

Pressure-Driven Phase Transitions in Bulk HfS₂

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The effect of hydrostatic pressure up to 27 GPa on Raman scattering in bulk HfS₂ is investigated. There are two transformations of Raman scattering spectra which take place during compression at a pressure between 5.7 GPa and 9.8 GPa as well as between 12.8 GPa and 15.2 GPa. Seven vibrational modes can be observed after the transformation, as compared to four modes before the transformation. The observed change suggests a structural change in the material of yet unknown nature. The frequencies of the Raman scattering modes observed above the transformation change linearly with pressure and the corresponding pressure coefficients have been determined. The other transition manifests itself as a change in the Raman scattering lineshape. While a series of well-defined Raman scattering modes are observed under the pressure below the transition, broad spectral bands can be seen at higher pressure. The overall lineshape of the spectra resembles that of disordered materials. The lineshape does not change during decompression, which suggests the permanent nature of the high-pressure transition.

topics: Raman scattering, hydrostatic pressure, transition metal dichalcogenides

1. Introduction

Layered transition metal dichalcogenides (TMDs), and in particular their few-layer structures, have been drawing the attention of researchers for more than a decade. While about 60 layered TMDs are recognized, until now, the attention of researchers is focused on Mo- and W-based compounds. Basic properties of several TMDs in their bulk form are known for years [1], however, there is still room for studies including their properties under hydrostatic pressure.

In this work, we address the effect of hydrostatic pressure on hafnium disulphide (HfS₂) — a member of group IVB TMD. Recently, it has been shown that HfS₂ has a very effective electrical response [2, 3], which justifies the need to uncover the basic properties of the material. The evolution of

lattice dynamics of HfS₂ with hydrostatic pressure is studied. We follow Raman scattering (RS) spectra as a function of pressure to investigate possible structural transformations of the material as the first-order phase transition has been recently reported in [4].

2. Samples and experimental setups

Single crystals of HfS₂ have been synthesized in a two-zone chemical vapour transport (CVT) furnace. First, the precursor materials were sealed in quartz tubes 25 cm long and 8 cm in diameter. Iodine was used as a transport agent. The reaction and growth temperatures were set to 1050 K and 950 K, respectively. Growth was performed continuously for 120 h. With higher stability of HfS₂ against iodine, CVT growth starts first at elevated

temperatures. In the vapour phase, HfI and HfI_2 can also dominate the direction of the reaction. After 120 h, the reaction was stopped automatically and the reactor was cooled down to room temperature in 5 h. High quality HfS_2 single crystals of 0.8–1 cm² size were grown in the low-temperature part of the reactor. The pattern of powder X-Ray diffraction (XRD) of the investigated material was found to be in perfect agreement with that of the octahedral 1T phase of HfS_2 [5]. A very minor amount of the unidentified phase was also detected in the crystal by the XRD technique.

High-pressure RS measurements were conducted at room temperature in a nonmagnetic diamond anvil cell (DAC) made of BeCu alloy. Crystallographic oil was adopted as the pressure transmitting medium. The fluorescence line of ruby was used to calibrate pressure. The RS spectra were excited using $\lambda = 561$ nm (2.21 eV) radiation from a diode-pumped laser. Excitation light was focused by means of a 50 \times long-working distance objective with a 0.42 numerical aperture (NA) producing a spot diameter of about 1 μm . The signal was collected via the same microscope objective, sent through a 0.75 m monochromator and then detected by using a liquid nitrogen-cooled charge-coupled device (CCD) camera. The spectral resolution of the setup in the studied energy range of the RS experiment was 0.7 cm⁻¹.

3. Results

There are six normal vibrational modes at the Γ point of 1T- HfS_2 [5], given by

$$\Gamma = A_{1g} + E_g + 2A_{2u} + 2E_u. \quad (1)$$

The modes A_{1g} and E_g are Raman-active modes. The infrared-active modes A_{2u} and E_u are split into LO and TO branches (for the atom displacement pattern see, e.g. [6]), and other A_{2u} and E_u modes are acoustic [5].

The measured RS spectrum of bulk HfS_2 at ambient pressure consists of four modes (see Fig. 1), the frequencies of which equal \approx to 141 cm⁻¹, 266 cm⁻¹, 325 cm⁻¹, and 344 cm⁻¹. This is consistent with previous studies [4, 7, 8]. There is an agreement in the literature on the attribution of peaks at 266 cm⁻¹ and 344 cm⁻¹ to in-plane E_g and out-of-plane A_{1g} Raman-active modes, respectively. The peak at 325 cm⁻¹ is attributed to infrared-active E_u (LO) [6, 8] or A_{2u} (LO) [7] alike mode. Despite the formal Raman-inactivity, both the LO and TO components of infrared-active modes may be observed in the RS spectrum due to the long range Coulomb forces resulting from charges localised on atoms [7]. The resonant nature of RS involving such phonons was previously reported in [9]. Temperature-dependent RS measurements [10] or measurements with modulation of excitation light [11] might help to verify the attribution of the mode. For the sake of this work, we assume the latter attribution to A_{2u} (LO) [4].

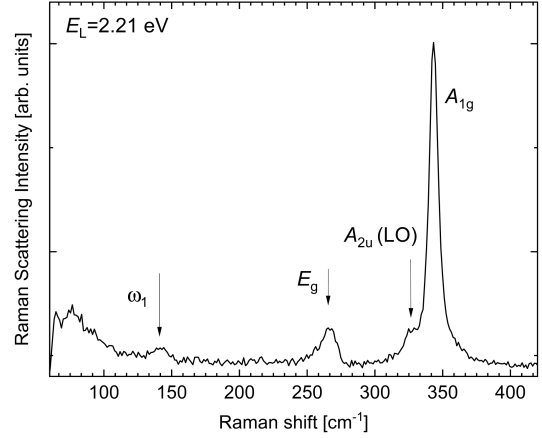


Fig. 1. Raman scattering spectrum of bulk HfS_2 at ambient pressure.

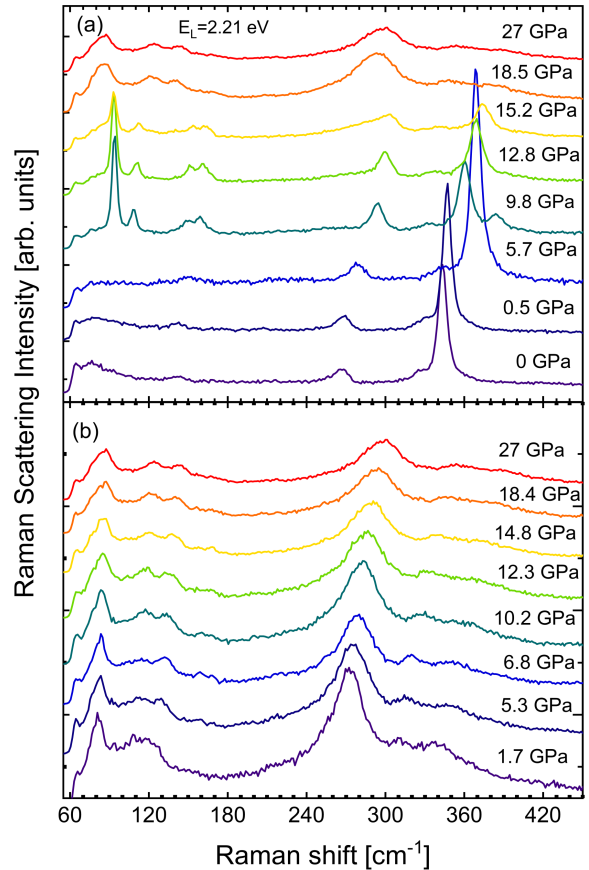


Fig. 2. Raman scattering spectra of bulk HfS_2 as a function of hydrostatic pressure for (a) compression and (b) decompression cycle.

The assignment of the weak feature at 141 cm⁻¹, previously reported in [4], is also unclear. It has been suggested to assign it to second-order difference processes, since such peaks can be observed in the RS spectra of some TMDs [12, 13]. Also, E_u (TO) was suggested as the mode signature [6, 7]. The peak in this work will be referred to as ω_1 .

TABLE I

Results of linear fits to the pressure evolution of the Raman scattering peaks in bulk HfS_2 .

Peak	E_0 [cm^{-1}]	α [$\text{cm}^{-1}/\text{GPa}$]
ω_1	141.4	1.59
E_g	266.1	2.14
$A_{2u}(\text{LO})$	325.5	2.63
A_{1g}	344.0	4.36
I	95.1	-0.13
II	101.8	0.69
III	142.0	0.75
IV	151.6	0.77
V	277.3	1.68
VI	315.3	1.69
VII	334.9	2.61

The effect of hydrostatic pressure on the RS spectra of bulk HfS_2 during compression and decompression can be appreciated in Fig. 2a and b, respectively. Let us first focus on the results obtained during the compression process. The lineshape of the RS spectra does not significantly change up to 5.7 GPa. The observed modes experience blueshifts with increasing hydrostatic pressure. Moreover, a substantial enhancement of the A_{1g} peak can be noticed in the spectrum at 5.7 GPa.

It was found that the energies of the observed modes increase linearly with increasing pressure, which can be appreciated in Fig. 3. Assuming a linear dependence of the energies on pressure

$$E(P) = E_0 + \alpha P, \quad (2)$$

one can fit the experimental data with the results shown in Table I.

The obtained pressure coefficients are in general agreement with those recently reported by Ibáñez and coworkers [4]. The initial values E_0 and pressure coefficients α for the observed modes span from $1.59 \text{ cm}^{-1}/\text{GPa}$ to $4.36 \text{ cm}^{-1}/\text{GPa}$ for A_{1g} mode.

A substantial change in the line-shape of the RS spectrum can be observed at pressure of 9.8 GPa. The corresponding spectrum is presented in Fig. 4. It can be seen there that the A_{1g} mode substantially weakens. Simultaneously, E_g , $A_{2u}(\text{LO})$, and ω_1 disappear from the spectra and a set of new lines emerge in their stead. The peaks are denoted with I–VII. A similar lineshape of the spectra can be observed under hydrostatic pressure up to 12.8 GPa with the A_{1g} mode completely vanishing above 10 GPa. The structural change of HfS_2 , which affects the RS spectra, was previously suggested in [4] with a new peak on the higher-frequency side of the A_{1g} mode. In our experiment, the transformation manifests itself in the emergence of the peak VII at the lower-frequency side of the A_{1g} , as well as in changes to the low-energy part of the spectrum, in which two pairs of lines I–II and III–IV can be observed. The pressure coefficients α of the I–VII

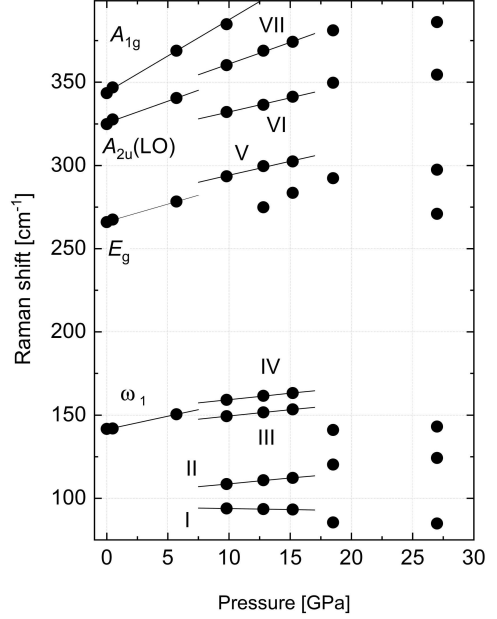


Fig. 3. The evolution of the Raman scattering peak energies in bulk HfS_2 with hydrostatic pressure. Straight lines correspond to linear fits to experimental data.

modes do not correspond to those of the modes detected at lower pressure. In particular, the pressure coefficient α ($2.61 \text{ cm}^{-1}/\text{GPa}$) for mode VII is substantially lower than the pressure coefficient for A_{1g} mode, although both linear energy evolutions have rather similar E_0 initial values (334.9 cm^{-1} for VII mode vs 344.0 cm^{-1} for A_{1g}). Similar effect can be observed for the E_g and V mode with E_0 and α . Their respective values are 266.1 cm^{-1} and 277.3 cm^{-1} for E_0 , and $2.14 \text{ cm}^{-1}/\text{GPa}$ and $1.68 \text{ cm}^{-1}/\text{GPa}$ for α (see Table I). Modes II–IV share relatively small pressure coefficient α equal to $\approx 0.7 \text{ cm}^{-1}/\text{GPa}$, which is significantly smaller than the lowest coefficient for modes below the pressure-induced transformation. Finally, the pressure coefficient for the I mode is negative. The properties substantially differ from those observed at lower pressure, so one can conclude that the phase transition of yet unknown origin takes place between 5.7 GPa and 9.8 GPa.

The next transformation of the RS spectrum can be observed above 15.2 GPa (see Fig. 2a). Instead of the seven well-defined vibrational modes present in the RS spectrum at lower pressure, broad spectral bands can be detected at 15.2 GPa or higher pressures. The overall lineshape of the RS spectra at the highest hydrostatic pressure resembles that of disordered materials [14, 15]. The disorder and/or defects affecting the crystalline structure can localize phonons allowing for momentum non-conserving processes. As a result, inelastic scattering is possible with phonons from the whole Brillouin zone. Therefore, the RS spectrum of disordered materials reflect the total density of phonon modes.

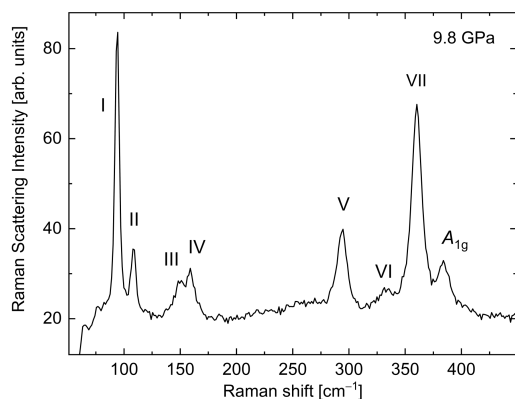


Fig. 4. Raman scattering spectrum of bulk HfS_2 in hydrostatic pressure of 9.8 GPa.

Adopting such an approach, one can conclude that the low-energy band (below 150 cm^{-1}) corresponds to acoustic phonons and the high-energy band (at $\approx 300 \text{ cm}^{-1}$) is due to optical vibrations. The emergence of a disorder-like RS under highest hydrostatic pressure may be related to the contribution of an undefined phase observed in X-ray diffraction measurements as it was mentioned earlier. As can be appreciated in Fig. 2b, the lineshape of the RS spectra does not change during the decompression process. It suggests a permanent nature of the high-pressure transition, most likely into the amorphous phase.

4. Conclusions

We have studied Raman scattering in bulk HfS_2 as a function of hydrostatic pressure up to 27 GPa. There are two transformations of the Raman scattering spectrum observed during compression between 5.7 GPa and 9.8 GPa as well as between 12.8 GPa and 15.2 GPa. The spectrum after the lower-pressure transformation consists of seven well-defined vibrational modes as compared to the four modes observed below the transformation. The modification in the spectrum suggests a structural change in the material. The frequencies of the modes observed above the transformation change linearly with pressure and the corresponding pressure coefficients have been determined. Relatively small (II–IV) or negative pressure coefficients (I) of the vibrational modes in the low-energy part of the spectra have been noticed. The high-pressure transformation of the Raman scattering spectrum results in the change of its lineshape. While a series of well-defined vibrational modes are observed under the pressure below the transition, broad spectral bands can be detected at higher pressure. The lineshape of the spectra resembles that of disordered materials, which suggests the amorphisation process involved. The lineshape does not change during decompression, confirming the permanent nature of the high-pressure transition.

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