

## Isosymmetric Reversible Pressure-Induced Phase Transition in Sodium Oxalate at 3.8 GPa

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Oxalates are widely used in the design of supramolecular structures with various desirable properties and as precursors in solid-state chemical reactions. Therefore, it is important to assess the sundry factors determining the crystal structures of oxalates and their response to external actions. In crystals, oxalate ions are usually considered as structure-forming units, defining the crystal packing (the framework) and the positions of other species, especially, metal cations [1, 2]. Structures of anhydrous metal oxalates, such as sodium oxalate, are of special importance, since they lack hydrogen bonds and their structures and general behavior under various conditions are entirely determined by oxalate anion–metal cation interactions.

In this work, the existence of a pressure-induced ( $P = 3.8$  GPa) first-order phase transition in crystalline sodium oxalate, previously proposed in [3], was demonstrated by Raman spectroscopy and by high-resolution X-ray powder diffraction. Structural and spectral

changes in the original and high-pressure polymorphs were studied as functions of hydrostatic pressure up to 8 GPa.

The high-pressure experiments were carried out in situ in diamond anvil cells. Raman spectra were measured with a Dilor OMARS 89 spectrophotometer equipped with a Princeton Instruments LN/CCD–1100PB multichannel detector; the excitation wavelength was 514.5 nm (Ar laser). Optical microscopy observations showed that the crystals of sodium oxalate retain their integrity after the pressure-induced phase transition. This allowed us to use the same crystal for all Raman spectroscopic measurements below and above the phase transition point. X-ray powder diffraction patterns were measured with synchrotron radiation ( $\lambda = 0.7$  Å) at ESRF, Grenoble, and recorded with an MAR345 2D-detector.

The nonpolarized Raman spectra of sodium oxalate show a very strong band at 1456  $\text{cm}^{-1}$ ; strong bands at 888 and 880  $\text{cm}^{-1}$  (in order of decreasing intensity); bands of medium intensity at 570, 482, 1653, and 1621  $\text{cm}^{-1}$ ; and weak low-frequency bands at 214, 227, and 245  $\text{cm}^{-1}$  (Fig. 1). The intensity of bands in the Raman spectra is highly anisotropically dependent on the polarization of scattering. This agrees with the low symmetry of the crystal. The frequencies in the Raman spectra change continuously with increasing pressure. At 3.8 GPa, the spectral pattern changes jumpwise. This change manifests itself, in particular, in the plots of frequencies versus pressure (Fig. 2). Frequency jumps were observed for most vibrational bands. At the phase transition point, the spectra essentially changed in the spectral range 160–250  $\text{cm}^{-1}$ . No low-frequency soft mode (in the range above 160  $\text{cm}^{-1}$ ) was detected.

The vibrational frequencies and forms of all optical modes of sodium oxalate were calculated at  $k = 0$  with the LADY computing program [4, 5] so that all experimentally measured bands in the Raman spectra could be interpreted. Thus, the following interpretation could be given to the modes for which the pressure-induced frequency shifts are plotted in Fig. 2. The  $A_g$  mode at

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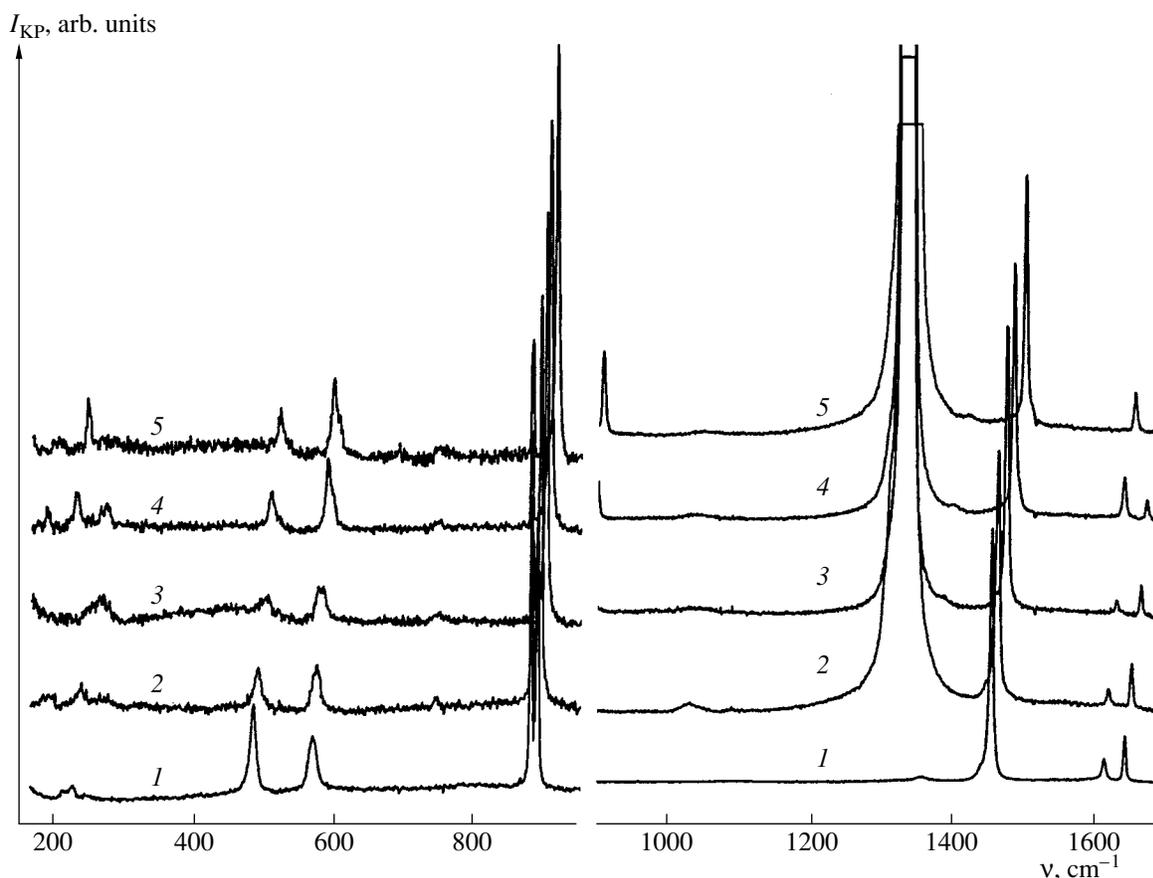
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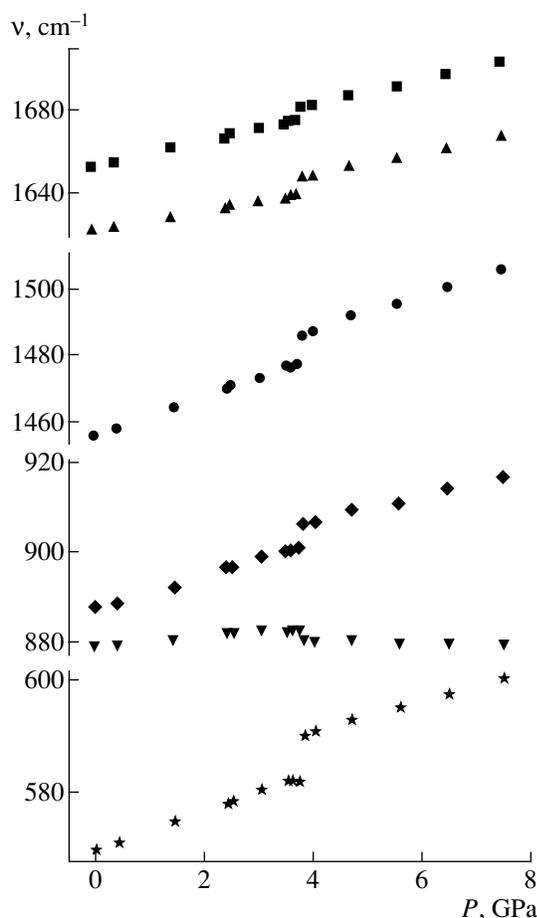
**Fig. 1.** Raman spectra of crystalline sodium oxalate at various pressures: (1) ambient pressure (free crystal, no diamond anvil cell) and (2) 1.46, (3) 3.75, (4) 3.85, and (5) 6.57 GPa.

482  $\text{cm}^{-1}$  is a rocking vibration of the type of an in-phase rotation of two  $\text{CO}_2$  groups almost in the plane of the  $(\text{O}_2\text{C}-\text{CO}_2)^{2-}$  molecule. The  $A_g$  mode at 570  $\text{cm}^{-1}$  corresponds to an in-phase bending vibration of the OCO angles. The bands at 880 and 888  $\text{cm}^{-1}$ —are assigned to  $B_g$  and  $A_g$  C–C stretching vibrations, which correspond to a fully symmetrical deformation of the whole molecule, so that the effective mass of this vibration is noticeably higher than the mass of a single C atom. As a rule, such fully symmetrical vibrations of organic molecules have high intensities in the Raman spectra. The  $A_g$  mode at 1456  $\text{cm}^{-1}$  is a stretching C–O vibration, which is symmetrical for  $\text{CO}_2$  groups and has a large contribution from the C–C vibration. The  $A_g$  and  $B_g$  modes at, respectively, 1621 and 1653  $\text{cm}^{-1}$  correspond to the C–O antisymmetric stretches. The low-frequency 160–250  $\text{cm}^{-1}$  range shows the translational modes of the cations. This range undergoes the most profound changes upon the phase transition.

Nonzero elastic constants of sodium oxalate under ambient conditions were calculated by the lattice dynamics method using the LADY program [4, 5]:  $C_{11} = 107.9$ ,  $C_{22} = 145.3$ ,  $C_{33} = 135.7$ ,  $C_{44} = 29.5$ ,  $C_{55} =$

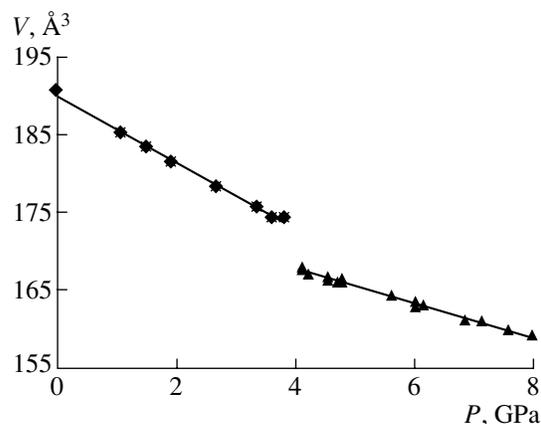
16.6,  $C_{66} = 41.6$ ,  $C_{12} = 79.3$ ,  $C_{13} = 55.9$ ,  $C_{23} = 74.3$ ,  $C_{15} = 2.73$ ,  $C_{25} = 9.5$ ,  $C_{35} = 10.8$ , and  $C_{46} = -0.73$  GPa. The last elastic constant, which is related to the interaction of angles, is anomalously low. The calculated bulk modulus is  $K = 83.5$  GPa. Diagonalization of the  $C_{ij}$  matrix gave the minimum value of a diagonal element as equal to 15 GPa. This allows us to conclude that the structure is stable with respect to acoustic modes at high pressures, at least, up to  $P \sim 15$  GPa [6]. The phase transition at 3.8 GPa is definitely not related to a possible elastic instability of the crystal structure at much higher pressures.

According to the X-ray diffraction evidence, the crystal structure of sodium oxalate [7] does not change its space group symmetry at the point of the phase transition (space group  $P2_1/c$  is preserved), although the unit cell parameters  $a$ ,  $b$ , and  $\beta$  and the cell volume change jumpwise at the phase transition point. For example, the cell volume is 185  $\text{\AA}^3$  at ambient pressure, 176  $\text{\AA}^3$  at 3.6 GPa, and 167  $\text{\AA}^3$  at 4.3 GPa (Fig. 3). The plot of the parameter  $c$  versus pressure has a pronounced kink at the phase transition point. The polymorphous transition is accompanied by a jumpwise



**Fig. 2.** Frequencies of selected vibrational bands in the Raman spectra of sodium oxalate vs. hydrostatic pressure up to 8 GPa.

change in the orientation of the oxalate anions and in the coordination of the sodium cations by oxygen atoms. At the same time, the packing of the centroids of the oxalate anions persists to a large extent. The unit cell parameters at 4.35 GPa are  $a = 3.160(1)$  Å,  $b = 5.300(2)$  Å,  $c = 10.001(4)$  Å, and  $\beta = 85.25(2)^\circ$ ; the fractional coordinates of the atoms from the asymmetric unit are Na(1) (0.437(8), 0.083(4), 0.336(3)), C(1) (0.073(19), 0.054(12), 0.066(6)), O(1) (0.013(10), -0.076(7), 0.173(5)), and O(2) (0.248(14), 0.271(5), 0.053(4)). The largest shifts in the course of the phase transitions were observed for the Na<sup>+</sup> cations. The shifts of the oxygen atoms were somewhat smaller and related mostly to the rotations of oxalate anions. The coordination number of Na in the original polymorph is 6, 3O(1) + 3O(2) (the Na–O distances are equal to 2.27(2), 2.28(2), 2.40(2), 2.25(3), 2.40(2), and 2.48(3) Å at 3.6 GPa). In the high-pressure polymorph, the coordination number of Na is equal to 7, 4O(1) + 3O(2)



**Fig. 3.** Cell volume of sodium oxalate vs. pressure.

(the Na–O distances are equal to 2.26(4), 2.35(5), 2.49(4), 2.50(4), 2.26(4), 2.33(5), and 2.87(4) Å at 4.3 GPa). A specific feature of the pressure-induced structural change in sodium oxalate is that the monoclinic angle  $\beta$  continuously decreases from  $92.25^\circ$  under ambient conditions to  $90.75^\circ$  at 3.6 GPa (just before the phase transition) and then changes jumpwise to  $85.25^\circ$  at the phase transition point at 3.8 GPa.

Thus, our findings allow us to draw the following conclusions:

(1) A reversible first-order phase transition takes place in crystals of sodium oxalate at 3.8 GPa.

(2) This phase transition is isosymmetric; i.e., space group  $P2_1/c$  is preserved.

(3) The anisotropic compression of the structure, the rotation of oxalate ions with their packing being retained to a large extent, and the jumpwise change in the coordination number of sodium cations from 6 to 7 at the phase transition point account for the changes observed in the Raman spectra with increasing pressure.

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