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Phonon spectrum, crystal structure, and stability of the ruthenocene molecule at high pressure

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The phonon spectrum, crystal structure, and stability of the ruthenocene molecule at ambient and high pressures were studied. The crystal had an orthorhombic structure $Pnma$, $Z = 4$. A change in the parameters at high pressure could be described by the Murnaghan equation of state $(V0/V)B = \{1 + P \cdot B'/B_0\}$ with $B_0 = 9.68$ GPa and $B' = 6.1$ up to a pressure of 4 GPa, above which a drastic increase in the mosaic parameters was observed in the X-ray diffraction patterns. The pressure dependence of phonon frequencies under hydrostatic compression changed abruptly at ~ 4, ~ 8 and ~ 5 GPa in the first, second, and third series of measurements, respectively. The results of all measurements for a decrease in the pressure differed from those for an increase in the pressure, the changes being irreversible. Under non-hydrostatic compression, the changes occurred gradually in the range of ~ 4 to ~ 10 GPa. The ruthenocene molecule was stable in the eclipsed conformation; however, jumps to the staggered conformation were possible under heating. The energy barrier between the conformations determined from the Arrhenius dependence of the bandwidth of intermolecular phonons on temperature was (273 ± 19) meV/mol.

Keywords: metallocenes, high pressure, Raman scattering, X-ray diffraction, phase transitions, molecular conformation stability.

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1. Introduction

Ruthenocene $RuC_{10}H_{10}$ relates to a family of metalorganic molecules consisting of two stacked cyclopentadienyl rings of C_5H_5 with an atom of metal between them. The first representative of metallocenes — ferrocene $FeC_{10}H_{10}$, was synthesized in 1951 and since then these materials have been actively studied [1]. The lower and upper cyclopentadienyl rings of Cp in metallocenes can change their mutual orientation relative to the central axis of the fifth order of the molecule, forming two stable conformations. In the eclipsed conformation with symmetry D_{5h}, the upper ring is located parallel to the lower one, and in the staggered conformation with symmetry D_{5d}, it is rotated 36 degrees relative to the lower one [2,3]. The free ferrocene molecule is stable in the eclipsed conformation, while both conformations of the molecule are available in the monoclinic crystalline phase and a conformational disorder is observed. In the low-temperature triclinic phase LT1, low-temperature orthorhombic phase LT2, and the high-pressure monoclinic phase, the molecules are ordered in the staggered conformation [4–8].

The ruthenocene crystal under normal conditions has an orthorhombic structure (space group $Pnma$, $Z = 4$), the molecule is stable in the eclipsed conformation [9]. Recent X-ray diffraction studies at high pressure showed that the orthorhombic phase α ($Pnma$ group) turns into orthorhombic phase β ($Pcmb$ group) at pressure of ~ 3.9 GPa, which is accompanied by a drastic worsening of crystallinity quality [10]. The studies of β phase of ruthenocene were carried out within the pressure range from 0.7 to 2.3 GPa on the single crystals grown at pressure of ~ 1 GPa from tetrahydrofuran solution of ruthenocene [10]. The studies demonstrated that the reverse transition into orthorhombic phase α occurred at 0.7 GPa with a large hysteresis, and the isostructural transition from α to β phase is related with the change of short contacts configuration of Ru...H between the molecules of ruthenocene [10].

In this study, the phonon spectrum and structure of a ruthenocene crystal were studied at normal and high pressure, pressure shear coefficients and Gruneisen parameters of phonon modes were determined, changes in the parameters of the crystal structure at high pressure and the stability of the conformation of the molecule were studied. The structure of the crystal in α phase (orthorhombic $Pnma$, $Z = 4$) was proved with the following cell parameters in normal conditions: $a = 7.119$ Å, $b = 8.9899$ Å, $c = 12.8084$ Å, $V_0 = 819.73$ Å^3. The change in crystal parameters at high pressure is described by Murnaghan equation of state $(V_0/V)^{B'} = \{1 + P \times B'/B_0\}$ from $B_0 = 9.68$ GPa and $B' = 6.1$ to a pressure of 4 GPa, above which the diffraction pattern deteriorates significantly due to a sharp broadening of diffraction maxima caused by increase in mosaic. The pressure dependence of the frequencies of intermolecular and intramolecular phonons changes abruptly during hydrostatic compression in a mixture of methanol/ethanol at ~ 4, ~ 5 and ~ 8 GPa in three independent series of Raman scattering (RS) spectra measurements. When the pressure is reversed, it is the same in all series and differs from the initial one, which indicates an irreversible phase transition. As the pressure increases, the frequency of phonon modes goes up: the baric shift coefficients range from 1 to 23 cm^{-1}/GPa. When the pressure reverses, the phonon frequencies decrease, and the baric dependence of the phonon modes and the shift coefficients differ from the initial ones. When the crystal is compressed under quasi-hydrostatic conditions in silicone oil, individual bands of intramolecular phonons split and a gradual redistribution of intensity occurs between the split components in the range from 4 to 10 GPa. These changes are irreversible and persist with the reverse pressure up to ~ 0.8 GPa, at which an abrupt transition to the initial state occurs.

The ruthenocene molecule is stable in the eclipsed conformation under normal conditions, but flips to the staggered conformation occur when heated. In RS spectra of ruthenocene crystals at temperatures up to 373 K, this leads to a broadening of the bands of intermolecular phonons compared with intramolecular phonons. The flips reduce the lifetime of the conformation of the molecule up to the period of lattice vibrations, which leads to a loss of coherence of intermolecular phonons and a significant broadening of the bands [4,6,11]. The energy barrier between the eclipsed and staggered conformations of ruthenocene molecule, found from the Arrhenius dependence of the intermolecule phonons widths on reciprocal temperature $1/k_{\text{B}}T$, makes (273 ± 19) meV/molecule [3,11–13].

2. Experimental procedure

High-quality single crystals of ruthenocene were grown from powder dissolved in hexane during slow solvent evaporation at room temperature. X-ray diffraction (XRD) analysis was performed at normal and high pressure using Oxford Diffraction Gemini-R four-circle diffractometer with an Atlas S2 two-dimensional CCD detector (Mo $K_{\alpha 1}$, $\lambda = 0.71073$ Å, graphite monochromator, ω-scanning) and a high-pressure chamber with Boehler-type diamond anvils.

RS spectra were measured in the back scattering geometry using Acton SpectraPro-2500i spectrograph with a CCD-detector Pixis2K cooled down to $-70\,^{\circ}$C and Olympus BX51 microscope using $\lambda = 532$ nm laser and edge filter with OD = 6 and bandwidth from 60 cm^{-1}. A laser beam with an intensity of ~ 2.1 mW in front of the anvils was focused on the sample with an Olympus lens 50× into a spot with a diameter of $\sim 1.3\,\mu$m. A chamber with diamond anvils of Mao–Bell type was used for measurements at high pressure and room temperature, and a chamber of the Merrill-Basset type was used in the temperature range of 80–370 K. A compact chamber in the form of a cylinder with a diameter/height of 39 mm was tightly placed in a cylindrical cavity inside the heat exchanger of a nitrogen cryostat with a temperature controller and a resistive heater that kept the temperature with an accuracy of ± 0.4 K [14]. A methanol/ethanol mixture in the ratio of 4 : 1 or silicone oil was used as the pressure transfer medium, and pressure calibration was performed using the spectral position of R1-line of luminescence of ruby microcrystals [15,16].

3. Experimental Results

RS spectra of ruthenocene crystal within the energies 40–495 cm^{-1} at room temperature and pressure of up to ~ 11 GPa are shown in Figure 1. The region up to 100 cm^{-1} stands for the intermolecular phonons, and the region 300–490 cm^{-1} incorporates the spectral bands of intramolecular breathing (328 and 335 cm^{-1}) and (390, 400 and 406 cm^{-1}) bending vibrational modes of the cyclopentadienyl rings relative to the molecule axis. The region 1100 cm^{-1} and 3100 cm^{-1} incorporates the intramolecular modes standing for the vibrational C–C and C–H oscillations of the cyclopentadienyl ring respectively (not shown in the figure). As the pressure increases, the spectrum shifts upward in energy: the bands of intermolecular phonons shift more strongly than those of intramolecular phonons, which is typical for crystals with a van der Waals bond [11,17].

The exception is vibrational C–H oscillations, the shift of which is close to the shift of intermolecular phonons, as, for example, in a molecular crystal of naphthalene [17]. The left panel of Figure 1 shows the spectra with increasing pressure, where the initial spectrum is identical to the spectrum at normal pressure and nitrogen temperature obtained earlier in [18]. As the pressure rises, the frequency of the bands increases monotonously to a pressure of ~ 8 GPa, at which the bands of intermolecular phonons shift downwards in energy, and the intramolecular mode 335 cm^{-1} shifts up in energy. With a further increase in pressure, a monotonous shift of all spectral bands towards higher energies continues. It should be noted that at $P > 8$ GPa slightly changes and the intensity ratio of the bands of intermolecular phonons and weak satellites appear near the bands. The right-hand side of Figure1 shows the spectra with decreasing pressure, where a monotonous shift of the bands towards lower energies is observed without changing the structure up to pressure ~ 0.8 GPa, when the spectrum drastically turns into an initial one in the forward pressure cycle.

Figure 2 shows the pressure dependence of the phonon mode frequencies for forward and reverse pressure in two independent measurement cycles. The half-filled symbols correspond to the forward pressure stroke, and the fully filled symbols — correspond to the reverse pressure stroke. The round red and square green symbols show the experimental results for the first and second series of measurements at high pressure, respectively. The frequency of phonons was found by approximating the bands profile by Voigt function with an accuracy of ± 0.3 cm^{-1}. The

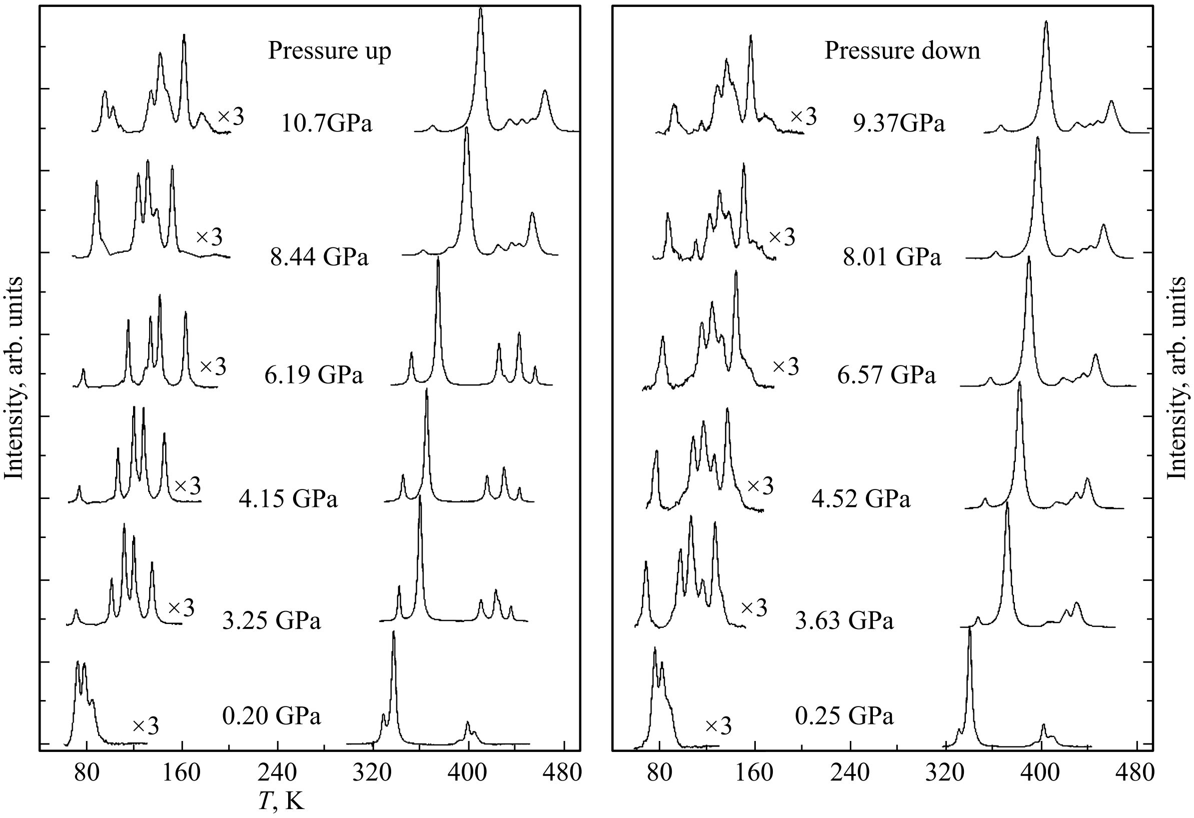

Figure 1. RS spectra of ruthenocene crystal within the range 40–495 cm^{-1} at a room temperature and pressure of up to $\sim$ 11 GPa.

lower-left part of Figure2 shows the pressure dependence of three bands of intermolecular phonons with frequencies of 78.6, 72.7 and 67.4 cm^{-1}, and the upper part shows data for intramolecular phonons 328 and 335 cm^{-1}. Abrupt changes in the baric dependence of frequencies near 4 and 8 GPa in the first and second series of measurements, respectively, are marked by vertical red and green hatching. For simplicity, the figure does not show the results of the third series of measurements, in which similar changes were observed at a pressure of $\sim$ 5 GPa. The results of two series of measurements for the forward pressure stroke completely coincide up to a pressure of $\sim$ 4 GPa, and the data of the second series between 4 and 8 GPa are a continuation of the pressure dependence of the first series of measurements. At the transition points, the frequency of intermolecular phonons decreases abruptly, while the frequency of the intramolecular mode 335 cm^{-1} goes up. The experimental results for the reverse pressure stroke in different measurement series are shown in solid round red and square green symbols and completely coincide with each other in the entire pressure range, but differ from the data of the forward pressure stroke below the transition points.

The central panel in Figure 2 illustrates the RS spectra of ruthenocene within 3050–3250 cm^{-1}, where C–H bands of the vibrational modes are located (top). Five C–H bands are observed in the spectrum, which indicates some difference in length of C–H bonds in the cyclopentadienyl ring, which was observed earlier in the ferrocene crystal [4,6]. With an increase in pressure, all bands smoothly shift towards higher energies, and at a pressure of $\sim$ 4 GPa in the first series of measurements and $\sim$ 8 GPa in the second, step-like changes are observed. We should emphasize that modes with frequencies $\sim$ 3095 and $\sim$ 3113 cm^{-1} are displaced towards short-wavelength region, similar to the intramolecular phonons, and the low-frequency mode $\sim$ 3080 cm^{-1} is displaced towards the long-wavelength region, similar to the intramolecular mode 335 cm^{-1}.

The values of the pressure band shift coefficients of intermolecular phonons range from 18 to 23.2 cm^{-1}/GPa for the forward pressure stroke and from 13.9 to 19.9 cm^{-1}/GPa for the reverse pressure stroke. For the intramolecular phonons they make 2.4–14.2 cm^{-1}/GPa under direct pressure stroke and 5.5–13.3 cm^{-1}/GPa in case of reverse pressure stroke. The decrease in the shear coefficients for the reverse pressure stroke is most likely due to the isostructural phase transition [10]. It's interesting to note that for modes $\sim$ 335 and $\sim$ 3080 cm^{-1} the coefficients grow, and for modes $\sim$ 3095 and $\sim$ 3113 cm^{-1} they decline, at that, the first ones have frequency jumps upwards, and the second ones - downwards. We should emphasize that the baric coefficients of the shift of 328 cm^{-1} mode that had no

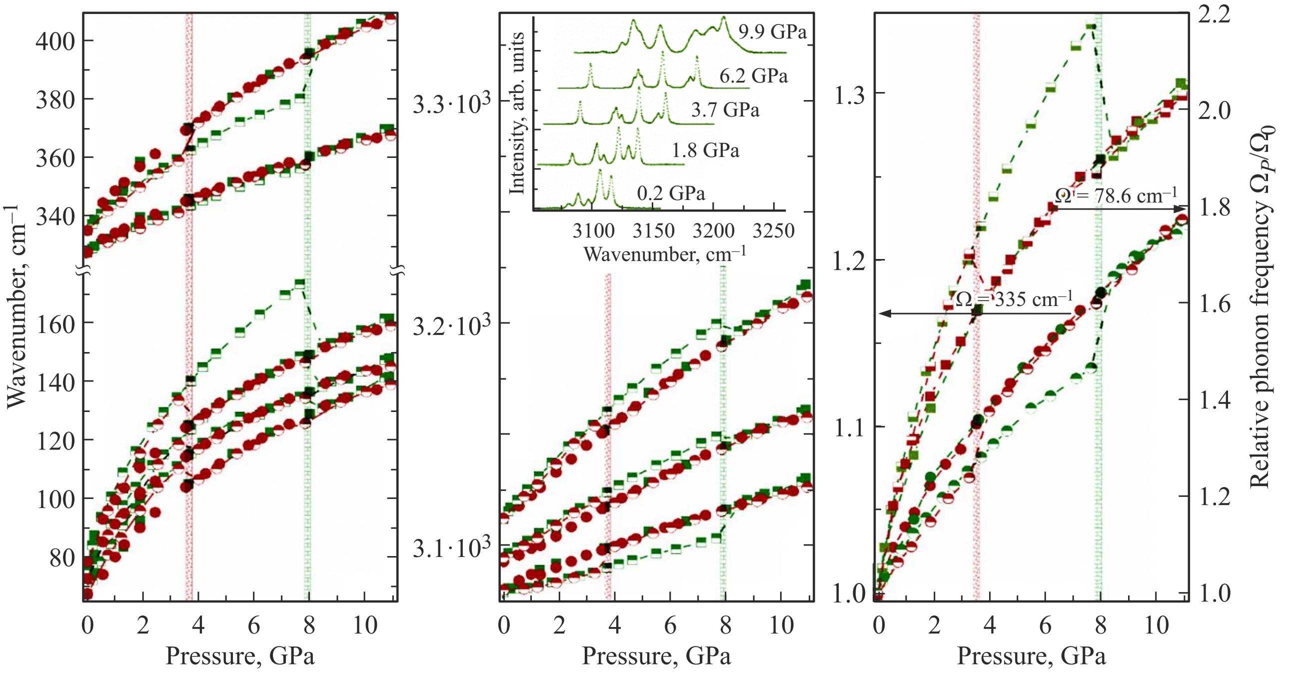

Figure 2. The pressure dependence of inter-molecular 78.6, 72.7 and 67.4 cm^{-1} and intramolecular 328 and 335 cm^{-1} modes of ruthenocene crystal (in the left). Raman spectra of ruthenocene in C—H oscillations region and the pressure dependence of the frequency of some phonon modes (in the center). Pressure dependence of frequency Ω_p/Ω_0 of modes 75 and 335 cm^{-1} (in the right). Round red symbols and hatching — transition at ~ 4 GPa, green square symbols and hatching — transition at ~ 8 GPa. The half- and fully filled-in symbols — represent the forward and reverse pressure strokes, respectively.

step-like variations are identical for the forward and reverse pressure strokes and make ~ 5.5 cm^{-1}/GPa.

Finally, the right panel of Figure 2 shows the changes in the relative frequency Ω_p/Ω_0 for the intermolecular mode 78.6 cm^{-1} and intramolecular mode 335 cm^{-1} under forward and reverse pressure strokes. The figure illustrates the abrupt weakening and tightening of these modes at critical pressure values and indicates an irreversible phase transition occurring at two different pressure values. With the reverse stroke of pressure the transition to the initial state occurs at $P \sim 0.8$ GPa with a hysteresis of ~ 3.2, ~ 4.2 and ~ 7.2 GPa as registered by three individual measurement cycles. The spectra variations, in our opinion, are caused by the irreversible isostructural phase transitions from α-phase $Pnma$ into β-phase $Pcmb$, which was first observed in the X-ray diffraction studies at a pressure of 3.9 GPa.

Most of the measurements at high pressure were carried out under hydrostatic compression conditions using a methanol/ethanol mixture, but some of the measurements used silicone oil, which solidifies at $P > 3.5$ GPa and stresses occur in the crystal. Figure 3 shows RS spectra of ruthenocene in the region of intramolecular oscillation 335 cm^{-1} obtained under these conditions. In the right part of Figure 3, the spectra are shown in red with a forward pressure stroke up to 10 GPa, and in blue with a reverse pressure stroke. Up to pressure ~ 4 GPa a band ν_1 with a frequency of 335 cm^{-1} is observed, and after that, its weak satellite $\nu_2 = 370$ cm^{-1} appears with an intensity rising up to maximum at $P \sim 10$ GPa. When the pressure reverses, the spectrum shifts unchanged down in energy to a pressure of ~ 0.8 GPa, and then abruptly returns to the initial one. It should be noted that the difference in the frequency bands ν_1 and ν_2 in the moment of the band splitting at ~ 4 GPa makes ~ 8 cm^{-1}, similar as the frequency jump at phase transition in conditions of the hydrostatic compression. The upper right insert shows the baric shift of the mode $\nu_1 = 335$ cm^{-1}: the half-filled red and blue symbols show the shift of the bands ν_1 and ν_2, respectively. At $P \geq 4$ GPa the shift of the weakened band ν_1 is shown by shaded symbols. Solid red and blue symbols show these two bands when the pressure is reversed, while the red symbols are also shaded due to the weakening of the band ν_1. It can be assumed that at a pressure of ~ 4 GPa the sample partially passes into a new phase and becomes a two-phase sample, and the share of each phase is proportional to the intensity of the ν_1 and ν_2 bands. The lower insert shows the dependence of the relative intensity of ν_2 band on pressure (half-filled red symbols), which shows a gradual increase in the proportion of the new phase to ~ 83 % with an increase in pressure to 10 GPa. During the reverse pressure stroke (solid blue symbols), the fraction of the new phase does not change until ~ 0.8 GPa, after which the entire sample transforms into initial phase.

Studies of the crystal structure of the ruthenocene under normal conditions and at high pressure were performed us-

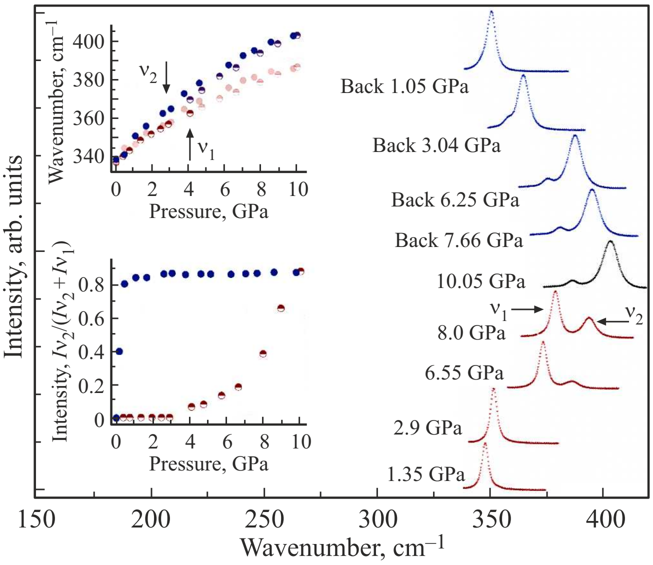

Figure 3. Raman spectra of a ruthenocene crystal near the band $\nu_1 = 335\,\mathrm{cm}^{-1}$ when compressed in silicone oil. Red and blue — forward and reverse pressure stroke, respectively. At $P \geq 4\,\mathrm{GPa}$ a satellite $\nu_2 = 370\,\mathrm{cm}^{-1}$ emerges, when the pressure declines the spectrum moves into initial state at $\sim 0.8\,\mathrm{GPa}$. Upper insert — pressure shift of modes $\nu_1 = 335\,\mathrm{cm}^{-1}$ and $\nu_2 = 370\,\mathrm{cm}^{-1}$, red and blue symbols respectively. Lower insert — change in the fraction of the new phase during the forward and reverse pressure strokes.

ing X-ray diffraction method on high-quality single crystals. According to the data obtained, the structure under normal conditions is orthorhombic $Pnma$, $Z = 4$, $a = 7.119\,\text{Å}$, $b = 8.9899\,\text{Å}$, $c = 12.8084\,\text{Å}$, $V_0 = 819.73\,\text{Å}^3$, which is in good consistency with the earlier obtained data [9,10]. Measurements at high pressure showed that the crystal structure is well defined up to a pressure of 4 GPa, above which the quality of the diffraction pattern deteriorates sharply. In the left part of Figure 4, different symbols show the baric dependence of the lattice cell volume on pressure. The squares show the results of this study, and the round symbols show similar data recalculated from the previously published dependence of specific molecular volume on pressure for α-phase [10]. The asterisks show the same dependence for β-phase, recalculated from the dependence of the specific molecular volume on pressure in the range from 2 to 0.9 GPa [10]. Both dependences for α-phase are smooth and agree well with each other, as well as the few data for β-phase. The insert window on the right side of the figure shows the diffraction spot width $\langle 060 \rangle$, obtained in our experiments at pressures up to 6 GPa. The pressure dependence of the diffraction spot FWHM is shown in the lower part of the figure: it changes little to $\sim 3.5\,\mathrm{GPa}$, and then begins to increase sharply. The broadening of the reflex is associated with a deterioration in crystal quality during the transition from α-phase $Pnma$ to β-phase $Pcmb$, accompanied by an abrupt change in the crystal parameters [10]. The change in cell volume with pressure is well described by the Murnaghan equation of state:

$$(V_0/V)^{B'} = \{1 + P \cdot B'/B_0\}, \qquad (1)$$

where $B_0 = 9.68\,\mathrm{GPa}$ — bulk module, and $B' = 6.1$ its derivative. Dotted lines on the left side of the figure — approximation of our experimental data and the data from [10] by the equation of state (1) up to pressure $\sim 4\,\mathrm{GPa}$.

These data are close to each other, as well as the resulting parameters of the Murnaghan equation of state. Using the previously obtained baric phonon mode shift coefficients $\partial\Omega_i/\partial P$, the Gruneisen parameters can be determined:

$$\gamma_i = (\partial\Omega_i/\Omega_i)/(\partial V/V) = (B_0/\Omega_i^0)/(\partial\Omega_i/\partial P). \qquad (2)$$

Their values for intermolecular phonon modes in α and β phases, calculated by the formula (2) for the forward and reverse pressure strokes and bulk modulus $B_0 = 9.68\,\mathrm{GPa}$ are given in the table.

Values for intermolecular phonon modes in α and β phases

Ω_i^0, cm^{-1}, pressure goes up	γ_i, α-phase	Ω_i^0, cm^{-1}, pressure goes down	γ_i, α-phase
67.6	2.25 ± 0.32	67.4	1.74 ± 0.24
72.2	2.18 ± 0.31	74.1	2.12 ± 0.3
75.3	2.48 ± 0.35	77.6	2.09 ± 0.29
67.6	2.25 ± 0.32	67.4	1.74 ± 0.24
72.2	2.18 ± 0.31	74.1	2.12 ± 0.3
75.3	2.48 ± 0.35	77.6	2.09 ± 0.29

The ruthenocene molecule in the free state and in a crystal under normal conditions has the eclipsed conformation [9,10], but when heated, flips to the staggered conformation can be observed, which has more energy. The flips between two conformations of a molecule reduce the lifetime of intermolecular phonons to the lifetime of the conformation and lead to bands broadening in RS spectrum. Thus, in a ferrocene crystal, conformational disorder leads to disruption of translational symmetry and broadening of the bands of intermolecular phonons, the magnitude of which depends on pressure and temperature [4,6,11]. In RS spectra of ruthenocene crystals, under normal conditions, the bands of intermolecular and intramolecular phonons have almost the same width. The band width of intermolecular phonons in a ruthenocene crystal is practically independent of pressure, but increases markedly with heating. The lower part of Figure 5 illustrates the RS spectra of the intermolecular phonons in the region 45–105 cm^{-1} and intramolecular breathing mode in the region 310–360 cm^{-1} when heated up to 373 K. The dotted line marks the shift of the band maxima of the intermolecular phonon $\Omega = 78.6\,\mathrm{cm}^{-1}$ and intramolecular phonon $\Omega = 335\,\mathrm{cm}^{-1}$: heating results in their weakening. In the inset of Figure 5, light circles and squares show the dependence of the bandwidth of the intermolecular phonon $\Omega = 78.6\,\mathrm{cm}^{-1}$ and the band of the intramolecular phonon

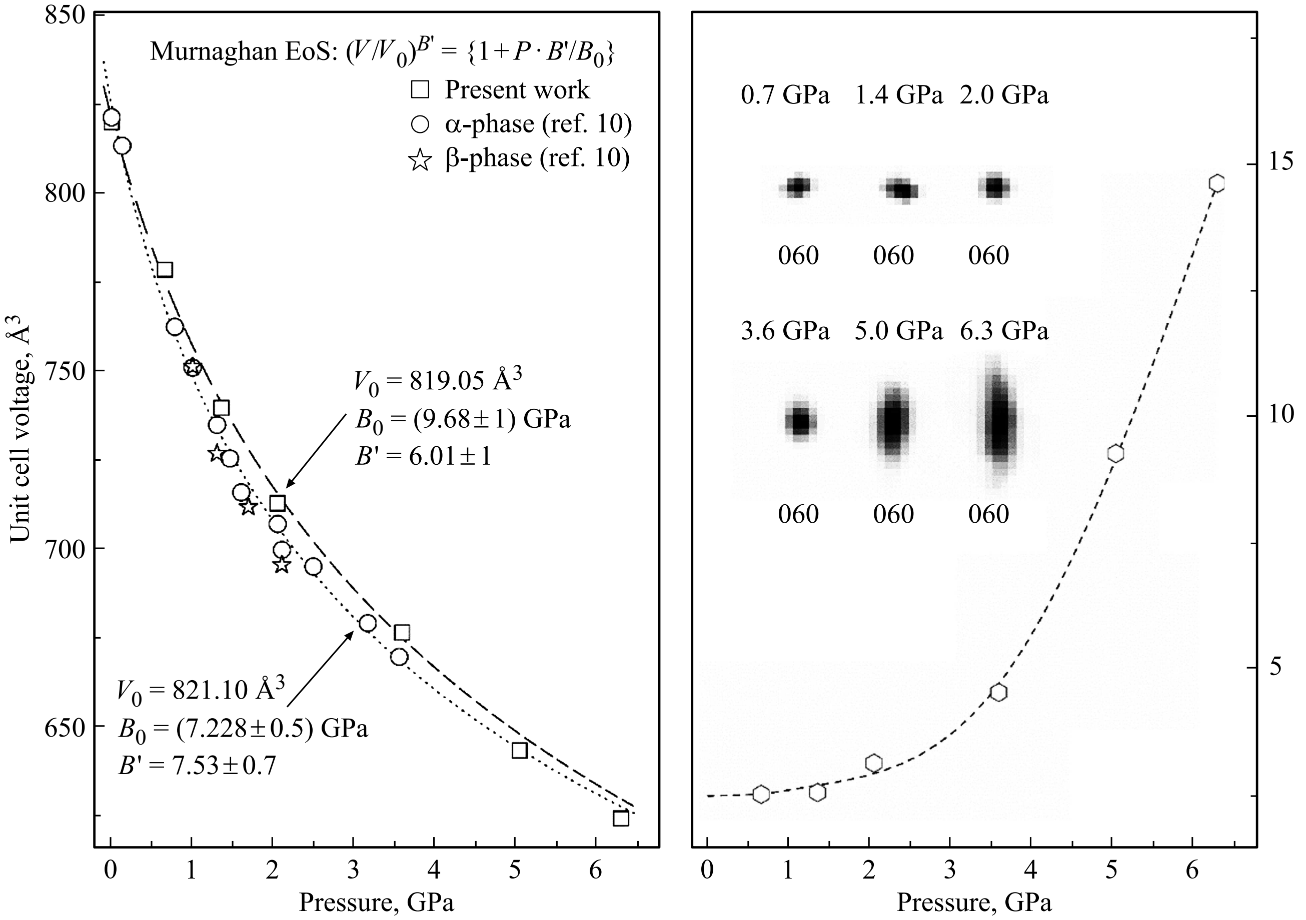

Figure 4. In the left: volume of the lattice cell versus pressure. Square and round symbols — results of this study and work data [10] for α-phase, respectively, asterisks — dependence for β-phase [10]. On the right: at the top — diffraction spot $\langle 060\rangle$ in conditions of increasing pressure, at the bottom — the spot's FWHM versus pressure.

$\Omega = 335\,\mathrm{cm}^{-1}$ on the reciprocal temperature $1/k_\mathrm{B}T$, where k_B is the Boltzmann constant. The width of the phonon $\Omega = 335\,\mathrm{cm}^{-1}$ linearly grows from $4.1\,\mathrm{cm}^{-1}$ at a room temperature up to $5.5\,\mathrm{cm}^{-1}$ at 373 K. The band width of the phonon $\Omega = 78.6\,\mathrm{cm}^{-1}$ grows from $4.9\,\mathrm{cm}^{-1}$ at a room temperature up to $10.1\,\mathrm{cm}^{-1}$ at 373 K. The dotted line shows the approximation of this dependence by the function $\Gamma = \Gamma_0 + A\exp(-E_A/k_\mathrm{B}T)$, where $\Gamma_0 = (4.1\pm0.4)\,\mathrm{cm}^{-1}$, $E_A = (276\pm50)$ meV. This dependence is typical for thermal activation processes and reflects a broadening of the band of intermolecular phonons due to a decrease in lifetime caused by the flips between conformations. Here E_A is the activation energy of flips between conformations and actually defines the barrier between them, and Γ_0 is the temperature-independent initial phonon bandwidth.

It includes the slit width of the spectral instrument $\sim 3\,\mathrm{cm}^{-1}$, as well as heterogeneous and uniform bands width. The inhomogeneous width in crystals is related to the scattering of phonons by crystal lattice defects and impurities, while the homogeneous width is related to phonon-phonon scattering. Under normal conditions, they are an order of magnitude smaller than the spectral slip width of the device, but they rise with increasing crystal defects and temperature [19]. The violation of translational symmetry due to conformational disorder leads to a loss of coherence of intermolecular vibrations and band broadening, while the coherence of intramolecular vibrations is not disrupted, and their width weakly depends on temperature [11]. The dependence of $1/(\Gamma-\Gamma_0)$ on the reciprocal temperature is shown in round dark symbols on the insert, and the dotted line is the Arrhenius dependence. $1/(\Gamma-\Gamma_0) = A\exp(E_A/k_\mathrm{B}T)$, where $E_A = (273\pm19)$ meV — energy of activation of the flips between the conformations. It should be underscored, that the broadening of phonon bands in RS spectra of NH_4ClO_4, crystals has been described earlier, which apparently was caused by libration of NH_4^+ ions in the lattice [19,20]. The lifetime of crystalline phonons τ, due to the flips between conformations, can be estimated from the width $(\Gamma-\Gamma_0)$. According to the ratio of uncertainty in the quantum mechanics $\Delta E\cdot\Delta t = \hbar$ the lifetime of phonons is equal $\tau = \hbar/(\Gamma-\Gamma_0)$, where $(\Gamma-\Gamma_0)$ — width of the phonon bands due to the flips between the conformations $\hbar$ — Planck constant [21,22]. The lifetime of phonons in crystals

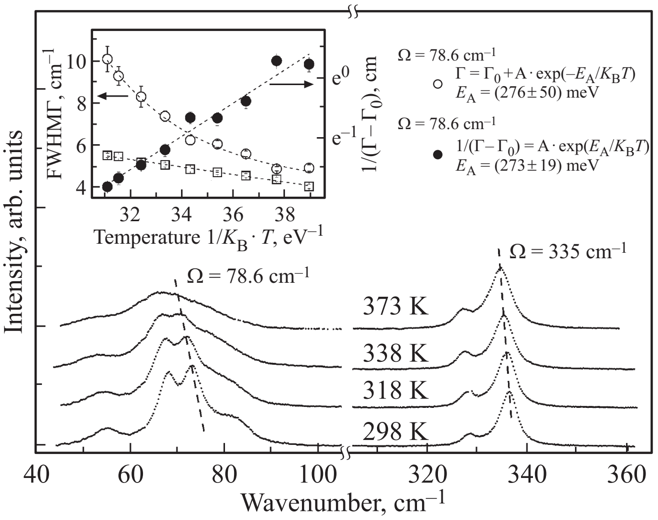

Figure 5. RS spectra of ruthenocene crystal in the region of $45-360\,\mathrm{cm}^{-1}$ at a temperature of up to 373 K. Dashed line — shift of the phonons bands $\Omega = 78.6\,\mathrm{cm}^{-1}$ and $\Omega = 335\,\mathrm{cm}^{-1}$. In the insert window — light round and square symbols — band width of the intermolecular phonon $\Omega = 78.6\,\mathrm{cm}^{-1}$ and intramolecular phonon $\Omega = 335\,\mathrm{cm}^{-1}$ versus reciprocal temperature $1/k_\mathrm{B}T$. Dark round symbols — experiment, dotted line — Arrhenius approximation for the phonon band $\Omega = 78.6\,\mathrm{cm}^{-1}$.

of aluminum, indium, and gallium nitrides was previously estimated in a similar way [19,22,23]. In our case, the time of flips between conformations, which limits the lifetime of phonons and determines the band width of intermolecular phonons declines with increasing temperature by a factor of seven and amounts to ~ 1 ps at 373 K.

4. Discussion

The Raman spectra of ruthenocene crystals at high pressure indicate an irreversible phase transition with a huge hysteresis, which implies the coexistence of two phases. The phonon spectra of these phases are close, but the frequency of the phonon modes changes abruptly during the transition. In three measurement cycles under hydrostatic compression, the transition was observed at pressure values of 4, 5, and 8 Gpa, respectively. The results for the reverse pressure stroke will differ from the forward one, but they match each other in all measurement cycles. Minimal pressure of 4 GPa, when the step-like changes were observed in the phonon spectrum, coincides with the pressure of 3.9 GPa for the isostructural phase transition from α-phase $Pnma$ in β-phase $Pcmb$, first discovered in [10]. This transition is associated with a rearrangement of the interaction between molecules, when there emerge additional coordination Ru–H bonds of hydrogen atoms of the cyclopentadiene ring of one molecule with the ruthenium atom of a neighboring molecule. According to [10], the length of these contacts in α-phase is the same for the lower and upper rings and makes 3.369 Å, and after transition to β-phase it decreases to 3.169 Å for the lower ring and goes up to 3.699 Å for the upper ring. These changes increase the effective mass and rigidity of the molecule, which leads to an abrupt decrease in the frequency of intermolecular phonons and an increase in the frequency of the intramolecular breathing mode. The reverse transition to the initial phase occurs at a pressure of 0.7 GPa according to XRD [10] and at a pressure of ~ 0.8 GPa according to our RS data. The phase transition has a significant hysteresis, the magnitude of which ranges from ~ 3.2 to 7.2 GPa. This suggests the possibility of two-phase states in the pressure region, where both phases are stable. This situation is observed in experiments on RS spectroscopy and X-ray diffraction analysis during quasi-hydrostatic compression in silicone oil, when mechanical stresses occur in the crystal during oil solidification. This is evidenced by the splitting of the intramolecular phonon band $335\,\mathrm{cm}^{-1}$, an increase in the intensity of the new component and, accordingly, the proportion of the second phase to 83 % at 10 GPa. With the reverse pressure stroke, this ratio remains stable to a pressure of ~ 0.8 GPa, when an abrupt transition to the initial phase occurs. Hysteresis and phase coexistence are quite common: for example, this was observed during the nematic-cholesteric phase transition in liquid crystals [24], or during the electro-crystallization of supercooled water entrapped between graphene layers under confinement [25]. The values of the volume modulus, baric shift of phonon modes, and Gruneisen parameters obtained in this study are typical for molecular crystals and correlate with data for other crystals of this type [13,26–29]. The X-ray diffraction data from [10] are insufficient to accurately determine the bulk modulus of β-phase, but if we assume that it is close to the value for α-phase, then the Gruneisen parameters for β-phase are somewhat less due to a decrease in the phonon mode shift coefficients in this phase.

The ruthenocene molecule in the free state and in the crystal is stable in the eclipsed conformation [9,10], but the flips between conformations are possible when the crystal is heated, which leads to a broadening of the bands of intermolecular phonons. A decrease in the conformation lifetime caused by the flips leads to a loss of translational symmetry of the crystal, a decrease in the lifetime of intermolecular phonons, and band broadening. RS spectra at temperatures up to 373 K demonstrate a weak broadening of the bands of intramolecular phonons, linearly dependent on the reciprocal temperature $1/k_\mathrm{B}T$, and a significant broadening of the bands of intermolecular phonons, exponentially dependent on $1/k_\mathrm{B}T$. The latter is characteristic of thermal activation processes and reflects a decrease in the lifetime of phonons due to the flips between conformations of the molecule. Energy of flips activation — barrier between conformations — makes $E_A = (273 \pm 19)$ meV. Its sufficiently outpaces the barrier of 16.9 meV in the ferrocene crystal under normal conditions and the value of 80 meV at 4.9 GPa [11].

5. Conclusion

Thus, the change in the crystal parameters of the ruthenocene at high pressure is well described by the Murnaghan equation of state $(V_0/V)^{B'} = \{1 + P \cdot B'/B_0\}$ with parameters $B_0 = 9.68$ GPa and $B' = 6.1$ at pressure 4 GPa, above which the diffraction pattern worsens due to a sharp broadening of diffraction patterns maxima. The pressure dependence of phonon frequencies in RS spectra demonstrates abrupt changes under hydrostatic compression near $\sim 4, \sim 5$ and ~ 8 GPa in three independent series of measurements. The change in the phonon frequency is associated with a characteristic change in the geometry of Ru−H coordination bonds of hydrogen atoms of the cyclopentadiene ring in one molecule with the ruthenium atom of the neighboring molecule [10]. The observed changes in RS spectra indicate an irreversible phase transition and confirm the findings of the study [10]. In the quasi-hydrostatic conditions at ~ 4 GPa the breathing mode 335 cm^{-1} is split into two components and the sample becomes a two-phase one. The proportion of the new phase increases to a maximum of 83 % at 10 GPa and remains unchanged when the pressure reverses to ~ 0.8 GPa, when an abrupt transition to the initial state occurs. The energy barrier between the eclipsed and staggered conformations of the ruthenocene molecule, determined by Arrhenius dependence of the width of intermolecular phonons bands, is an order of magnitude greater than in a ferrocene crystal and amounts to (273 ± 19) MeV/molecule.

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Conflict of interest

The authors declare that they have no conflict of interest.

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