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Raman spectroscopy and inelastic neutron scattering study of crystalline L-valine

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Abstract

Information about the strength of the hydrogen bond interactions in crystalline L-valine was obtained by Raman and inelastic neutron scattering spectroscopies. Raman studies were carried out from room temperature up to 423 K in order to examine both the external and the internal vibrations in L-valine. The structure seems to be stable above room temperature since no indication of a phase transition or clear indication of reorientation of L-valine molecules was observed. From the inelastic neutron scattering measurements, made between 270 and 320 K, for fully hydrogenated and partially deuterated L-valine, a better description of the low frequency modes was possible. Moreover it was possible to establish that the phase transition at low temperatures is related to the activation of an infrared mode in the Raman spectra. Additionally the low temperature phase of L-valine was further characterized by means of specific heat measurements between 5 and 350 K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Amino acids are the monomeric building blocks of proteins and exist as zwitterionic species in the crystalline state and in solution. The presence of hydrogen bonds and the polarity of amino acids is one of the forces responsible for the stability of the final protein structure, thus essential in the conformational characteristics of many polypeptides and proteins. The possibility of testing the structural-dynamic relationship in amino acids is viable by changing thermodynamics parameters such as temperature and pressure using different techniques such as adiabatic calorimetric measurements [1, 2], Raman [3–9] and neutron scattering [10–13], NMR [14, 15] as well as x-ray diffraction [16–18].

Among the various studies of amino acids some revealed striking results emphasizing the fact that subtle changes in the hydrogen bond arrangements give rise to important motions, as well as to the fact that how functional groups are arranged in a sequence will define the dynamics of complex systems. For instance, a remarkable kinetic effect in the pressure-induced phase transition in γ -glycine was observed after the sample was kept at 0.8 GPa for an hour [12]. An irreversible transition into a high-pressure form took place, although previous in x-ray diffraction [16] and Raman spectroscopy [19] experiments indicated a γ - to δ -glycine phase transition above 3.5 GPa only. Similarly, although no substantial structural modifications are observed in fully hydrogenated L-alanine as a function of temperature, by using selective deuteration [10] the anomalies

in the Debye–Waller behavior at about 160 K and at 220 K, related to reorientations of the NH₃ and CH₃ moieties, could be evidenced. Moreover, the pressure effects are remarkable in L-alanine; a structural phase transition from orthorhombic to tetragonal symmetry at 2.2 GPa was observed by both Raman spectroscopy [20] and synchrotron x-ray diffraction [21]. Additionally, Raman studies of deuterated L-alanine obtained at high-pressure conditions [22] indicated a phase transition at ~ 1.5 GPa, most likely related to a symmetry change, and a second transition at ~ 4.4 GPa, which may be associated to conformational changes of the molecule. Furthermore, Raman scattering studies on L-leucine point towards a phase transition at high temperature [9] as well as at least three phase changes at high pressures conditions [23]. However, similarly to L-alanine, the structure of L-isoleucine seems to be stable from 30 to 290 K as reported by Almeida *et al* [24]. Interestingly, chiral and racemic (L- and DL-) serine and valine crystals have different physical behavior. On cooling from room temperature to 3 K, new lattice modes appeared at ~ 140 K in L-serine and various changes in the O–H stretching vibrations were observed in the same temperature range [11]; however, no significant modifications were observed for the racemic mixture [25]. Low temperature studies of L-valine indicate one phase transition [26] at ~ 120 K, while DSC-investigations show no evidence for a phase transition on both forms of valine between 233 and 423 K [27]. On the other hand, while L-valine undergoes two phase transitions [28] at ~ 3.0 and ~ 5.0 GPa, even if a substantial reduction in the intensity of the N–HO librational mode is observed at ~ 3.0 GPa [29], DL-valine seems to be stable at least up to 7.9 GP. In summary, such findings can certainly be interpreted in terms of changes in the hydrogen bonding interaction.

To the best of our knowledge no Raman data is available for the high temperature phase of L-valine. In order to close this gap, we present, in this work, the Raman spectra of a L-valine crystal from room temperature up to 423 K. The stability of the structure and the behavior of most of the modes active in the Raman spectrum are discussed. Moreover to better analyze the dynamics of the NH₃ group inelastic neutron scattering (INS) data were collected in fully hydrogenated L-valine and partially deuterated L-valine between 270 and 320 K. Finally to enhance the understanding of our previous low temperature Raman data [26] heat capacity measurements are presented between 5 and 350 K, one expects that a disorder–order transition will manifest itself in the temperature dependence of the calorimetric data.

2. Experimental details

Samples: colorless and elongated plates of L-valine ((CH₃)₂CHCH(NH₂)CO₂H) crystal were obtained from an aqueous solution by the slow evaporation technique. The solution was kept at 295 K for about 6 weeks. X-ray diffraction measurements were performed to verify the crystal structure of the samples [23].

The L-valine-*d*₈ powder sample ((CD₃)₂CDCD(NH₂)CO₂H) was synthesized by Dr Ehrenstorfer GmbH (Augsburg, Germany). The samples were quoted to have a purity better

than 99%. All powder samples used in the neutron experiments were loaded into their containers in a glove bag flooded with helium.

Calorimetric measurements: heat capacity measurements were performed between 5 and 320 K. In order to achieve appropriate heat capacity using the Physical Property Measurement System (PPMS), L-valine was alloyed with the grease Apiezon H in 1:1.01 ratio. The option quantum design heat capacity of PPMS allows to measure the heat capacity $C_p = (\frac{dQ}{dT})_p$ at constant pressure. Therefore the sample with a weight of 1.01 mg was mounted on a sample platform, which is in contact with the heater and a thermometer. After heating the sample platform, a cooling period occurs and the emerging evolution of the temperature of the platform T over time t satisfies the equation $C_{\text{total}} \frac{dT}{dt} = -K_w(T - T_b) + P(t)$, where C_{total} is the heat capacity of the sample and the sample platform; K_w the thermal conductance of the supporting wires; T_b the temperature of the thermal bath and $P(t)$ the power applied by the heater. Exponential functions with the characteristic time constant $\tau = C_{\text{total}}/K_w$ are possible solutions.

Inelastic neutron scattering (INS) measurements: INS data were obtained on polycrystalline samples using the time-of-flight (ToF) spectrometer NEAT located at the BENSC facility in Berlin, Germany. Using this spectrometer, a good resolution for low energy excitations can be achieved due to the selected incident wavelength ($\lambda = 5.1$ Å) plus the fact that the instrument is located in a cold neutron source. However due to the fact that data are collected in energy gain of the scattered neutrons limits are set to work at lower temperatures. For instance, for a sample temperature of 50 K only excitations up to 240 cm⁻¹ (~ 30 meV) can be followed. After correcting the data for sample holder and background contributions and Bragg peaks were removed, a one-dimensional spectrum, $S(E)$, was obtained by summing the spectra collected over the scattering region covered by a solid-angle determined by the angular range covered by the instrument, here from 13.35° to 136.65°. Then the spectral information contained in $S(E)$ was divided by the Bose population factor $n(E) = (eE/k_B T - 1)^{-1}$, with k_B representing the Boltzmann constant, giving the dynamical susceptibility function, $\chi''(E)$ [30]. Such approach allows for the inspection of the vibrational information. For excitations following the Bose dependence with temperature, their susceptibility should overlap. Moreover, it is of particular importance in this work that the scattering cross sections of H and deuterium (D) differ by a factor of 20. Therefore, isotopic replacements will cause significant changes in the observed intensities, and the use of selectively deuterated samples allows contributions arising from different parts of the molecules to be distinguished. Besides the simplicity of the neutron–nucleus interaction has one important consequence: that there are no selection rules in contrast to Raman and infrared spectroscopy, and all modes can in principle be observed.

Raman scattering measurements: Raman spectra were obtained with a T64000 Jobin-Yvon triple spectrometer equipped with an N₂-cooled CCD detection system. Due to the shape of the crystals it was possible to obtain good spectra at the $z(yy)z$ scattering geometry. The slits

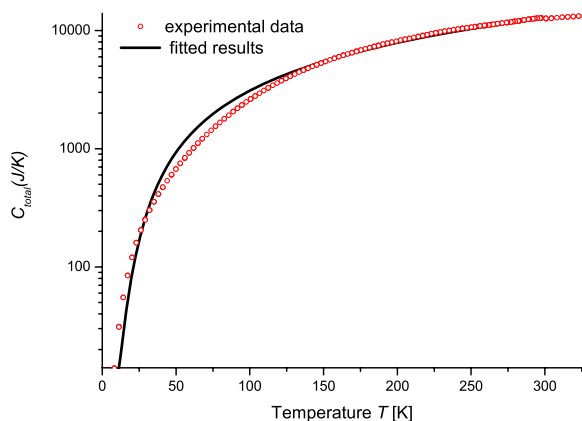


Figure 1. Temperature dependence of heat capacity, C_{total} , of L-valine.

were set for a resolution of 2 cm^{-1} . Temperature Raman scattering experiments were carried out using a Linkan TS1500 microfurnace. The 514.5 nm line of an argon laser was used as excitation source.

3. Results and discussions

At room temperature L-valine crystallizes in a monoclinic structure, belonging to $P2_1$ (C_2^2) space group, with four molecules per unit cell. As observed in other amino acids [31–33] L-valine also has two crystallographic independent molecules in the unit cell, being two in the *gauche I* conformation and the other two in the *trans* conformation [34].

PPMS calculated C_{total} in a temperature range of 5–350 K. The data were analyzed using a program written in IDL to verify if the total heat capacity follows a Debye behavior. As shown in figure 1 a small anomaly is observed between 50 and 150 K. Our results agree with previous studies of fully hydrogenated L-valine where neither changes in the NMR spectra over the temperature range from 298 to 248 K nor anomalies were detected in the heat capacity measured by standard DSC between 220 and 340 K [35]. Furthermore our results confirm changes in the Raman spectra observed around 120 K [26]. A similar anomaly in the heat capacity data was observed for the crystalline L-cysteine and was interpreted as non-simultaneous changes in the dynamics and the orientation of the numerous thiol groups in the structure [36].

Comparison of the INS spectra of L-valine and L-valine- d_8 is a powerful tool for highlighting the modes of a particular molecular group. The INS spectra of L-valine and L-valine- d_8 is presented in figure 2(a). Clearly the intense band at $\sim 480 \text{ cm}^{-1}$ in the spectra of L-valine- d_8 (deuterium-labeled valine retains the amino ($-\text{NH}_2$) and the OH groups) confirms the assignment of to vibrations involving the $\text{N-H} \cdots \text{O}$ hydrogen bonds, while the overall decrease of signal below 450 cm^{-1} substantiates that the lower frequency modes are related to the CH_3 and CO_2 groups as well to the N-C-C unit [37]. Interestingly, and as indicated by the arrow, the mode at about 120 cm^{-1} that appears in the Raman spectra of L-valine below 120 K is

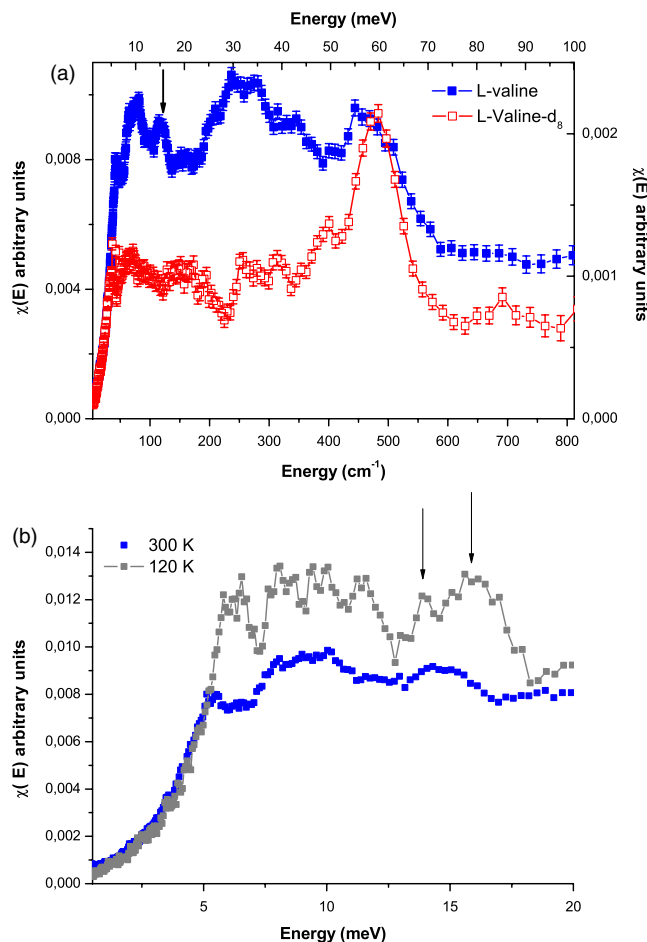


Figure 2. (a) Dynamical susceptibility ($\chi''(E)$) of the L-valine (full square) and L-valine- d_8 (open squares) samples measured on the NEAT spectrometer using a 5.1 \AA incident wavelength. (b) Dynamical susceptibility of the L-valine at 300 and 120 K. The arrow in (a) indicates the mode at 120 cm^{-1} (15 meV) observed at 120 K in the Raman spectra, suggesting that the phase transition observed at low temperatures can be related to activation of an IR mode.

clearly observed in the INS spectra of fully hydrated L-valine at 300 K, indicating that this mode is related to the CH group, and most likely IR active [38, 39]. Moreover as shown in figure 2(b) this mode shows a splitting, thus supporting the idea of a phase transition [26] at lower temperatures, since symmetry change should lead to the activation in the Raman (IR) spectra of modes which were non-active in the Raman (IR) in the monoclinic $P2_1$ phase. In fact, the new band appeared in the Raman spectra from a $z(yy)z$ scattering geometry (A symmetry) at low temperature [26], possibly originated from the T_x or T_y infrared modes from the B symmetry. Figures 3(a) and (b) represent the susceptibility of L-valine and L-valine- d_8 measured at 270, 300 and 320 K. For excitations following a Bose dependence with temperature, their susceptibility should overlap which is observed for the high temperature range analyzed in this experiment. The fact that at low temperatures the susceptibility does not follow in the same master curve, i.e. a re-distribution of the intensity of the bands is noticeable, indicates that below room temperature the system is no longer harmonic. This observation, additionally, highlights the fact

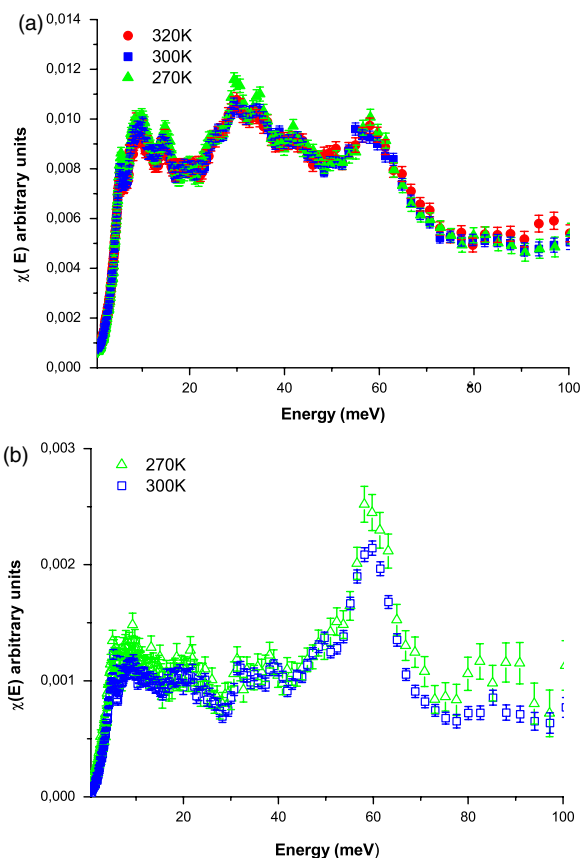


Figure 3. (a) Dynamical susceptibility of the L-valine (full symbols) and (b) L-valine- d_8 (open symbols) at 270 K (triangles), 300 K (squares) and 320 K (circles). Note that the excitations follow the Bose dependence with temperature.

that molecular conformation of L-valine changes below room temperature.

Figure 4 shows the Raman spectra of L-valine crystal in the spectral range (40–700) cm^{-1} at several temperatures from 295 to 423 K. We remember that a phase transition observed in L-valine crystal at high-pressure measurements was supported mainly by modifications of the Raman spectra in the region of the lattice modes [28]. By inspecting the inset of figure 4 it is possible to observe in detail the Raman spectra of L-valine in this low frequency spectral region. As can be seen, no significant changes were observed on warming above room temperature: the number of modes remains the same and their intensities practically do not change. Moreover, even with low intensity it is possible to observe that the mode at $\sim 60 \text{ cm}^{-1}$, which vanishes between 120 and 100 K supporting the idea that crystalline L-valine undergoes one phase transition [26] at $T \sim 110 \text{ K}$, keeps practically unchanged as the temperature increases. The asymmetric band centered at $\sim 85 \text{ cm}^{-1}$ can be adjusted by two Lorentzian peaks that at 423 K are almost separated. It is interesting to cite that on cooling [26], a change in the intensity of these modes was observed. In the present work, the fact that the intensity of the bands of low frequency—which are associated to translational motions of the molecule—remains approximately constant indicates that the L-valine molecules in the crystalline lattice above

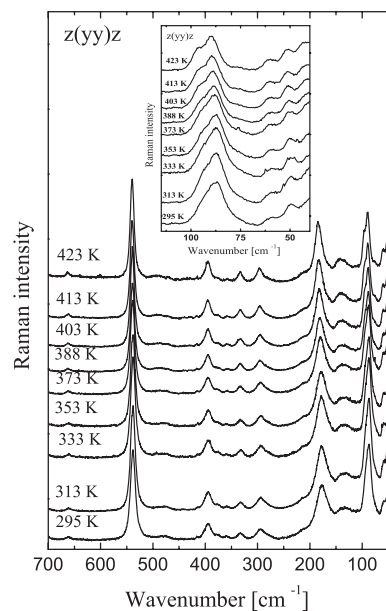


Figure 4. Raman spectra of L-valine crystal in the region between 40 and 700 cm^{-1} for several temperatures for the $z(yy)z$ scattering geometry. Inset: detailed view of the Raman spectra of L-valine between 40 and 120 cm^{-1} .

room temperature do not undergo reorientation motions. In crystalline L-valine the oxygen atoms of one molecule form hydrogen bonds with the hydrogens of the adjacent molecules. And as pointed out by x-ray diffraction measurements the two oxygens of one molecule are located in approximately tetrahedral directions with two hydrogen atoms situated nearly on the lines between the amino nitrogen atom and the oxygen atoms [31]. Additionally, the other amino hydrogen atom participates in a bifurcated hydrogen bond. For the second molecule in the unit cell, all three oxygen atoms participate in the hydrogen bonds [31]. The band observed at the Raman spectrum at $\sim 185 \text{ cm}^{-1}$ is associated to the torsion of CO_2^- , $\tau(\text{CO}_2)$ [26] thus carrying information about the hydrogen bond between the CO_2^- and NH_3^+ groups. The observation of a slight increase of the frequency of $\tau(\text{CO}_2)$ vibration on heating points towards a possible increase of the distance between adjacent L-valine molecules. Finally, the mode assigned as rocking of $\text{CO}_2[\rho(\text{CO}_2)]$ at $\sim 540 \text{ cm}^{-1}$ is practically not affected by increasing temperature. Such a fact is different from what is observed at the low temperature [26] and the high-pressure [28] measurements where a splitting of the mode is very clear. The splitting could be understood as a break of degeneracy, as mentioned above, due to the phase transition undergone by the crystal.

Raman spectra of L-valine crystal for several temperatures in the spectral range (700–1000) cm^{-1} can be seen in figure 5(a). In this region one can expect modes associated with vibrations of wagging of CO_2 , deformation of CO_2 and stretching of C–C. As can be observed the spectrum is almost the same for all the temperatures. However, one point worth mentioning is that for L-leucine [9] it was observed that a band associated to stretching vibration of C–C, which was seen as a doublet at room temperature, was observed for

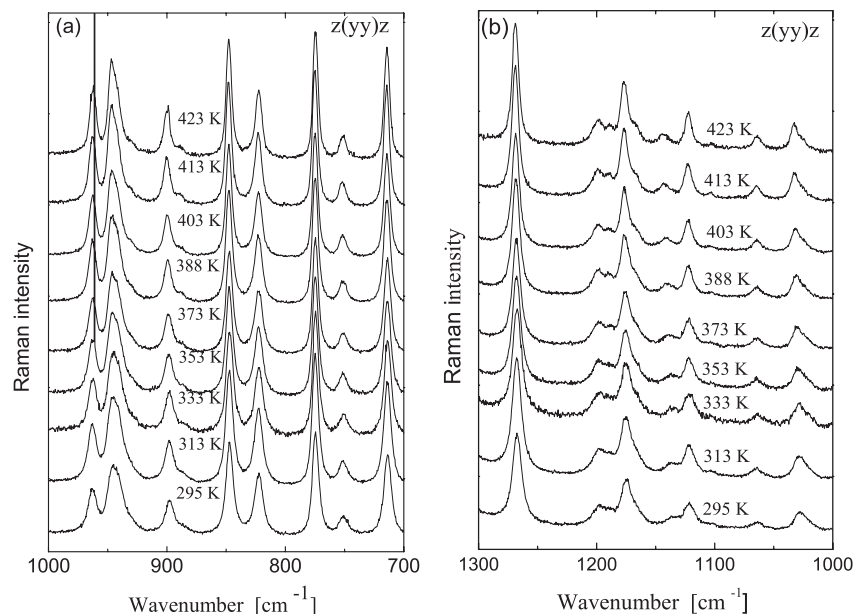


Figure 5. Raman spectra of L-valine crystal for several temperatures for the $z(yy)z$ scattering geometry in the region between 700 and 1000 cm^{-1} in (a) and in the region between 1000 and 1300 cm^{-1} in (b).

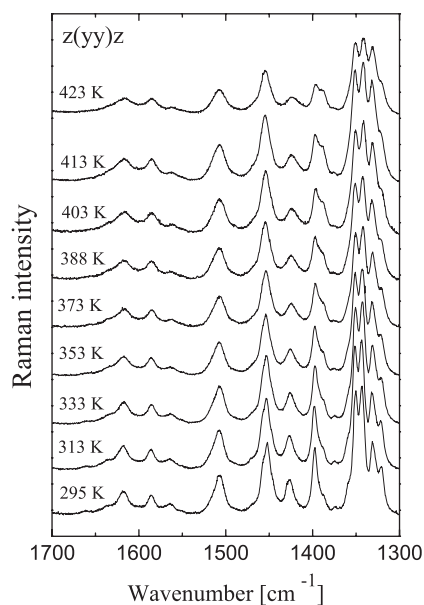


Figure 6. Raman spectra of L-valine crystal in the region between 1300 and 1700 cm^{-1} for several temperatures for the $z(yy)z$ scattering geometry.

$T > 360\text{ K}$ as a single band. Here, for L-valine under high temperature, such a phenomenon is absent, indicating that the effect of temperature on the stretching vibration of C–C is more important for crystalline L-leucine than for L-valine. Moreover, the intensity of the mode centered at $\sim 1270\text{ cm}^{-1}$, associated with a deformation of C–H, increases on warming, while the intensity for all other modes is practically unchanged—see figure 5(b).

Figure 6 presents the Raman spectra of L-valine crystal in the spectral range (1300 – 1700 cm^{-1}) at several temperatures

from 295 to 423 K. Under heating the number of modes remains the same and their intensity decreases. Interestingly, although no great change is observed for this region, a small modification, referring to the intensity of bands at 1300 – 1350 cm^{-1} , was noted. These bands are associated to the bending vibrations of CH and CH_3 . Observe, for example, that the band at $\sim 1330\text{ cm}^{-1}$ has the half intensity of the band at $\sim 1340\text{ cm}^{-1}$ when $T = 295\text{ K}$. For high temperature ($T = 423\text{ K}$) the intensities of these two bands are approximately the same. Such an increase of relative intensity of a band related to bending vibration of CH or CH_3 was also observed in crystalline L-leucine [9] on heating, and can be associated to a small coupling of this high frequency band with a band of lower frequency.

Raman spectra of L-valine crystal at several temperatures in the spectral range (2800 – 3050 cm^{-1}) are shown in figure 7(a) and the wavenumber versus temperature plot for the same regions is presented in figure 7(b). It is observed that there is a small decrease in the intensity of the modes especially between 413 and 423 K but the number of modes does not change. Additionally, there no change of the relative intensity among the several bands was observed, indicating that the conformation of the molecules remains approximately unchanged in all temperatures investigated. The wavenumber of all bands presents a linear dependence with the temperature parameter not only for this spectral region but for the previous ones as well, moreover no discontinuities in $\omega \times T$ plot were observed. Again, it is important to mention that the increasing temperature seems to not have any influence in the stretching of CH and CH_3 modes. This is in contrast with the results of high-pressure measurements which show that these modes are severely affected: the bands associated suffer drastic changes in the intensities, in the slopes of the linear adjust of $\omega \times P$ and in the number of modes [28].

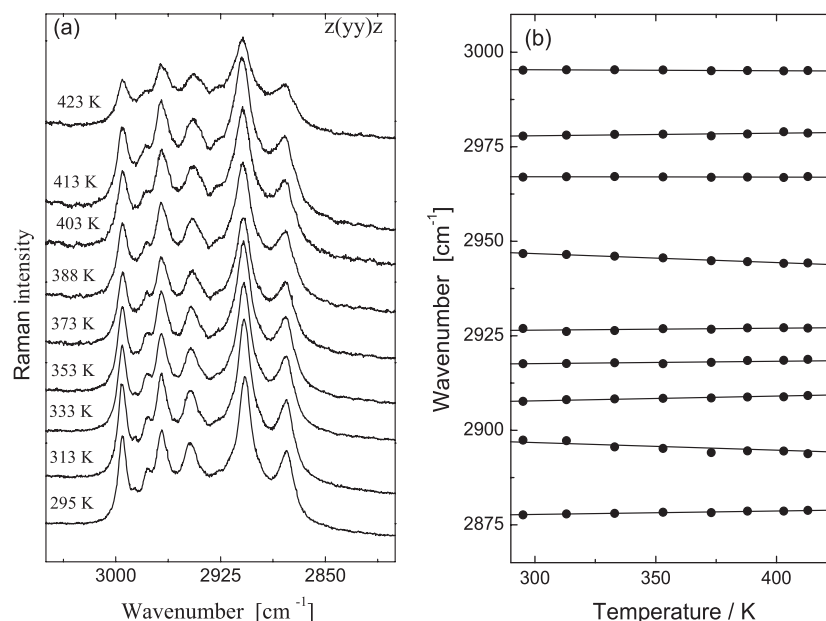


Figure 7. Raman spectra of L-valine crystal in the region between 2800 and 3050 cm⁻¹ for several temperatures for the $z(yy)z$ scattering geometry in (a) and wavenumber versus temperature plot for the same region in (b).

One possible explanation for the stability of L-valine at high temperatures is related to the hydrogen bonds of the crystal. L-valine crystallizes in a monoclinic system and the tridimensional arrangement build up by double layers linked by hydrogen bonds along (001) axes [31]. As the side chain of L-valine is short [27] cooling will induce symmetry changes [23]; however, for high temperatures, the bonds can vary their lengths in a great range without the structure being forced to undergo a symmetry change.

4. Conclusions

In this work we have extended our methodical approach of combining vibrational and structural properties to the aliphatic amino acid: L-valine. Calorimetric measurements, and INS and Raman data were collected on fully hydrated and partially deuterated L-valine as a function of temperature. While the specific heat results confirmed the instability of the structure at low temperatures, from the Raman spectroscopy results it is possible to infer that the structure of L-valine is stable between 295 and 423 K. No modification in the number of modes or on the slope of ω versus T plot were observed, the number of modes in the Raman spectra did not change and the behavior of the frequency of all modes was shown to vary linearly with the temperature without any discontinuity. The behavior of the band associated to τ (CO₂) vibration on heating suggests that the hydrogen bonds among the molecules in the unit cell are softened, most likely due to the increasing of the distance between adjacent L-valine molecules. Differently from that observed by Raman spectroscopy on crystalline L-valine at low temperatures and high pressures, the band associated to the rocking of CO₂[ρ (CO₂)] practically is not affected by changing the thermodynamic parameter. Additionally, from the observation of the high frequency bands, we can conclude

that the conformation of the L-valine molecule in the unit cell does not change substantially above 300 K. Moreover from the INS results we can infer that around room temperature L-valine follows the Bose dependence with temperature. Finally, from the comparison of the Raman and INS spectra it was possible to identify that in the low temperature phase IR active modes are observed, thus implying a change in the symmetry below 120 K in crystalline L-valine. Further structural studies as a function of temperature are now under way in order to clearly identify the role of the hydrogen bonds in the structural change.

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