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Difference in the Dynamic Properties of Chiral and Racemic Crystals of Serine Studied by Raman Spectroscopy at 3–295 K

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Single-crystal polarized Raman spectra ($60\text{--}4000\text{ cm}^{-1}$ at $3 \leq T \leq 295\text{ K}$) were measured for chiral L- and racemic DL-serine, α -amino- β -hydroxypropionic acid, $(\text{NH}_3)^+\text{CH}(\text{CH}_2\text{OH})(\text{COO})^-$. The Raman spectra of DL-serine do not show any striking changes with temperature or on storage. In contrast to that, the dynamical properties of L-serine change at about 140 K. These changes can be interpreted as the reorientation of the side chain $-\text{CH}_2\text{OH}$ fragments of the zwitterions with respect to the backbone C–C bonds, resulting in the positional disorder of the $\text{O}=\text{H}\cdots\text{O}$ intermolecular H-bonds. The redistribution in the intensities of the Raman spectra of the crystals of L-serine stored for a long time (about a year) indicates the changes in the orientation of the molecular fragments in the direction normal to the axes of the head-to-tail chains. The difference in the thermodynamic functions of L- and DL-serine reported previously [Drebushchak, V. A.; Kovalevskaya, Yu. A.; Paukov, I. E.; Boldyreva, E. V. *J. Therm. Anal. Calorim.* 2007, 89 (2), 649–654] is explained by the difference in the spectra of external vibrations of the crystals.

1. Introduction

Temperature-induced changes in crystalline amino acids are of interest for their ferroelectric, piezoelectrical, and nonlinear optical properties and reveal the intrinsic motions of these structural fragments and their contribution to the dynamic properties of the proteins.¹ The structure-forming units in the crystals of amino acids are similar to those in the biopolymers (head-to-tail chains of amino acids mimicking polypeptide chains, two-dimensional layers mimicking β -sheets^{2,3}). The functions of proteins require some flexibility, and the unique physical characteristics of proteins is that they display such flexibility over a large range of time scales, from femtoseconds (individual bond vibrations) to picoseconds (small group fluctuations) to microseconds and longer (collective motions). All these motions are thermally driven, and temperature is a potential probe for the functional role of these motions.⁴ Vibrational studies of the crystalline amino acids help to understand the dynamics of the individual fragments, from which the biopolymers are built, in relation to the structural changes in the same systems characterized by diffraction techniques. It is not surprising that a vast literature is devoted to vibrational spectroscopy of crystalline amino acids (see refs 5–16 as examples of reviews on the topic and entry points).

The amino acid serine ($\text{NH}_3^+\text{CH}(\text{CH}_2\text{OH})\text{COO}^-$) (Figure 1) provides an example of chiral and racemic crystals (L- and DL-forms) differing strikingly in their properties. Understanding the structure–property relation in this system is interesting by itself and because of the biological applications. Serine–serine interactions account for many biochemical processes, in par-

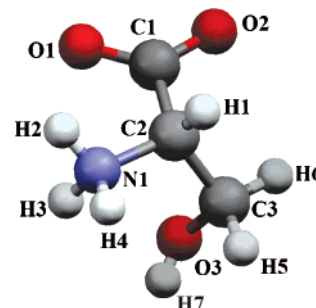


Figure 1. A zwitterion of serine. Numeration of atoms used in the present paper (the same as in refs 18, 21, 24, and 25).

ticular for the functioning of polar clamps and serine zippers in membrane proteins.¹⁷

L-Serine is denser than DL-serine,¹⁸ which contradicts the so-called “Wallach rule”,^{19,20} stating that racemic compounds tend to be denser than their chiral counterparts. At the same time, the denser structure of L-serine is about 4 times more compressible on cooling at ambient pressure than that of DL-serine.^{18,21} The isothermal bulk compressibility with increasing pressure is the same for L- and DL-serine, up to about 5 GPa,^{18,21} after which, with further increasing pressure, the crystal structure of DL-serine remains stable, whereas that of L-serine undergoes two reversible phase transitions at 5.5 and at 7.8 GPa.^{22–26} The difference between the heat capacity $C_p(T)$ of the chiral and the racemic forms increases rapidly from $-0.01\text{ J mol}^{-1}\text{ K}^{-1}$ at 5 K to $+6.5\text{ J mol}^{-1}\text{ K}^{-1}$ near 130 K, which is larger compared to that of other studied chiral/racemic pairs or polymorphs.²⁷

The difference in the properties of the chiral and racemic crystals of serine should be sought in the intramolecular dynamics in relation to the crystal structures. Crystal structures of L- and DL-serine were refined repeatedly at several temperatures and pressures.^{18,21–26,28–34} Serine is prone to form clusters

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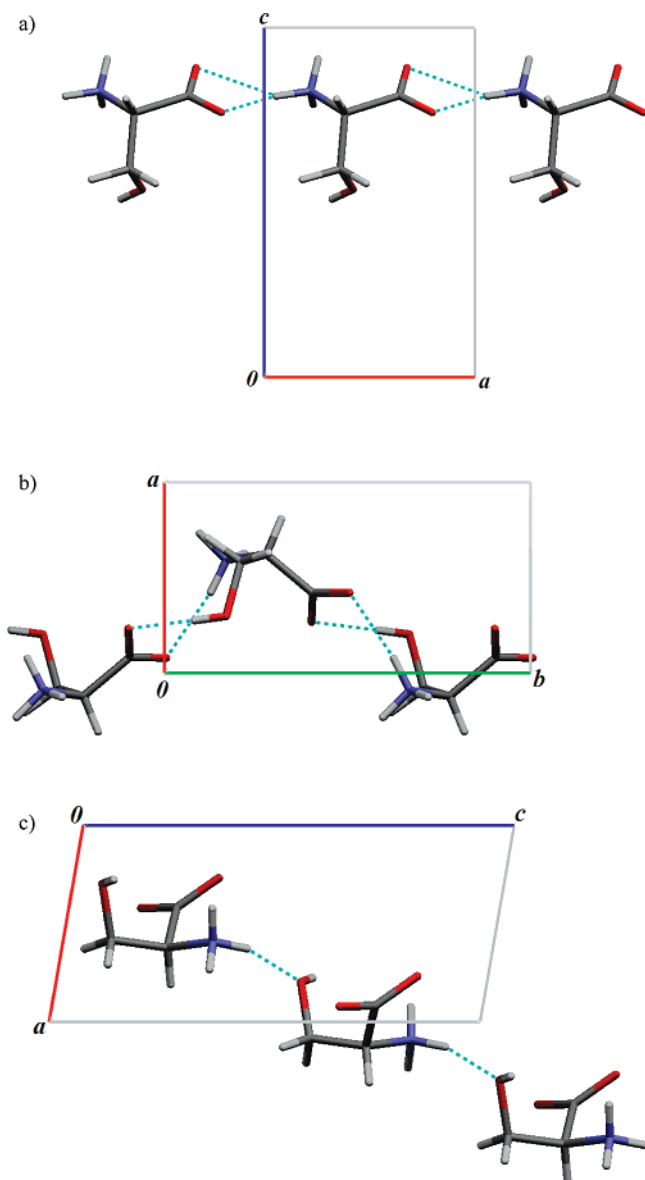


Figure 2. Hydrogen-bonded chains formed by L-serine zwitterions in the crystals of L-serine (a) and by zwitterions of the same (b) and of different (c) chiralities in DL-serine.

of molecules of the same chirality even in racemic mixtures in solutions.³⁵ In the crystals of DL-serine one can find the chains and the two-dimensional arrays of L-serine molecules alternating with chains and layers formed by D-molecules, but their structures are different from those in the crystals of L-serine (Figure 2).^{18,21} The conformations of the serine zwitterions are different in the crystals of the L- and DL-forms, and the reason for this is that the hydroxy groups of the side chains are involved in the formation of different types of intermolecular hydrogen bonds with close neighbors: $\text{OH}\cdots\text{OH}$ in L-serine and $\text{OH}\cdots\text{O}=\text{C}$ in DL-serine.^{18,21} In the structure of L-serine, the head-to-tail chains are linked further to give a three-dimensional H-bonded framework,²¹ whereas in the structure of DL-serine a combination of hydrogen-bonded L-chains, D-chains, and DL-chains of the zwitterions gives a structure in which double layers can be clearly seen, although the hydrogen bond network is also three-dimensional¹⁸ (Figure 3).

Vibrational spectra of serine as individual neutral molecules in inert matrixes and as zwitterions in solutions and in the crystalline state for nondeuterated and deuterio-substituted samples were studied by computational and experimental

techniques in a large number of papers.^{36–52} Still, there are “knowledge gaps” that can be filled. For example, although the IR spectra for L- and DL-serine were measured not only at room but also at low temperatures (at 10 K^{48,50} and in the range from room temperature down to 100 K⁵²), only a room-temperature Raman spectrum of L-serine was reported.⁵⁰

Assignment of the vibrational bands observed in IR and Raman spectra of L- and DL-serine powder samples was discussed previously in several papers,^{36–52} most recently in 2007.^{50–52} Therefore, we have concentrated our attention on the variations of vibrational modes in L- and DL-serine single crystals *with temperature* in relation to the structural phenomena occurring in these compounds on heating from 3 K to ambient temperature. We measured not powder but *single-crystal polarized Raman spectra*, which can be correlated reliably with the crystallographic orientation (i.e., the direction of individual chemical bonds in the crystal). At low temperatures, some vibrational bands, which are broad and overlapping at room temperature, become narrow and well-resolved, and this permits better insight into the nature of the intermolecular interactions to be reached.

The aim of the present single-crystal polarized Raman spectroscopy investigation is to compare the effect of temperature (from 3 K up to room temperature) on the Raman spectra of the crystalline L- and DL-serine in relation to the structural strain on cooling studied previously by diffraction techniques^{18,21,34} and to low-temperature calorimetry²⁷ and low-temperature IR spectroscopy^{49,51,52} studies. We also compare the variations in the low-temperature Raman spectra with the previously reported pressure-induced spectral changes.²³

2. Materials and Methods

L-Serine and DL-serine were obtained from ICN Biomedicals (batches 56-45-1 and 302-84-1, chemical purity 99%). Single crystals of anhydrous L-serine (transparent white elongated prisms, $1.0 \times 0.6 \times 0.5$ mm, without visible imperfections) were precipitated from 1:1 EtOH/H₂O solution as described in ref 21. The crystal structure (space group $P2_12_12_1$)²¹ was confirmed by single-crystal X-ray diffraction. The long axis of a crystal corresponds to the direction of the head-to-tail chains formed by zwitterions along the shortest crystallographic axis *a*. Single crystals of DL-serine (prisms, $1.0 \times 0.9 \times 0.16$ mm) were crystallized by slow evaporation of aqueous solutions.¹⁸ The crystal structure (space group $P2_1/n$)¹⁸ was also confirmed by single-crystal X-ray diffraction. The large face (001) of a prism was strictly normal to *c*, and the smaller faces had indices (011) and (110). The crystal structures were studied and the faces of the crystals were indexed using a four-circle X-ray diffractometer, STOE STADI-4. Thermal analysis measurements have proved that there were no solvent inclusions in the crystals. The crystals were not hygroscopic and could be stored without special precautions.

The Raman spectra were collected using a triple-grating spectrometer with a CCD detector, LN-1340PB, from Princeton Instruments. The lines of a Ne lamp were used for spectral calibration of the spectrometer. The 488 nm line of an Ar⁺ laser was used for spectral excitation with a diameter of the laser spot on the sample surface of 1–2 μm . The laser power at the sample was typically 5 mW. The spectra at all temperatures were measured in 180° backscattering collection geometry with a Raman microscope. The low-temperature spectra were recorded by mounting the crystal on a cold finger of a helium cryostat (MicrostatHe) from Oxford Instruments. The precision of the measured temperatures of the cold finger is 0.1 K, but

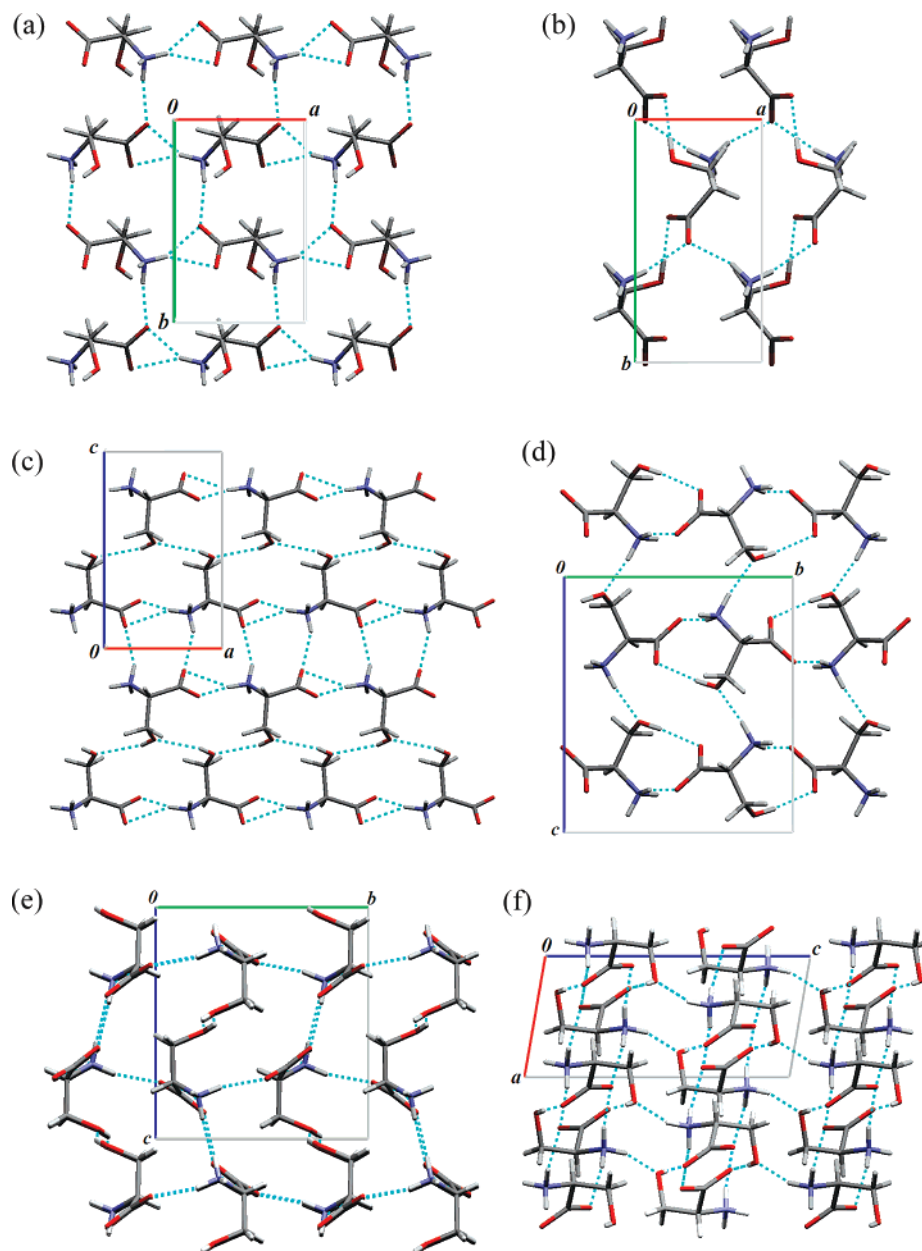


Figure 3. Fragments of the crystal structures of L-serine (a, c, e) and DL-serine (b, d, f).

the true temperature of the sample can differ from the measured one due to some heating of the sample in the laser spot. We estimate this heating as 4–5 K for transparent crystals. All measurements were performed with a spectral resolution of 2 cm^{-1} .

3. Results

Polarized Raman spectra of L- and DL-serine at 3 K and at room temperature are shown in Figure 4. Some modes (87, 852, 1324, and 3468 cm^{-1}) are strongly polarized and exhibit a high intensity for only one combination of incident and scattered light polarization. This information is related to the directions of atomic and molecular motions contributing to these normal vibrations in the crystal. A full set of vibrational spectra collected at 12 temperatures in the range 3–300 K are available as Supporting Information. The selected representative spectra at three temperatures are shown in Figure 5. They reflect the changes in molecular and crystal structure at different temperatures. Figure 6 illustrates the effect of temperature on the

vibrations related to the side $-\text{CH}_2\text{OH}$ groups, indicating at a dynamic transition around 140 K. Figure 7 shows the redistribution of the intensities of all the modes in the Raman spectra of L-serine crystals after one year of storage, which is a manifestation of long-term instability of the crystal structure.

4. Discussion

Polarized Spectra. Polarized spectra contain information on the mode symmetry and can be used to correlate an observed mode and the direction of the atomic motions in the lattice. Both L- and DL-serine crystals are, however, of low symmetry (orthorhombic and monoclinic, respectively), and a definition of the symmetry of their vibrations is of little help for band assignment. In addition, some normal modes of serine molecules in the range of stretching vibrations of C–C, C–N, and C–O bonds can involve motion of all these atoms, since the values of their force constants and atomic masses are close to each other. For this reason, only several “strong” modes can be assigned with a fair degree of confidence. We consider the

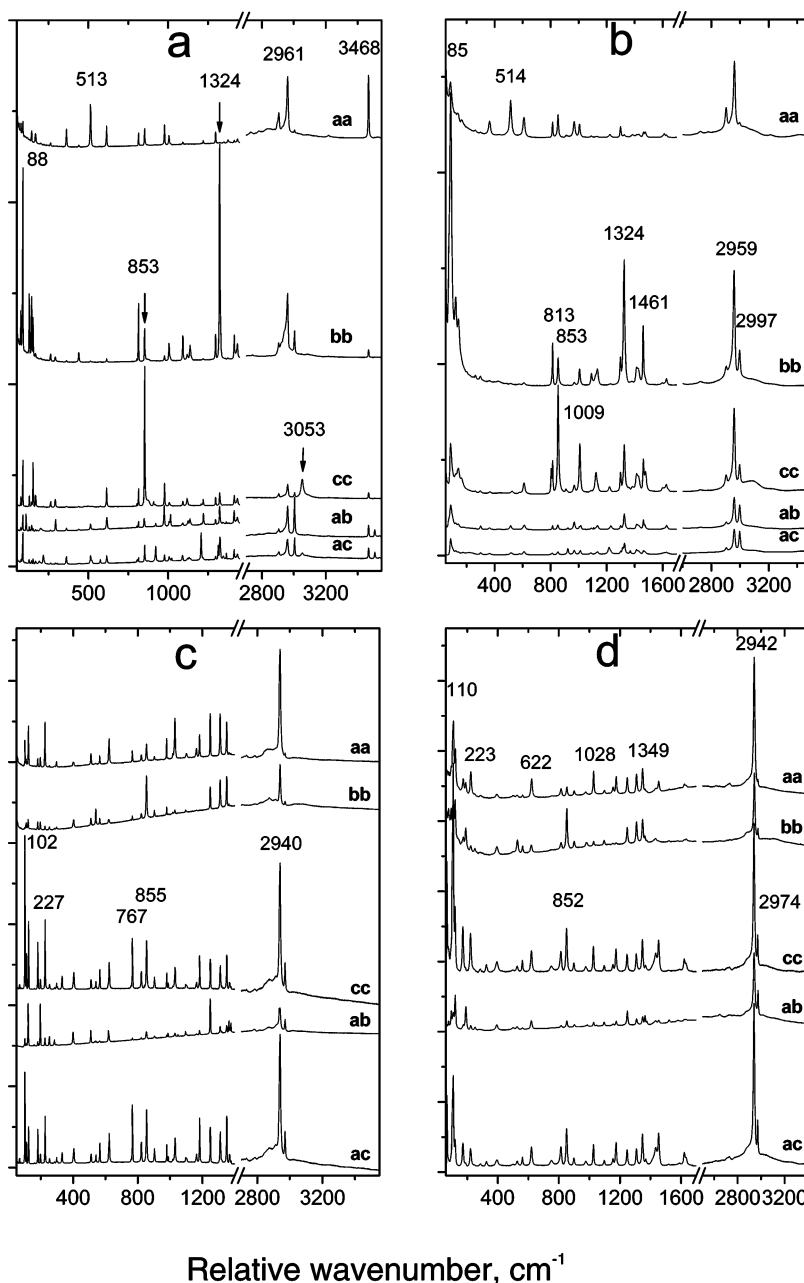


Figure 4. Polarized Raman spectra of L-serine (a, b) and DL-serine (c, d) single crystals at 3 K (a, c) and at 295 K (b, d). The abbreviations **aa**, **bb**, etc. imply the direction of the polarization vector of incident (first symbol) and scattered (last symbol) light compared to the crystal axes.

assignment reliable if a vibrational mode is observed in only one polarized spectrum (**aa**, **bb**, or **cc**), because in this case the normal coordinate of the mode involves vibration of only one bond. Besides, it is easy to define this bond via its crystallographic direction in the unit cell. This holds for the following bands (Figure 4): bands at 100–200 cm^{-1} in L- and DL-serine assigned to external [translational ($\sim 100 \text{ cm}^{-1}$) and rotational ($150\text{--}200 \text{ cm}^{-1}$)] motions of serine molecules, the band at 852 cm^{-1} (855 cm^{-1} in DL-serine), intensive in the **cc** spectrum of L-serine, assigned to C2–C3 stretching (the numeration of atoms is explained in Figure 1), the band at 1324 cm^{-1} , intensive in the **bb** spectrum of L-serine, assigned to C3–O3 stretching, and the band at 1460 cm^{-1} (1450 cm^{-1} in DL-serine) assigned to the symmetric COO stretching vibration of the carboxyl group.

Vibrations of the N–H and O–H groups involved in the hydrogen bonds are of a special interest. The suggested assignments of the corresponding modes (Table 1) were made using the well-known relationship between N–H \cdots O and

O–H \cdots O distances and N–H and O–H stretching frequencies in hydrogen-bonded systems^{53,54} and the polarization behavior of the various N–H and O–H bands observed in the Raman spectra for different crystal orientations. The directions of all the intermolecular hydrogen bonds can be well correlated with one of the crystallographic axes. Only two of five different types of hydrogen bonds in L-serine,^{18,21,24,25} i.e., N–H \cdots O (3053 cm^{-1} at 3 K, type 4) and O–H \cdots O (3468 cm^{-1} at 3 K, type 5) (numeration of H-bonds is the same as in refs 18, 21, 24, and 25), are represented in the spectra by intensive bands (Figure 4, Table 1). The other three bands are very weak, but a detailed analysis of the origin of this weakness is beyond the scope of the present study. The bands corresponding to the vibrations of hydrogen-bonded groups in the crystals of DL-serine could not be observed due to a low Raman intensity. According to the IR spectroscopy data,⁵² the hydrogen bonds in DL-serine are stronger than those in L-serine, and this agrees with the X-ray diffraction data on the shorter interatomic distances in these

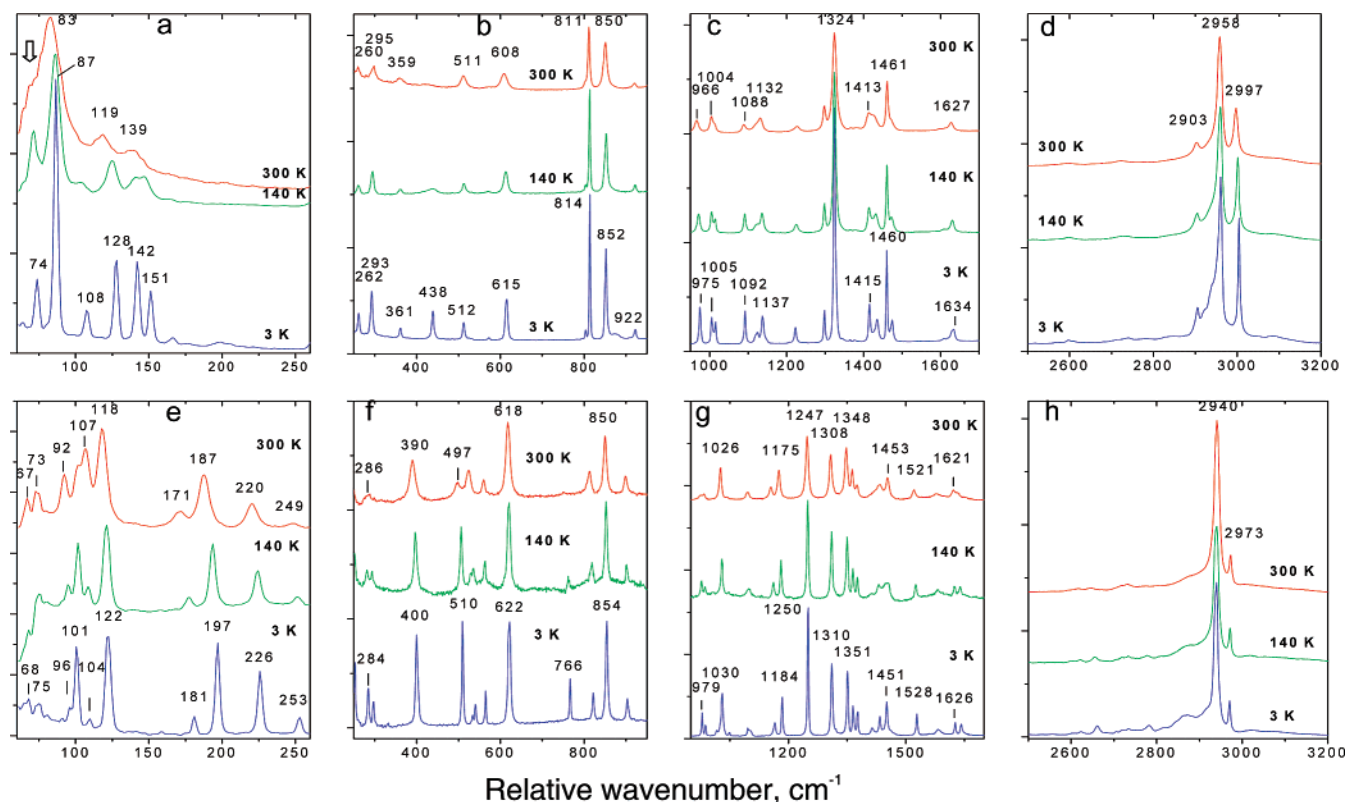


Figure 5. Unpolarized Raman spectra of L-serine (a–d) and DL-serine (e–h) at several temperatures in selected spectral ranges. The double arrow marks an envelope of many lines observed at $T > 140$ K for the low-frequency vibration of the hydrogen bond itself (at 60–80 cm^{-1} at low temperatures). A full set of spectra collected at 12 temperatures in the range 3–300 K are available (*.doc). This material can be downloaded as Supporting Information.

bonds (Table 2).^{18,21} The frequencies of the stretching vibrations of C–H bonds observed in the spectra of L- and DL-serine in the range of 2900–3100 cm^{-1} do not differ from the expected values for the CH groups not involved in hydrogen bonds at all temperatures and for all the orientations of the crystals. Thus, Raman spectroscopy data, as well as the IR spectroscopy data,⁵² do not confirm the hypothesis on the presence of $\text{CH}\cdots\text{O}$ hydrogen bonds in the crystals of serine, which was based on the distances between the C and O atoms calculated from the diffraction data.^{22,26} From the analysis of the polarized spectra and the direction of the bonds in the unit cell, one can conclude that the intensive band at 2961 cm^{-1} (3 K) should be assigned to the C3–H5–H6 symmetric stretching mode and the mode at 3004 cm^{-1} to the C2–H1 stretching vibration.

Additional information, which can be retrieved from the analysis of the polarized spectra, will be discussed in the next section (“Temperature Dependence”).

Temperature Dependence. With a few exceptions, the effect of temperature on the frequencies of most vibrational bands in L- and DL-serine is small (Figure 5). The data on the vibrational frequencies at several temperatures are summarized in Tables 3 and 4. Most of the inter- and intramolecular modes remain practically constant in the range 3–100 K and show a slight decrease in frequency on further heating, in agreement with the IR data.⁵² This behavior is “quite regular” and relates to the decrease of the cell volume on cooling in the 100–295 K range.^{18,21} The changes in the cell volume of L-serine on cooling are more than 3 times larger than those of DL-serine.^{18,21} However, the frequency shifts measured for the nonpolarized spectra of the two crystals are comparable. This may result from the fact that nonpolarized spectra give averaged information for the atomic displacements in all the crystallographic directions and do not reflect the anisotropy of structural strain induced by

temperature changes. In the case of L- and DL-serine, different values for bulk thermal expansion result from a radical difference in the strain anisotropy.^{18,21}

The temperature variations of Raman spectra of DL-serine do not show any striking features. The low-frequency modes at 90–120 cm^{-1} in DL-serine change their intensity with temperature: the intensity of the modes at 96 and 104 cm^{-1} increases, and that of the mode at 101 cm^{-1} decreases on heating. The modes are assigned to translation motions of serine molecules, and the changes in their intensity can be attributed to a small mutual molecular reorientation in the lattice. The stretching C–H and N–H vibrations do not show noticeable changes with temperature, while the vibrations of the O–H groups were not observed in the whole temperature range.

The most remarkable change in the spectrum of DL-serine with temperature is observed for the $\tau(\text{NH}_3)$ vibration, which is related to the frozen rotations of the NH_3^+ groups around the C–N bond (510 cm^{-1} at 3 K): this band loses intensity with increasing temperature above 200 K and is very weak at 300 K (presumably due to population of the excited torsion states or the transition from restricted to free rotations of the NH_3^+ group, which was observed earlier in this temperature range by the NMR technique⁵⁵). A similar effect is observed for the $\tau(\text{NH}_3)$ vibration (at 290–300 cm^{-1}) in the spectrum of L-serine at somewhat lower temperatures, which also agrees with the NMR data.⁵⁵ The hydrogen bonding of the NH_3^+ groups in L-serine is weaker than that in the DL-form^{18,21} (see also “Low-Frequency Lattice Vibrations and Heat Capacity”), and respective potential barriers are lower.⁵⁵ For a comparison, the peaks of the $\tau(\text{NH}_3)$ vibration in the Raman spectra of L-alanine, which are well resolved at low temperatures, start broadening rapidly at similar temperatures, above ~ 220 K,⁵⁶ in agreement with NMR,^{56–58} IR,⁵⁹ and IINS⁵⁹ data. Interestingly, the temperature

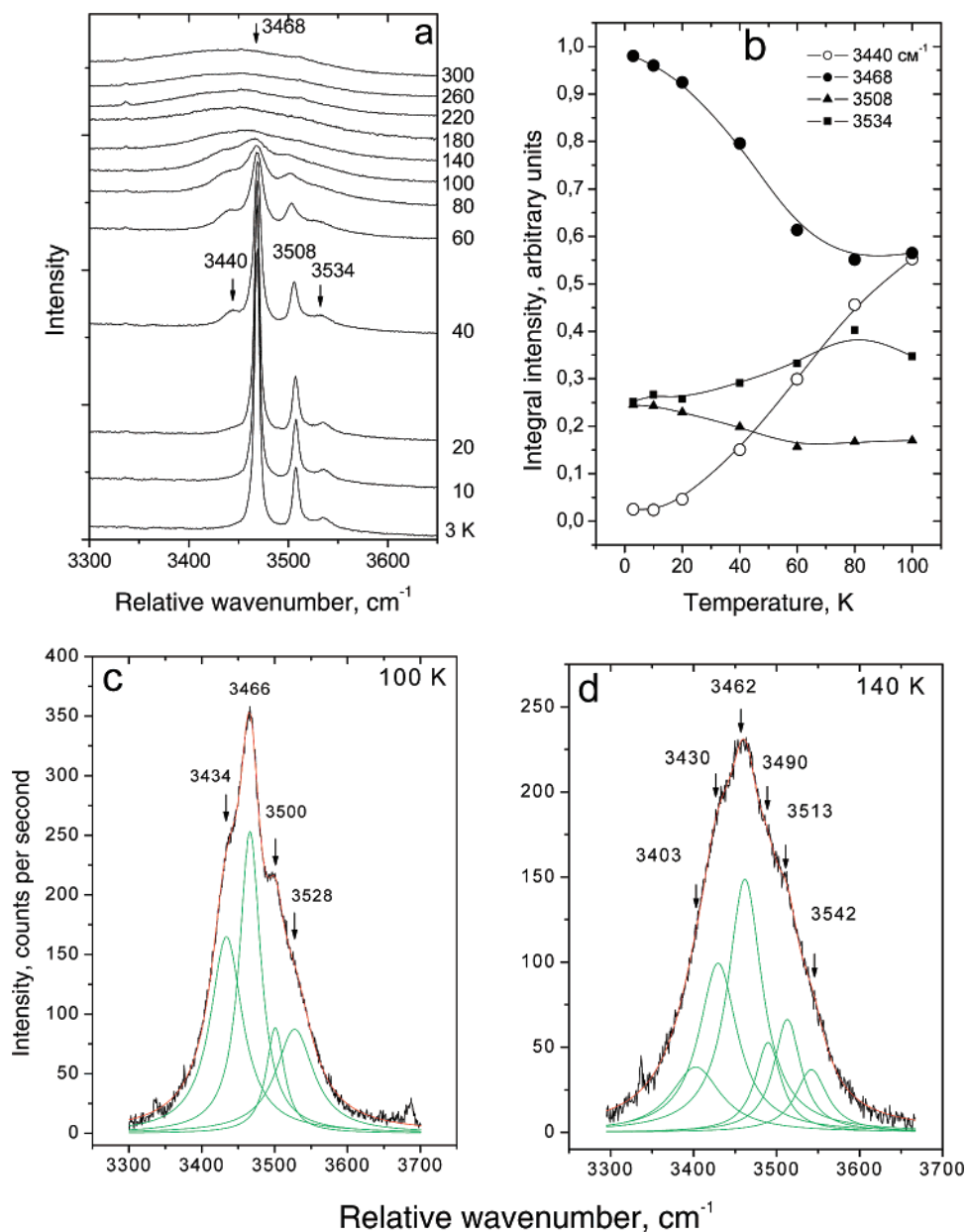


Figure 6. Effect of temperature on the unpolarized spectra of L-serine in the range of O—H···O stretching vibrations: spectra recorded at several temperatures (a); temperature dependence of the normalized to unity integral intensity of the modes observed in panel a (b); deconvolution of the 100 K (c) and 140 K (d) spectra of L-serine with Lorentzian components.

TABLE 1: Wavenumber (cm⁻¹) of the Stretching Vibration of Hydrogen-Bonded Bonds in L-Serine

bond number ^a	bond	type of bond	D—A distance (Å) at 100 K ^b	direction in the crystal	wavenumber at 3 K	intensity ^c	Raman spectrum
1	N—H···O, shorter H-bond in the head-to-tail chains	bifurcated	2.830(1)	a	3217	w	aa
2	N—H···O, longer H-bond in the head-to-tail chains	bifurcated	3.129(1)	a	3534	w	aa
3	N—H···O, H-bond between antiparallel chains within a layer	normal	2.862(1)	b	3087	w	bb
4	N—H···O, H-bond between the ab layers	normal	2.820(1)	c	3053	m	cc
5	O—H···O, along the head-to-tail chains	normal	2.907(8)	a	3468	s	aa

^a Bond numeration is as in refs 18, 21, 24, and 25. ^b Structural data for $T < 100$ K are not available. ^c Key: w, weak; m, middle; s, strong.

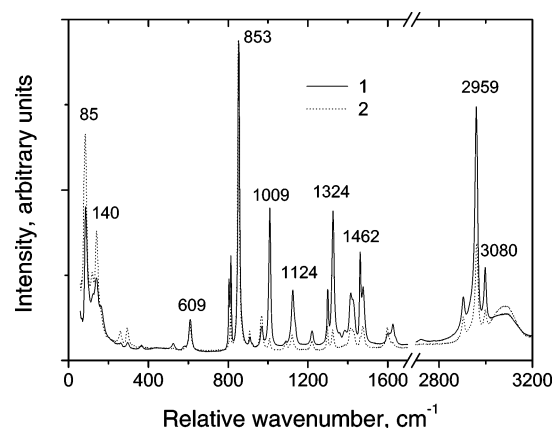
range 200–220 K is the region where dynamic transitions are typically observed in proteins and their complexes.⁴

Torsional vibrations of the NH₃⁺ terminal group play an important role in the dynamic transitions in the crystals of amino acids on cooling^{55–61} and with increasing pressure.^{62–64} According to the NMR data,^{55–58,65} the activation energies of NH₃⁺ group reorientation in the crystals of amino acids range from 28 to 40 kJ/mol. This suggests that together with intramolecular

forces (which determine the staggered positions for the NH₃ groups as preferable) the barriers are to some extent intermolecular in origin, dependent on the details of the packing, hydrogen bonding, and electrostatic interactions;⁵⁸ in particular, lowering the temperature may increase packing interactions that will limit the freedom of rotation. Different values of the activation barriers for the unfreezing of the rotations of the NH₃ groups in different polymorphs of the same amino acid and in

TABLE 2: Geometric Parameters of Hydrogen Bonds in DL-Serine at Several Temperatures Based on X-ray Diffraction Data^{18,32–34}

bond number ^a	bond	D–A distance (Å)			
		at 300 K ^{18,32,34}	at 200 K ^{18,32,34}	at 100 K ^{18,32,34}	at 20 K ³⁴
1	O–H···O (between –OH and COO [–] groups)	2.677(2)	2.673(2)	2.666(1)	2.663(1)
2	N–H···O (between NH ₃ [–] and COO [–] groups)	2.878(2)	2.869(2)	2.857(2)	2.853(1)
3	N–H···O (between NH ₃ [–] and COO [–] groups)	2.821(2)	2.812(2)	2.801(2)	2.795(1)
4	N–H···O (between NH ₃ [–] and –OH groups)	2.774(2)	2.769(2)	2.761(2)	2.765(1)

^a Bond numeration is as in ref 18.**Figure 7.** *cc* spectra of L-serine taken just after synthesis of the crystal (1, solid curve) and one year later (2, dotted curve). The spectra are normalized to the intensity of the band at 853 cm^{–1}.

the crystals of different amino acids can, among other factors, account for different stabilities of the structures with respect to variations in temperature and pressure, which was reported in the literature.^{1,18,21–27,55–78} For example, the structure of α -glycine is very stable with respect to any variations of temperature (no phase transitions on cooling or on heating^{79,80}) or pressure (no phase transitions, at least up to 23 GPa⁶²). In the Raman spectra of α -glycine, the NH₃⁺ torsional motion remains nondegenerate (and the torsional mode split) even at room temperature.⁶⁰ Another polymorph of glycine— β -glycine—is very unstable, and several phase transitions were observed (e.g., on cooling to ~ 250 K⁶¹ or with increasing pressure to 0.76 GPa^{75,81}), which were supposed to be interrelated with the torsional motions of the NH₃⁺ groups of glycine zwitterions.

The temperature effect on the spectra of L-serine is very different from that for DL-serine. This holds, first of all, for the vibrations related to the –CH₂OH groups.

The mode at 293 cm^{–1} in L-serine shows the opposite temperature trend (i.e., it slightly increases in frequency on heating in the 100–295 K range, in agreement with the IR data⁵²). The mode can be assigned to the bending vibration C2–C3–O3H7; this molecular fragment undergoes a slight structural transformation (see “Structural Instability of L-Serine”).

The mode at 1324 cm^{–1} in the spectra of L-serine is assigned to the C3–O3 stretching vibration. It appears in the **bb** spectrum only at 3 K and in the **bb** and **cc** spectra at room temperature, while the C2–C3 stretching mode at 852 cm^{–1} does not change its polarization vs temperature. The polarization of most COO[–]-related modes (i.e., 1000–1500 cm^{–1}), as well as of the C3H5H6 symmetric stretching mode at 2961 cm^{–1}, also changes with temperature in the same way as the mode at 1324 cm^{–1}, suggesting that the –(C3H5H6)–O3H7 molecular fragment turns slightly with respect to the C2–C3 bond on heating (Figure 4).

Some modes (i.e., 361 and 438 cm^{–1} in L-serine and 400, 510, 766, and 979 cm^{–1} in DL-serine) broaden significantly on

TABLE 3: Peak Position (cm^{–1}) of the Observed Raman Modes in the Crystals of L-Serine at Different Temperatures^a

3 K	60 K	140 K	220 K	300 K
74 m	73	71	70	
87 s	87	86	85	83
108 m	107	104	sh	sh
128 m	127	125	121	119
142 m	142	141	142	139
151 m	151	147		
166 w	166	165		
177 w	177	177		
198 w	199	199	199	
207 w	205 (sh)			
221 w				
262 w	262	260	260	260
293 m	293	294	295	295
361 w	361	361	361	359
438 m	439	438	433	
512 m	512	513	512	511
573 w	573	572	571	
615 m	614	613	611	608
803 w	803	803	803	sh
814 s	813	813	812	811
852 s	852	852	852	850
922 w	922	922	921	
975 m	974	971	968	966
1005 m	1005	1005	1005	1004
1015 m	1015	1014	1014	1013 (sh)
1092 m	1092	1091	1090	1088
1119 w	1119	1123	1121	sh
1124 w	1124			
1137 m	1137	1136	1134	1132
1208 m	1208			
1223 m	1223	1225	1227	1227
1298 m	1298	1298	1298	1298
1324 s	1324	1324	1324	1324
1415 m	1415	1414	1414	1413
1435 m	1435	1432	1429	1426
1460 s	1460	1460	1461	1461
1470 (sh)				
1474 m	1474	1473	1472	sh
1629 (sh)				
1634 m	1632	1630	1629	1627
2905 m	2905	2904	2904	2903
2922 (sh)				
2940 (sh)				
2960 s	2960	2960	2959	2958
3004 s	3004	3001	2999	2997
3442				
3468 s	3468			
3508 m	3504			
3534 w	3530 (sh)			

^a Key: w, weak; m, middle; s, strong; sh, shoulder.

heating and almost disappear at room temperature. Possibly, they are related to torsion vibrations of the NH₃ groups.

The temperature behavior of the O–H stretching mode at 3468 cm^{–1} (i.e., corresponding to the O3–H7···O3 hydrogen bond) in L-serine is exceptional and will be considered separately in “Structural Instability of L-Serine”.

TABLE 4. Peak Position (cm⁻¹) of the Observed Raman Modes in the Crystals of DL-Serine at Different Temperatures^a

3 K	60 K	140 K	220 K	300 K
96 w	96	95	94	92
101 s	101	102	102	102
110 m	110	108	108	107
122 s	122	121	120	118
159 w	158	158	158	
181 m	180	177	174	171
197 s	196	194	191	187
226 s	226	224	222	220
253 m	252	251	250	249
284 m	284	281	278	282
297 w	296	293	289	
400 m	399	397	394	390
510 m	509	506	502	497
533 w	533	529	528	524
541 w	539	535		
565 w	565	563	561	560
620 (sh)	620 (sh)	619 (sh)	619	618
622 m	622	621		
766 w	765	762	756	751
822 w	821	818	815	813
854 m	853	852	851	850
903 w	903	901	899	899
979 m	979	977	975	975
988 w	987	986	984	983
1016 w	1015	1006		
1030 m	1030	1029	1028	1026
1049 w	1048	1045	1045	1043
1095 w	1095	1098	1097	1095
1102 w	1102			
1165 m	1164	1161	1158	1155
1184 m	1183	1181	1178	1175
1250 s	1250	1249	1248	1247
1310 s	1311	1310	1309	1308
1351 s	1351	1350	1349	1348
1365 m	1365	1365	1364	1363
1377 m	1377	1376	1375	1375
1414 w	1413	1412		
1434 m	1433	1431	1428	1421 (sh)
			1436	1433
1451 m	1451	1452	1454	1453
1528 m	1528	1526	1523	1521
1583 w	1582	1581	1580	1578
1626 m	1626	1624	1623	1621
1642 m	1641	1639	1636	1632
2869 (sh)	2870 (sh)	2870 (sh)	2873 (sh)	2877 (sh)
2936 (sh)	2937 (sh)	2937 (sh)	2940	2940
2940 s	2940	2940		
2970 s	2970	2971	2972	2973

^a Key: w, weak; m, middle; s, strong; sh, shoulder.

Structural Instability of L-Serine. The major changes with temperature involve the OH stretching vibrations, $\nu(\text{O-H})$, in the range 3300–3600 cm⁻¹ (Figure 6). The low-temperature spectrum of L-serine shows one intensive band at 3468 cm⁻¹ and two weak bands at 3508 and 3534 cm⁻¹. The two former bands are totally symmetric and antisymmetric, respectively, and the third band is too weak in intensity to determine its symmetry. When the temperature raises, a new mode appears in the spectra (i.e., 3440 cm⁻¹ in the 40 K spectrum, Figure 6a, and 3434 cm⁻¹ in the 100 K spectrum, Figure 6c). At temperatures higher than 100 K, at least three new Raman bands can be found in the spectra, as can be seen from a Lorentz deconvolution (Figure 6c,d). Figure 6b shows the integral intensity of the bands vs temperature in the 3–100 K range. The intensity gain of the mode at 3434–3440 cm⁻¹ unambiguously correlates with the intensity loss of the mode at 3468 cm⁻¹ (the frequency of the latter mode changes slightly from 3468 cm⁻¹ at 3 K, Figure 6a, to 3462 cm⁻¹ at 140 K, Figure 6d). In

other words, part of the states ($\sim 1/2$ of the total amount at 3 K) related to the mode at 3468 cm⁻¹ transform into other states corresponding to the modes at 3434–3440 cm⁻¹ at 100 K. On further heating, new modes appear in the spectra (Figure 6), and all these modes merge. Above 140 K only one broad band (an envelope of several modes) is observed. The low-frequency vibration of the hydrogen bond itself (at 60–80 cm⁻¹ at low temperatures) transforms to an envelope of many lines upon heating (Figure 5a, marked by a double arrow), giving another piece of evidence of the appearance of other energy states of hydrogen bonding.

The spectral changes described above can be interpreted in terms of the reorientation of the $-\text{CH}_2\text{OH}$ groups resulting in the positional disordering of the $\text{O-H}\cdots\text{O}$ intermolecular H-bonds on heating. Considering the temperature behavior of the polarized Raman spectra, we have concluded that the molecular fragments in L-serine turn slightly with respect to the axis parallel to the C2–C3 bond when the temperature changes (see “Temperature Dependence”). This temperature-dependent rotation of serine molecules accounts very well for the observed effect on the O3–H7 \cdots O3 hydrogen-bonding instability. Indeed, the rotation of the $-\text{CH}_2\text{OH}$ side chains of the molecules relative to each other should lead inevitably to changing the O3–H7 \cdots O3 geometry (configuration) and thus to changing the frequency of the O3–H7 \cdots O3 vibration. The rotation does not occur continuously, but a molecule can adopt a few different conformations. The transition of a molecule from one conformation to another is equivalent to a transition into another potential well. The rotation of the side chains can, in principle, be accompanied by (i) changing the energy of the hydrogen bonding, (ii) occurrence of bifurcated hydrogen bonding instead of normal hydrogen bonding with a single acceptor, and (iii) creation of new hydrogen bonding with the carboxyl oxygen atom. The dynamic transition on cooling manifests itself also in the IINS spectra: the estimates of the atomic mean-square displacement from the incoherent inelastic neutron scattering measurements for L-serine as a function of temperature have shown a clear deviation from linearity near 150 K.⁸²

Unfortunately, at this stage it is not possible to test the conclusion based on Raman and IINS spectra by diffraction data, since the latter are not available for temperatures below 100 K, when the changes in the hydrogen bonding of the $-\text{CH}_2\text{OH}$ groups can be expected from the Raman spectra. At the same time, X-ray and neutron diffraction studies at nonambient pressures show that rotation of side chains in the crystals of L-serine can really be observed and plays an important role in pressure-induced phase transitions. Two phase transitions were observed in the crystals of L-serine with increasing pressure.^{22–26} These phase transitions are of a “cascade type”²³ and, as evidenced by single-crystal X-ray diffraction^{22,24} and powder X-ray²⁵ and neutron²⁶ diffraction studies, are related to cooperative jumpwise rotation of the $-\text{CH}_2\text{OH}$ side groups, resulting in a change of the hydrogen bonding (in particular, during the first phase transition at about 5 GPa, hydroxyl–hydroxyl hydrogen bonds are substituted by hydroxyl–carboxyl hydrogen bonds,^{22,23,25} and although the hydroxyl–carboxyl bonds are preserved during the second phase transition at about 8 GPa,^{24–26} the jumpwise rotation of the $-\text{CH}_2\text{OH}$ fragment makes the hydrogen bond formed by this group even more multicentered, adding a new hydrogen bond, $\text{NH}\cdots\text{O}$, between the $-\text{NH}_3^+$ group and the $-\text{CH}_2\text{OH}$ side chain^{24,25}).

The changes in the Raman spectra of L-serine with increasing pressure,²³ accompanying the rotations of the $-\text{CH}_2\text{OH}$ side

chains, can be compared with those on cooling. Large positive jumps ($36\text{--}9\text{ cm}^{-1}$) were observed for the NCC (363 cm^{-1}), CH_2 (1462 cm^{-1}), and OH (1228 cm^{-1}) bending modes. Large red shifts (from -16 to -12 cm^{-1}) were measured for the COO^- symmetric stretch (1414 cm^{-1}), NH_3 antisymmetric rock (1133 cm^{-1}), COO^- bend (611 cm^{-1}), and NH_3 antisymmetric bend (1628 cm^{-1}). The intensity of the OH stretching vibration (about 3400 cm^{-1}) decreased on the phase transition at about 5 GPa, in agreement with a transfer from the $\text{OH}\cdots\text{OH}$ bond to the bond between the $-\text{OH}$ and carboxyl groups. On the second pressure-induced phase transition at about 7.8 GPa, most bands in the spectrum experience positive frequency jumps, in agreement with the increasing density of the structure. The largest jumps were observed for the bands at about 1250 cm^{-1} (OH bend) and 1430 cm^{-1} (COO^- symmetric stretching), consistent with the strengthening of the $\text{OH}\cdots\text{O}_2\text{C}$ bonds.²³ A comparison of the changes in the Raman spectra on cooling and with increasing pressure allows one to suggest that the state of the $\text{O}_3\text{--H7}\cdots\text{O}_3$ hydrogen bonding at ambient temperature and pressure in L-serine can be considered as an intermediate one as compared to that of the pure $\text{O}_3\text{--H7}\cdots\text{O}$ (hydroxyl) hydrogen bonding at low temperatures and pure $\text{O}_3\text{--H7}\cdots\text{O}$ (carboxyl) hydrogen bonding at high pressures. It is remarkable that, in the crystals of orthorhombic L-cysteine, $\text{NH}_3^+\text{CH}(\text{CH}_2\text{SH})\text{COO}^-$ (to some extent, a structural analogue of L-serine, with much weaker hydrogen bonds $\text{SH}\cdots\text{O}$ and $\text{SH}\cdots\text{S}$ formed by side chains $-\text{CH}_2\text{SH}$), the molecules are ordered at low temperatures⁸³ and get disordered on heating to about 60–70 K (the extended phase transition shows pronounced kinetic effects).⁸⁴ Rotation of the $-\text{CH}_2\text{SH}$ side chains in L-cysteine is supposed to account for pressure-induced phase transitions in this system.⁸⁵ An intermediate high-pressure phase was described as a structure with alternating thin domains with different orientations of thiol groups typical for another high-pressure phase and the ambient-pressure phase.⁸⁵ For L-serine, formation of a similar nanostructured state (or, alternatively, of a superstructure with tripled a and c cell parameters) at pressures between 6 and 8 GPa was suggested on the basis of powder X-ray diffraction data.²⁵

The disordering of the L-serine molecules in the crystal (e.g., the formation of domains with alternating orientations of side chains) can account also for another very unusual phenomenon observed in the present study: the structural instability on storage at ambient conditions. Whereas the **aa** and **bb** spectra of L-serine remain almost unchanged with time for crystal storage of over one year at ambient conditions, the relative intensities of almost all the bands (intra- and intermolecular) in the **cc** spectrum changed significantly, although the frequencies remained constant (Figure 7). All the modes in which atomic motion occurs in the direction normal to the c axis of the crystal became weaker in intensity on storage of the crystal. A weaker intensity of vibrations normal to the polarization plane is typical for nonchiral crystals. Thus, the spectral changes in L-serine on storage suggest that the optical activity of L-serine crystals with respect to the incident light polarized along the c axis decreases with time as the freshly grown crystals are stored. Earlier, the proton motion in a hydrogen bond associated with the NH_3^+ group, leading to the dynamic disorder in a crystal, was observed to result in depolarizing all the Raman lines associated with the hydrogen bonding in the crystals of L-alanine, and this phenomenon was supposed to be intrinsic for all hydrogen-bonded systems.⁵⁷

Low-Frequency Lattice Vibrations and Heat Capacity. Recently, a pronounced difference in the thermodynamic

functions of chiral (D) and racemic (DL) serine was found by adiabatic calorimetry.²⁷ The difference between the $C_p(T)$ of the chiral and the racemic forms increases rapidly from $-0.01\text{ J mol}^{-1}\text{ K}^{-1}$ at 5 K to $+6.5\text{ J mol}^{-1}\text{ K}^{-1}$ near 130 K. The results were interpreted in terms of a hypothetical presence of an additional Einstein mode at about 129 cm^{-1} in the vibrational spectrum of D-serine. Our Raman data in the low-frequency range of lattice vibrations (though obtained not for D-serine but for the isostructural L-serine) allowed us to understand the origin of the observed difference in the heat capacity values (Figures 4 and 5). The spectra of L- and DL-serine in the $70\text{--}250\text{ cm}^{-1}$ range (i.e., the range where the Einstein mode was supposed to occur) are very similar, but the frequencies of all the observed modes in DL-serine are shifted to higher values, as compared to the frequencies in L-serine (Figure 5). Low-frequency modes are assigned to intermolecular (translational and librational) motions of serine molecules. Their frequencies are determined by force constants of all intermolecular hydrogen bonds ($\text{N}\cdots\text{H}\cdots\text{O}$, $\text{O}\cdots\text{H}\cdots\text{O}$) and the shortest van der Waals contacts. $\text{N}\cdots\text{H}\cdots\text{O}$ and $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonds are noticeably shorter in DL-serine than in L-serine;^{18,21} see also Tables 1 and 2. Therefore, it is not surprising that low-frequency lattice modes in DL-serine are shifted to higher energies. As a result, the heat capacity C_p of the chiral form of serine is larger at low temperatures than that of DL-serine; i.e., $\Delta C_p (C_p(\text{L}) - C_p(\text{DL}))$ shows a maximum at 100–200 K (Figure 3 from ref 27). Thus, the low-frequency shift of *all* lattice modes in L-serine plays the role of the hypothetical “Einstein mode at around 129 cm^{-1} ”.

5. Conclusions

Variable-temperature single-crystal Raman spectroscopy contributes to our understanding of the different dynamic properties of the chiral crystals of L-serine and of the racemic crystals of DL-serine. Despite a higher bulk density of the structure as a whole, the mobility of zwitterions and their fragments is higher in the crystals of L-serine with a three-dimensional H-bonded framework than in the crystals of DL-serine, in which the more densely packed H-bonded double layers alternate with relatively looser spacing in the structure. A dynamic transition occurs in the crystals of L-serine at about 140 K and can be related to the reorientation of the side chains $-\text{CH}_2\text{OH}$ of the zwitterions. The changes in the orientation of the side chains occur also on long-term storage of L-serine single crystals at ambient conditions.

It is remarkable that unfreezing of rotations of $-\text{NH}_3^+$ groups and disordering of $-\text{CH}_2\text{OH}$ side chains in L-serine are activated in different temperature ranges. Selective activation of a particular motion in a characteristic temperature interval is of primary importance for the protein flexibility responsible for protein function.⁴ Crystalline amino acids mimic well this feature of proteins: different classes of motions (related to the $-\text{CH}_3$, $-\text{NH}_3^+$, $-\text{CH}_2\text{OH}$, etc. groups) are frozen in different temperature ranges on cooling or at different pressures on squeezing. Different experimental techniques (IR and Raman spectroscopy,^{7–15,36–52,59,60,62–64,66–71,73–79} picosecond coherent Raman scattering (ps CARS),^{86,87} terahertz spectroscopy,¹⁶ NMR,^{55–58,65} electron spin echo,⁸⁸ pulsed ESR spectroscopy,⁸⁹ adiabatic calorimetry,^{27,61,72,79,80,84,88} X-ray diffraction,^{18,21,22,24,26,81,83–85} IINS^{43,59,82}) are sensitive to the motions with different relaxation times and can, therefore, detect selectively different types of disorder in the crystals of amino acids. This often leads to confusion and seeming discrepancies in the conclusions on the occurrence of a phase transition based on using different experimental techniques. At the same time,

this selectivity can be used on purpose, and a complementary study of an amino acid crystal in a wide temperature/pressure range with as many experimental techniques as possible can be most helpful to elucidate the nature of the multiple dynamic transitions in these systems and the relation of these transitions to the conformational changes in biopolymers.

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Supporting Information Available: A full set of nonpolarized Raman spectra for L- and DL-serine (60–4000 cm⁻¹) collected at 12 temperatures in the range 3–300 K (*.doc). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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