized as the ground state above $p = 14$ kbar. Furthermore, the corresponding fully incoherent low-energy optical conductivity is almost temperature independent below $T = 300$ K. For intermediate pressures, the onset of the low-temperature insulating phase is reflected by the sudden drop of the reflectivity and by the emergence of sharp phonon resonances.

**Acknowledgement**

The authors are grateful to L. Mihály for useful comments and discussions. They are also greatly indebted to L.V. Gasparov for sending recently published ambient-pressure reflectivity spectra. This work was supported by the Hungarian Scientific Research Funds OTKA under grant Nos. F61413 and K62441, by the Swiss NSF, and its NCCR "MaNEP" and by the DOE under contract number DE-AC02-98CH10886. I. K. was a grantee of Bolyai János Fellowship.