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ORIGINAL PAPER

Raman study of phase transitions in the ruthenocene crystal at high pressure

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Abstract: The phonon spectrum and phase transitions with an extremely large hysteresis in the ruthenocene crystal were studied by Raman spectroscopy at high pressure. The pressure dependence of phonon frequencies under hydrostatic compression changed abruptly at ~ 4, ~ 5, and ~ 8 GPa in three independent series of Raman measurements. The results of all measurements for compression and decompression runs were different up to 0.8 GPa when the transition to the initial phase occurred. Under non-hydrostatic pressure, the transformation occurred gradually, and the sample became a mixture of two phases starting from ~ 4 GPa. The content of the high-pressure phase gradually increased to a maximum at ~ 10 GPa. It remained stable upon a decrease in the pressure up to 0.8 GPa when the reverse transition to the initial phase occurred.

Keywords: Metallocenes; Raman scattering; High pressure; Phase transitions; Hysteresis

1. Introduction

Ruthenocene $RuC_{10}H_{10}$ is an organometallic molecule consisting of two stacked cyclopentadienyl rings C_5H_5 with a metal atom between them. The first representative of metallocenes, ferrocene $FeC_{10}H_{10}$, was synthesized in 1951 [1]. The lower and upper cyclopentadienyl rings in metallocenes can change their mutual orientation relative to the fifth-order central axis of the molecule, thus forming two stable conformations. In the eclipsed conformation with D_{5h} symmetry, the upper ring is parallel to the lower ring. In the staggered conformation with D_{5d} symmetry, the upper ring is rotated 36° relative to the lower ring [2, 3]. A free ferrocene molecule is stable in the eclipsed conformation; in the monoclinic crystal phase, however, both molecular conformations are present. In several other crystal phases, ferrocene molecules are ordered in the staggered conformation [4–8].

Under ambient conditions, the ruthenocene crystal has an orthorhombic structure (space group Pnma) with four molecules per unit cell in the eclipsed conformation [9]. Recent high-pressure X-ray diffraction studies demonstrated that the orthorhombic α-phase (Pnma space group) undergoes a transition to the orthorhombic β-phase (Pcmb space group) at ~ 3.9 GPa; this transition is accompanied by a significant deterioration in crystallinity [10]. Investigations of the β-phase of ruthenocene in the pressure range of 0.7–2.3 GPa were carried out on high-quality single crystals grown from a ruthenocene solution in tetrahydrofuran at ~ 1 GPa [10]. They revealed that a transition to the orthorhombic α-phase occurs at a pressure of 0.7 GPa with a significant) hysteresis. A detailed study demonstrated that the transition from the α-phase to the β-phase is accompanied by a change in the packing and configuration of short Ru…H contacts between neighboring ruthenocene molecules [10]. In addition, the ruthenocene crystal undergoes a phase transition to the γ-phase at 394 K and normal pressure, which is characterized by the disorder of cyclopentadienyl rings between the eclipsed (50%) and staggered (50%) conformations. A similar transition to the γ-phase occurs in osmocene crystals at 421.5 K and normal pressure [11].

In this paper, we present the results of a Raman study of the phonon spectrum and phase transitions of the ruthenocene crystal at high pressure. The pressure dependence of the phonon frequencies changes abruptly under hydrostatic pressure in a methanol–ethanol 4:1 mixture at ~ 4, ~ 5, and ~ 8 GPa in three independent series of Raman measurements. With a decrease in the pressure, the pressure dependence is the same in all series and differs from

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the initial one, indicating a reverse transition to the initial phase at 0.8 GPa with an extremely large hysteresis. The frequency of the phonon modes increases with pressure, and the pressure shift coefficients vary from 2 to 23 cm^{-1}/GPa. With a decrease in the pressure, the phonon frequencies exhibit different pressure dependencies and smaller pressure shift coefficients. Under quasi-hydrostatic compression in silicone oil, several bands of intramolecular phonons split, accompanied by a gradual redistribution of intensity between the split components in the range of 4–10 GPa. The observed changes in the Raman spectrum are preserved in a pressure-down run up to a pressure of $\sim$ 0.8 GPa, at which an abrupt transition to the initial state occurs.

2. Experimental methods

Ruthenocene single crystals were grown from powder dissolved in hexane by slow evaporation of the solvent at room temperature. The Raman spectra were measured in the back-scattering geometry using an Acton SpectraPro-2500i spectrograph equipped with a Pixis2K CCD detector cooled down to $-$ 70 °C and an Olympus BX51 microscope. The measurements were performed using a single-mode laser with λ = 532 nm, an edge filter with OD = 6, and a transmission band from 60 cm^{-1}. The spectral resolution was $\sim$ 3 cm^{-1} for all Raman measurements. The laser beam with an intensity of $\sim$ 2.1 mW before the anvils was focused on the sample using an Olympus 50$\times$ objective in a $\sim$ 1.3 μm spot. A Mao–Bell-type diamond anvil cell was used for the measurements at high pressure and room temperature. A methanol–ethanol 4:1 mixture or silicone oil was used as a pressure-transmitting medium, and pressure was calibrated according to the spectral position of the R_1 luminescence line of ruby chips [12, 13]. The accuracy of pressure calibration under hydrostatic compression in the methanol–ethanol mixture was about $\pm$ 0.05 GPa. However, under quasi-hydrostatic compression in the silicone oil at pressures $>$ 3.5 GPa, the accuracy decreased to $\pm$ 1 GPa.

3. Results and discussion

Figure 1 shows the Raman spectra of the ruthenocene crystals in the region of 60–490 cm^{-1} at room temperature and pressures up to $\sim$ 10.7 GPa. The initial region of the spectra up to $\sim$ 100 cm^{-1} corresponds to intermolecular phonons similar to those of the ferrocene crystal [6]. The region of 300–490 cm^{-1} contains bands of intramolecular breathing (328 and 335 cm^{-1}) and bending (390, 400, and 406 cm^{-1}) vibration modes of the cyclopentadienyl rings relative to the C5 axis of the molecule. The high-energy regions of 1100 cm^{-1} and 3100 cm^{-1} contain intramolecular modes corresponding to the C–C and C–H stretching vibrations of the cyclopentadienyl ring, respectively (not shown in the figure). As the pressure increases, the spectrum shifts upward in energy: the shift of the intermolecular phonon bands is stronger than that of the intramolecular phonon bands, which is typical of crystals with a van der Waals interaction [14, 15]. An exception is the C–H stretching vibrations, whose shift is close to that of the intermolecular phonons, as in the naphthalene crystal [15].

The left panel of Fig. 1 depicts the Raman spectra of the ruthenocene crystal as the pressure increases. The spectrum measured under ambient conditions is identical to the Raman spectrum recorded earlier at normal pressure and liquid-nitrogen temperature [16]. With an increase in the pressure, the wavenumber of the bands increases up to $\sim$ 8 GPa. At this pressure, an abrupt shift of the intermolecular phonon bands downwards in energy occurs, while the intramolecular 335 cm^{-1} mode abruptly shifts upwards in energy. With a further increase in the pressure, a monotonic shift of all bands in the spectrum toward higher energies continues. At $P > 8$ GPa, the intensity ratio of some intermolecular phonon bands also changes, and weak satellite bands arise. The right panel of Fig. 1 shows the Raman spectra with a decrease in the pressure. Here, one can observe a monotonic shift of the spectrum toward lower energies without a change in its structure or band intensity up to a pressure of $\sim$ 0.8 GPa, where it changes abruptly and takes the structure of the initial spectrum.

Figure 2 illustrates the pressure dependence of the phonon mode frequencies for an increase and a decrease in the pressure in two independent series of measurements. The phonon frequency was determined by fitting the band profile with the Voigt function with an accuracy of $\pm$ 0.3 cm^{-1}. The half-solid and solid symbols denote the pressure-up and pressure-down runs, respectively. The red circles and green squares show the experimental results for the first and second series of measurements at high pressure, respectively. The lower left part of Fig. 2 depicts the pressure dependence of three bands of the intermolecular phonons with frequencies of 78.6, 72.7, and 67.4 cm^{-1}, and the upper part illustrates the data for the intramolecular phonons of 328 and 335 cm^{-1}. The pressure dependence of the frequencies shows abrupt changes near 4 and 8 GPa in the first and second pressure runs, respectively; they are marked with vertical red and green hatching. For simplicity, the figure does not show the results of the third pressure run, in which similar changes were observed at $\sim$ 5 GPa. All pressure-up runs were performed under similar conditions of compression, and the difference in the transition pressure is most likely not due

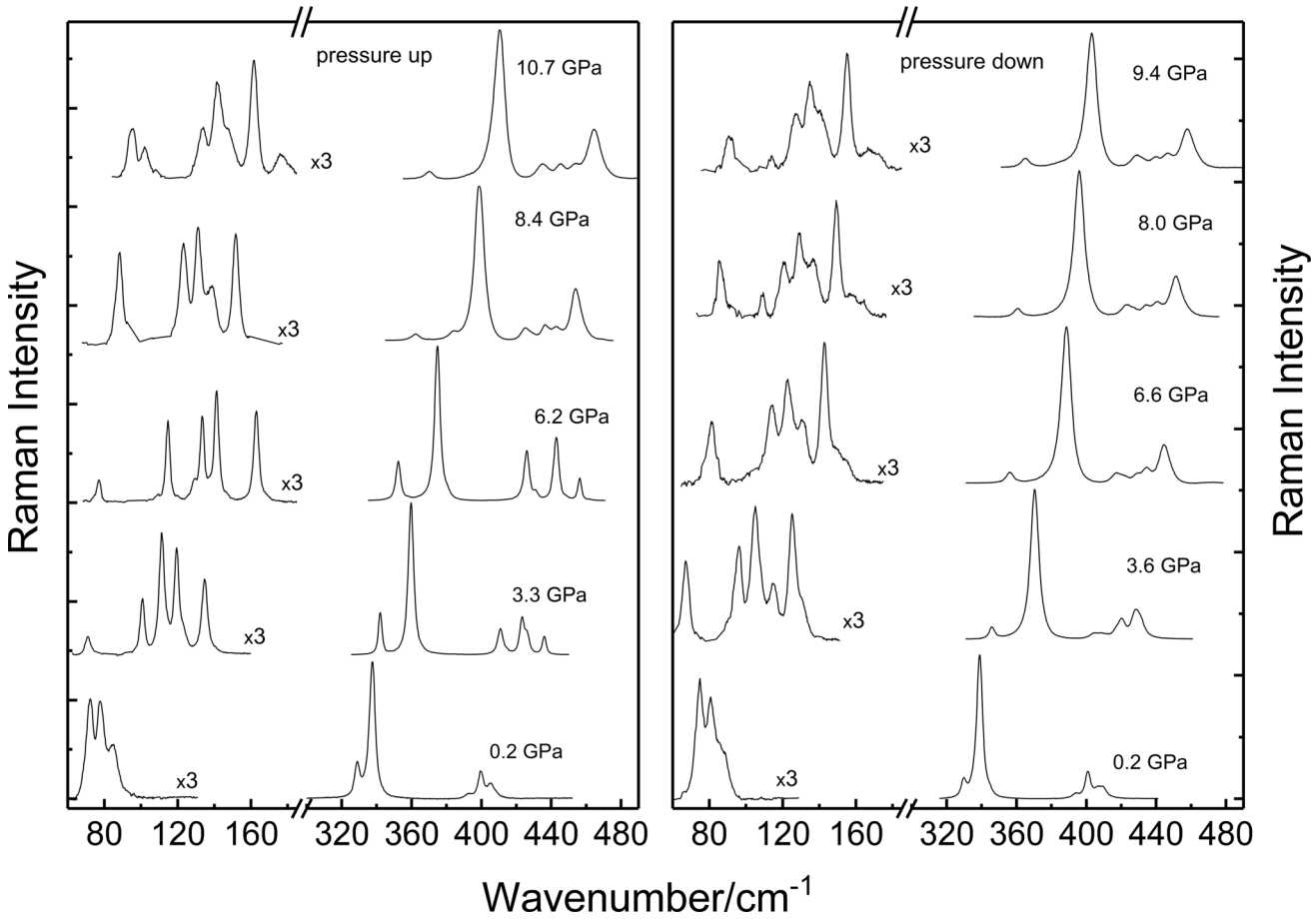

Fig. 1 Raman spectra of the ruthenocene crystals in the energy range of 60–490 cm^{-1} at room temperature and pressures up to 10.7 GPa

to kinetic effects. Unfortunately, we do not know the reason for this behavior. The results of the first and second series of measurements for the increasing pressure are the same up to $\sim$ 4 GPa. The data of the second measurement series between 4 and 8 GPa are, in fact, the continuation of the pressure dependence of the first measurement series. At the transition points, the frequency of the intermolecular phonons decreases abruptly, whereas the frequency of the intramolecular 335 cm^{-1} mode increases. The data for the pressure-up and pressure-down runs are different below the transition points but fully coincide above them. The values of the pressure shift coefficients of the intermolecular phonon bands vary from 18 to 23.2 cm^{-1}/GPa for the pressure-up run and from 13.9 to 19.9 cm^{-1}/GPa for the pressure-down run. The pressure shift coefficients for various intramolecular phonons are 2.4–14.2 cm^{-1}/GPa for the pressure-up runs and 5.5–13.3 cm^{-1}/GPa for the pressure-down runs. The abrupt changes in the pressure dependence of the phonon frequencies and the decrease in the pressure coefficients for the pressure-down run are most likely due to the phase transition [10]. The FWHM of the intermolecular and intramolecular bands does not change noticeably under compression and decompression runs, as well as under discontinuous changes at the transition pressure. Their value remains rather stable within the hydrostatic pressure range up to 10 GPa in the methanol–ethanol mixture and is close to the spectral width of the spectrometer slit. The compression in the silicone oil under non-hydrostatic conditions at pressures above 3.5 GPa results in the readily visible broadening of bands. In the right panel of Fig. 2, the same symbols show changes in the relative frequency Ω_p/Ω_0 for the intermolecular 78.6 cm^{-1} and the intramolecular 335 cm^{-1} modes for the pressure-up and pressure-down runs. Here, one can clearly see the details of the abrupt softening and hardening of these modes at critical pressure values. Hence, the jumps of phonon mode frequencies, the difference in the pressure dependence for the pressure-up and pressure-down runs, and the coincidence of all the data in the series of pressure-down runs indicate a phase transition that occurs in three independent pressure runs. With a decrease in the pressure, the transition to the initial phase occurs at $P \sim 0.8$ GPa with a hysteresis of $\sim$ 3.2, $\sim$ 4.2, and $\sim$ 7.2 GPa in various pressure runs. The changes in the Raman spectra

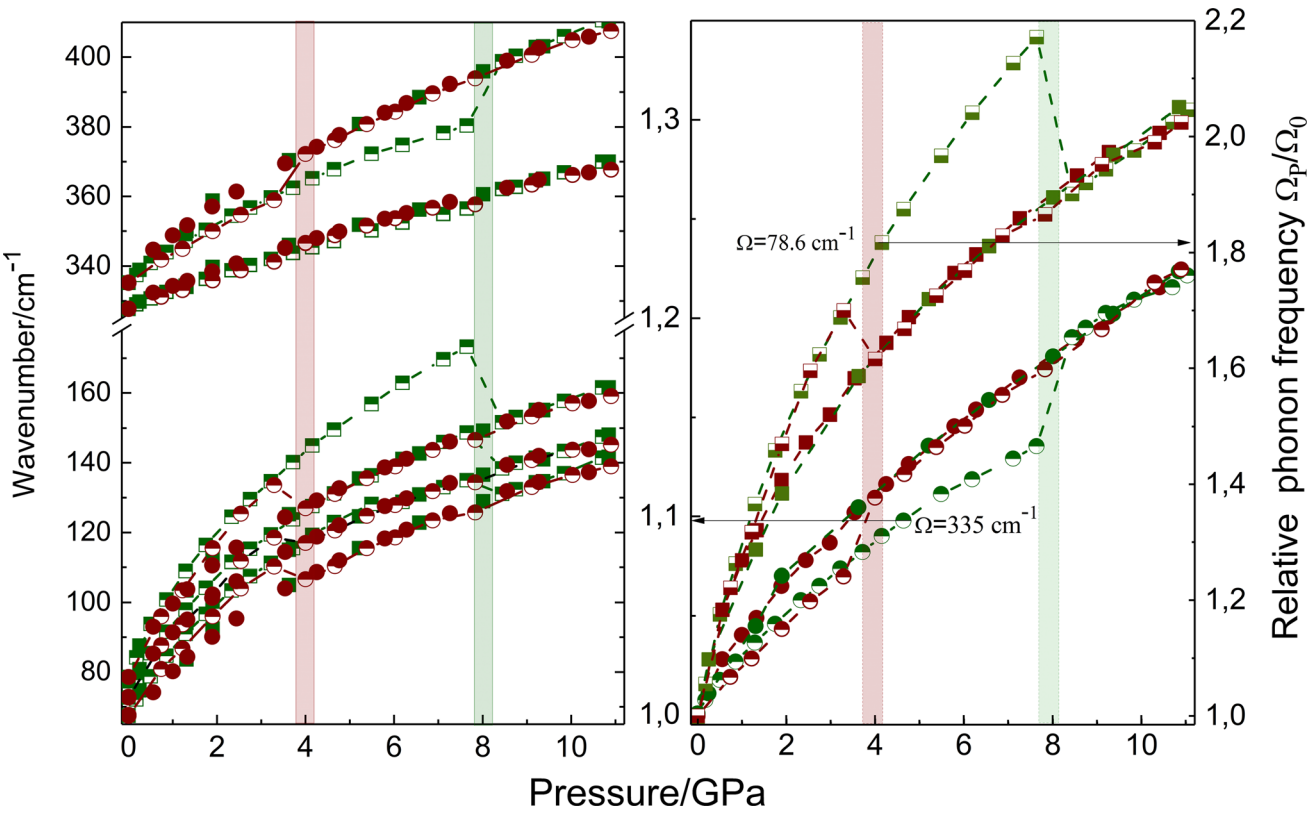

Fig. 2 Pressure dependence of the intermolecular 78.6, 72.7, and 67.4 cm^{-1} modes and the intramolecular 328 and 335 cm^{-1} modes of the ruthenocene crystal (left panel). Pressure dependence of the relative frequency Ω_p/Ω_0 of the intermolecular mode 75 cm^{-1} and the intramolecular mode 335 cm^{-1} (right panel). Red circles and red hatching—a transition at ~ 4 GPa, green squares and green hatching—a transition at ~ 8 GPa, half-solid and solid symbols—pressure-up and pressure-down runs, respectively (Color figure online)

are most likely due to the phase transition with an extremely large hysteresis from the α-phase Pnma to the β-phase Pcmb, which was observed for the first time in [10] at a pressure of 3.9 GPa.

The left panel of Fig. 3 depicts the Raman spectra of ruthenocene in the region of 3050–3250 cm^{-1}, where the bands of the C–H stretching vibrations are located. The spectra contain five C–H bands, indicating some difference in the lengths of five C–H bonds in the cyclopentadienyl ring, as in the ferrocene crystal [4, 6]. The right panel of Fig. 3 shows the pressure dependence of these modes. As the pressure increases, the entire bands shift toward higher energies, and abrupt changes can be observed at ~ 4 GPa in the first pressure run and at ~ 8 GPa in the second one. It is worth noting that two modes with frequencies of ~ 3095 and ~ 3113 cm^{-1} abruptly shift downwards, similar to the intermolecular phonons, and the low-frequency ~ 3080 cm^{-1} mode abruptly shifts upwards, similar to the intramolecular 335 cm^{-1} mode. The pressure shift coefficients in the pressure-down run increase for the ~ 335 and ~ 3080 cm^{-1} modes and decrease for the ~ 3095 and ~ 3113 cm^{-1} modes, whose frequencies jump up and down at the transition pressure, respectively. The 328 cm^{-1} mode does not undergo abrupt changes, and its pressure shift coefficients are the same for compression and decompression pressure runs and are ~ 5.5 cm^{-1}/GPa.

Three independent high-pressure runs were carried out under hydrostatic conditions up to ~ 10 GPa using a methanol–ethanol mixture as a pressure-transmitting medium. Some measurements were performed using silicone oil, which solidifies at $P > 3.5$ GPa and introduces stresses into the crystal. Figure 4 shows the Raman spectra of the ruthenocene crystal near the intramolecular vibration of 335 cm^{-1} obtained using silicone oil as a pressure-transmitting medium. The left part of Fig. 4 depicts the spectra for the compression run to 10 GPa in red and the decompression run in blue. At pressures below 4 GPa, the spectrum contains a single intense band ν_1 with an initial frequency of 335 cm^{-1}. Near 4 GPa, when its frequency increases to 362 cm^{-1}, a weak satellite ν_2 = 370 cm^{-1} appears, whose intensity gradually increases to a maximum at P ~ 10 GPa. As the pressure decreases, the spectrum containing weak ν_1 and intense ν_2 bands shifts downward in energy without noticeable changes in intensity or structure. At ~ 0.8 GPa, it abruptly transforms into the

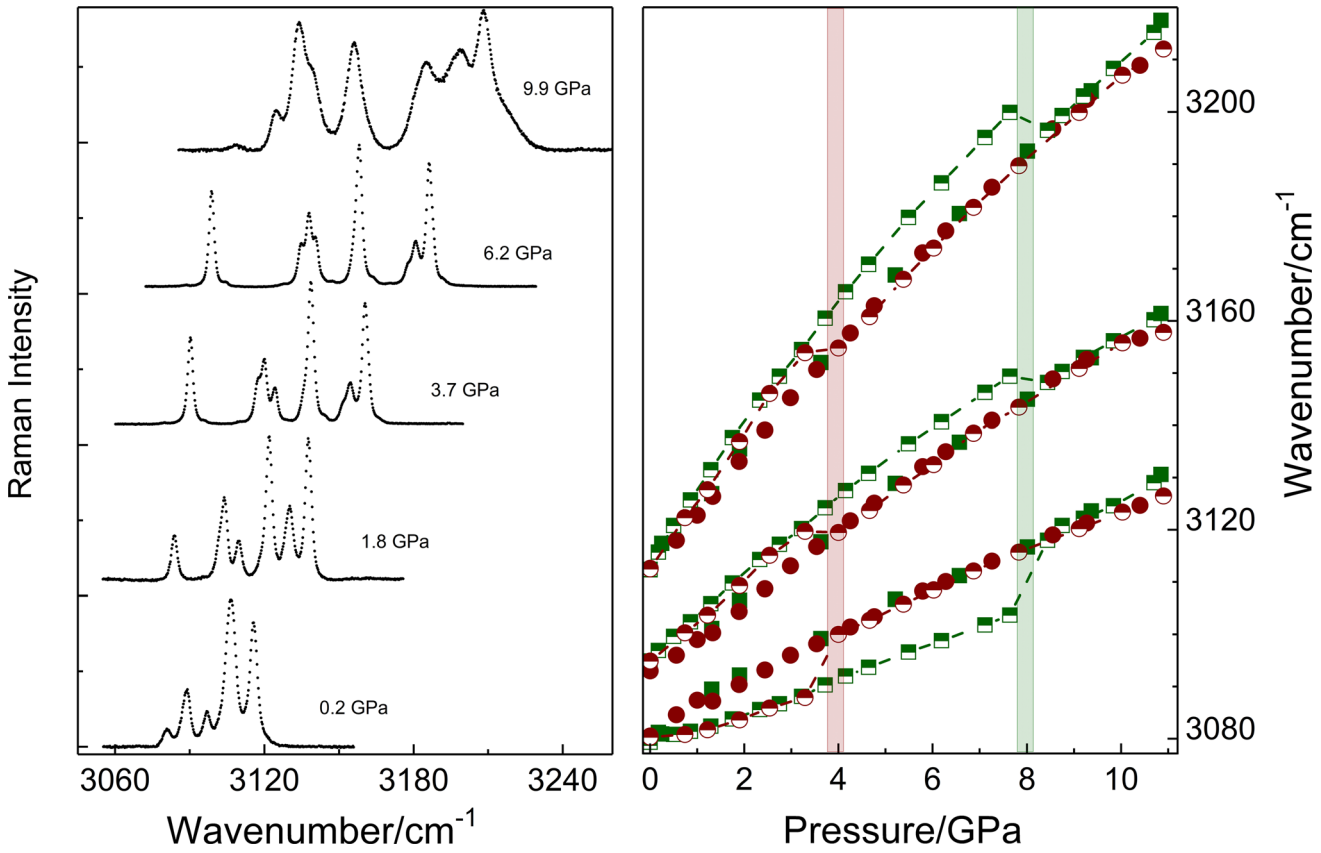

Fig. 3 Raman spectra of the ruthenocene crystal in the region of C–H vibration modes (left panel). Pressure dependence of some C–H phonon mode frequencies (right panel). Red circles and red hatching—a transition at ~ 4 GPa, green squares and green hatching—a transition at ~ 8 GPa, half-solid and solid symbols—pressure-up and pressure-down runs, respectively (Color figure online)

initial spectrum**.** When the band splits at ~ 4 GPa, the difference between the frequencies of the components ν_1 and ν_2 is ~ 8 cm^{-1}, which is exactly equal to the frequency jump upon the transition near ~ 4 GPa under hydrostatic compression. The upper inset in Fig. 4 shows the pressure shift of the mode ν_1 = 335 cm^{-1}: the half-solid red and blue symbols denote the shift of the ν_1 and ν_2 bands, respectively. At $P > 4$ GPa, the shift of the weakened ν_1 band is marked with the shaded half-solid symbols. The solid red and blue symbols show these two bands with a decrease in the pressure, the red solid symbols also being shaded due to the weakening of the ν_1 band. The lower inset in Fig. 4 depicts the pressure dependence of the relative intensity of the ν_2 band (half-solid red symbols). It reflects a gradual increase in the fraction of the new phase from 0% at 4 GPa to ~ 83% with an increase in the pressure to 10 GPa. It can be assumed that the sample partially undergoes a transition to a new phase at ~ 4 GPa: it becomes two-phase, and the fraction of each phase is proportional to the intensity of the ν_1 and ν_2 bands. With a decrease in the pressure (solid blue symbols), the fraction of the new phase does not change up to ~ 0.8 GPa. Then, it decreases sharply when the sample undergoes a transition to the initial phase.

The Raman spectra of the ruthenocene crystals in the pressure range of 4–10 GPa show a phase transition with an extremely large hysteresis, suggesting the coexistence of two phases. The structure of the phonon spectra of these phases is similar; however, the frequency of the phonon modes changes abruptly at the transition pressure. In three series of measurements under hydrostatic compression, the phase transition was observed at 4, 5, and 8 GPa, respectively. The results for a decrease in the pressure always differ from those for an increase in the pressure; however, they coincide in all series of measurements in overlapping pressure ranges. Abrupt changes in the Raman spectrum are observed at a minimum pressure of 4 GPa. This pressure coincides with a pressure of 3.9 GPa for the phase transition from the α-phase Pnma to the β-phase Pcmb discovered in [10]. This transition is related to a transformation of the interaction between the molecules: additional coordination Ru–H bonds are formed between the hydrogen atoms of the cyclopentadienyl ring of one molecule and the ruthenium atom of the neighboring molecule [10]. In the α-phase, the length of these contacts is the same for

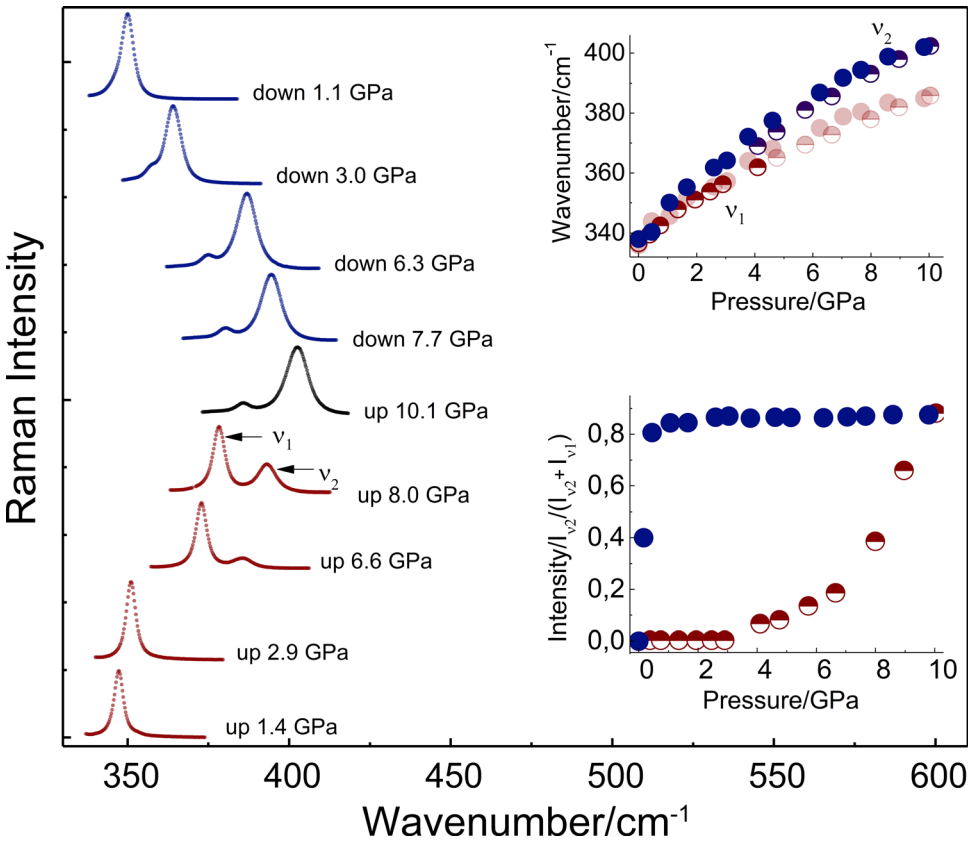

Fig. 4 Raman spectra in the region of the band $\nu_1 = 335\ cm^{-1}$ under compression in silicone oil. Red color – pressure up, blue color – pressure down. Upper inset: pressure shift of the modes $\nu_1 = 335\ cm^{-1}$ and $\nu_2 = 370\ cm^{-1}$, red and blue symbols, respectively. Lower inset: a change in the fraction of the new phase with an increase and a decrease in the pressure (Color figure online)

the lower and upper rings and is 3.369 Å. After the transition to the β-phase, it decreases to 3.169 Å for the lower ring and increases to 3.699 Å for the upper ring. These changes may increase the effective mass and rigidity of the molecule, leading to an abrupt decrease in the frequency of the intermolecular phonons and an increase in the frequency of the breathing mode, respectively. According to the X-ray diffraction data from [10], the reverse transition to the initial phase occurs at 0.7 GPa. The Raman spectroscopy data reported in the present work yield a value of ∼ 0.8 GPa. The phase transition has a giant hysteresis with a minimum value of ∼ 3.2 GPa. Since in our experiments the transition also occurs at 8 GPa, the value of the hysteresis is even higher and reaches 7.2 GPa. This suggests that two-phase states may arise in the corresponding pressure range, where both phases are stable. The two-phase state was observed in the Raman experiments under quasi-hydrostatic pressure when mechanical stresses arose in the crystal during the solidification of silicone oil. This is evidenced by the splitting of the phonon 335 cm^{-1} band, as well as an increase in the intensity of the new component and, accordingly, in the fraction of the second phase to 83% at 10 GPa. With a decrease in the pressure, this ratio holds up to a pressure of ∼ 0.8 GPa when the abrupt transition to the initial phase occurs. Hysteresis and the coexistence of phases are quite common phenomena; they were observed, e.g., upon the nematic-cholesteric phase transition in liquid crystals [17] and during electrocrystallization of supercooled water confined between graphene layers [18].

4. Conclusion

The pressure dependence of the phonon frequencies in the Raman spectra reveals abrupt changes under hydrostatic compression near ∼ 4, ∼ 5, and ∼ 8 GPa in three independent series of measurements. The pressure dependence of the phonon frequencies for the pressure-down run is the same in all series of measurements and differs from that observed for the pressure-up run. This indicates a phase transition and confirms the results of the X-ray structural investigation at high pressure [10]. The change in the phonon frequency is most likely related to a change in the coordination Ru–H bonds between the hydrogen atoms of the cyclopentadienyl ring of one molecule and the ruthenium atom of the neighboring molecule [10]. Under quasi-hydrostatic conditions at 4 GPa, the breathing 335 cm^{-1} mode splits into two components, indicating that the sample becomes a mixture of the α-phase and β-phase. The fraction of the new phase increases to a maximum of 83% at 10 GPa and remains the same with a decrease in the

pressure to $\sim$ 0.8 GPa, at which an abrupt transition to the initial state occurs. These peculiarities in the Raman spectra of the ruthenocene crystal at high pressure are associated with a phase transition that exhibits a giant pressure hysteresis.

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