Self–trapped NH vibrational states in the polymorphs of glycine, L– and DL–alanine

2 AUTHORS:

Boris Kolesov
Russian Academy of Sciences
135 PUBLICATIONS **1,574** CITATIONS

SEE PROFILE

Elena Boldyreva
Institute of Solid State Chemistry and Mech…
240 PUBLICATIONS **3,006** CITATIONS

SEE PROFILE

Self-trapped N–H vibrational states in the polymorphs of glycine, L- and DL-alanine

Boris A. Kolesov[a,b]* and Elena V. Boldyreva[b,c]*

The polarized Raman spectra of the oriented single crystals of L- and DL-alanine, α-, β- and γ-polymorphs of glycine have been studied at 3–300 K. Regularly spaced band packets have been observed in the spectral range of 2500–3000 cm^{-1}, with intensity decreasing noticeably on heating. These band packets were interpreted as the manifestations of the existence of N–H self-trapped states in these systems at low temperatures. The analysis of the polarized spectra has shown that the self-trapping is observed exclusively for the NH stretching vibration of the amino groups, which is related to the NH$\cdots$O hydrogen bonds along the head-to-tail chains of zwitterions in the crystal structures. The wavenumber of this NH stretching vibration, however, was proposed to depend not solely on the length of this NH$\cdots$O hydrogen bond, but also on the lengths of all the other NH$\cdots$O hydrogen bonds formed by the NH$_3^+$ and the COO$^-$ groups in the structure linking the head-to-tail chains with each other. The arguments in favor of the hypothesis that the self-trapping in these systems can be mediated by zero-point quantum motions, and not by lattice phonons, are considered. The unusually low wavenumber (2500 cm^{-1}) observed for the NH stretching vibration and indicating at the formation of a very strong NH$\cdots$O bond is interpreted based on considering the effect of the crystalline environment on the formation and properties of the NH$\cdots$O bonds in the head-to-tail chains of amino acid zwitterions. The results are interesting for understanding the factors determining the dynamics and structural instability of crystalline amino acids and also for biophysical chemistry, as the hydrogen bonded chains formed by amino acid zwitterions in the crystals can mimic the peptide chains. Copyright © 2009 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: low temperature; amino acid crystal; hydrogen bonds; self-trapped states

Introduction

A large interest in the crystalline amino acids can be explained by their applications as molecular materials and biomimetics.[1] Many crystalline amino acids are piezoelectrics or have nonlinear optical properties (see references in Ref. [1]). In most crystal structures of amino acids, the zwitterions are linked with each other via the NH$\cdots$O hydrogen bonds in the head-to-tail chains. Already in the early publications,[2,3] it was suggested to consider these chains as mimics of the peptide chains. The chains are very robust and are preserved during solid-state transformations in the crystals of amino acids on variations of temperature and pressure, even if the three-dimensional crystal structure rearranges radically.[4]

For the applications of amino acids either as molecular materials or as biomimetics, it is important to understand the interrelation between the motions of the individual molecular fragments and the response of the hydrogen bond network. In our recent articles,[5–8] we have shown that the measurements of the polarized Raman spectra of the oriented single crystals at variable temperatures can be very helpful for studying this problem. In the crystals of serine, $^+$NH$_3$-CH-(CH$_2$OH)-COO,[5,6,9–12] and cysteine, $^+$NH$_3$-CH-(CH$_2$SH)-COO,[7,8,13,14] the motions of the side chains and the changes in the type of hydrogen bonding, in which these chains were involved, were shown to play the key role in the phase transitions on cooling[5–8] and with increasing pressure.[9–14] It was interesting to consider the dynamics of other crystalline amino acids, in particular of those, which either have no side chains at all, like glycine, $^+$NH$_3$-CH$_2$-COO$^-$, or have a small hydrophobic side chain, which is not able to form any

hydrogen bonds, like alanine, $^+$NH$_3$-CH-(CH$_3$)-COO$^-$, to see the lattice dynamics effects related solely to the hydrogen bonds between the terminal NH$_3^+$ and COO$^-$-groups of the zwitterions.

Glycine and alanine are the smallest and the simplest possible nonchiral and chiral amino acids. At ambient conditions, glycine is known to crystallize as three polymorphs.[15–17] The head-to-tail chains of zwitterions are present in all the three polymorphs (Fig. 1). No polymorphs have been described for the crystal structures of L- and DL-alanine at ambient pressure; the two structures are orthorhombic (space groups P2$_1$2$_1$2$_1$ and Pna2$_1$, respectively)[18–20] (Fig. 2). The vibrational [Fourier transform infrared (FT-IR) and Raman] spectra of the glycine polymorphs and of L-alanine have been repeatedly reported for polycrystalline and single-crystalline samples, including variable-temperature and high-pressure studies (see Refs. [1,21–31], as examples and entry

* Correspondence to: Boris A. Kolesov, Institute of Inorganic Chemistry SB RAS, pr. Lavrent'eva, 3, Novosibirsk, 630090, Russia. E-mail: kolesov@che.nsk.su

Elena V. Boldyreva, REC-008 Novosibirsk State University & Institute of Solid State Chemistry and Mechanochemistry SB RAS, ul. Kutateladze, 18, Novosibirsk, 630128, Russia. E-mail: eboldyreva@yahoo.com

a   Institute of Inorganic Chemistry, SB RAS, pr. Lavrent'eva, 3, Novosibirsk, 630090, Russia

b   REC-008 Novosibirsk State University & Institute of Solid State Chemistry and Mechanochemistry SB RAS, ul. Kutateladze, 18, Novosibirsk, 630128, Russia

c   Institute of Solid State Chemistry and Mechanochemistry, SB RAS, Novosibirsk, Russia
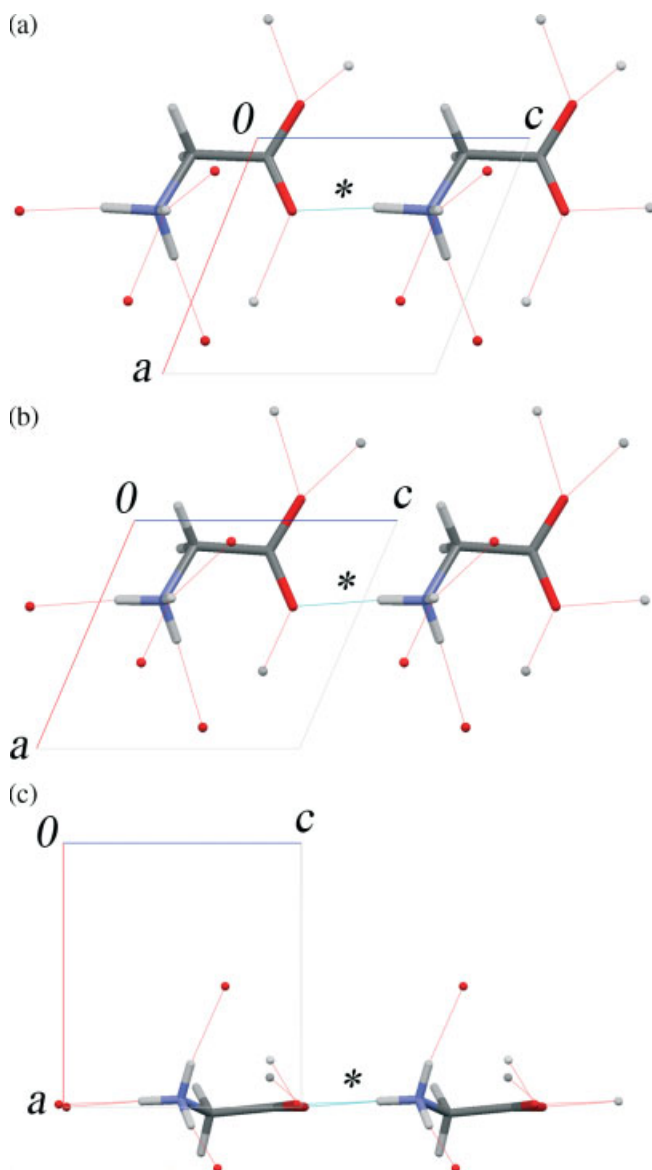
Figure 1. The fragments of the crystal structures of α- (a), β- (b) and γ-(c) glycine. The head-to-tail chains formed by zwitterions are shown, hydrogen bonds are represented by dashed lines, the shortest hydrogen bonds N*−H*···O* are marked with an asterisk.

points); the Raman spectra of DL-alanine have been reported for powder samples only in a poorly accessible journal.[32] The findings described in different articles on glycine and L-alanine do not always agree with each other. The richness of these systems leaves many questions open. We have revisited the problem and have measured the polarized Raman spectra of oriented single crystals of the three polymorphs of glycine and of L- and DL-alanine in the temperature range of 3–300 K. The aim of the present contribution is to discuss a very interesting phenomenon, that we have observed for all the five systems studied (α-, β- and γ-glycine, L- and DL-alanine), which seems to have escaped the attention of those who previously reported the low-temperature vibrational spectra: a few groups of the overlapped bands spaced at approximately 100 cm^{-1} from each other, corresponding to the polarization in one crystallographic direction only are present in the Raman

spectra in the wavenumber range of 2500–3000 cm^{-1}, with intensity increasing on cooling.

Materials and Methods

Samples

The crystals of α-, β-, γ-glycine and of L- and DL-alanine were grown as was described elsewhere.[15–20,33,34] The starting polycrystalline samples of α-glycine, L- and DL-alanine have been purchased from Aldrich and Fluka. The crystal structures of the samples were confirmed by single-crystal X-ray diffraction (STOE IPDS-II). The crystal faces were indexed using the X-SHAPE.[35]

Raman spectroscopy

The polarized single-crystal Raman spectra were collected using a triple-grating spectrometer with a charge coupled device 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 argon ion laser was used for the spectral excitation with 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 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}.

Results

Polarized Raman spectra (2400–3300 cm^{-1}) of L-alanine single crystals at 3 K are shown in Fig. 3(a). In addition to C−H stretching vibrations (2900–3000 cm^{-1}) and conventional N−H stretching modes (3000–3090 cm^{-1}), there are at least four groups of overlapped modes centered approximately at 2520, 2620, 2710 and 2820 cm^{-1} in the **cc**-spectrum. The decomposition of these band groups into Lorentz components is shown in Fig. 3(b) and the band positions are listed in Table S1 (supporting information). The changes of the **cc**-spectra of L-alanine *versus* temperature are plotted in Fig. 4. As each group consists of a few overlapped bands and its deconvolution into Lorenz components cannot be quite unambiguous, especially at high temperatures, we have calculated the integral intensity of each band group as a whole. The integral intensity of each packet of bands *versus* temperature is shown in Fig. 5. In each case, the intensity was normalized to integral intensity of the CH stretching modes. The latter was considered as independent on temperature. The spectra of DL-alanine and their temperature dependence are very similar to those of L-alanine [Fig. S1 (supporting information)].

The measured spectra agree very well with the Raman and IR-spectra published previously,[21–31] at least in those spectral ranges, for which the data have been reported. In particular, the series of bands in the spectral range of 2500–3000 cm^{-1} is present in the IR-spectra (Raman spectra either of glycine polymorphs, or of L- or DL-alanine in the spectral range of 2500–3000 cm^{-1} have never been reported) of L-alanine published in Refs. [27,30],
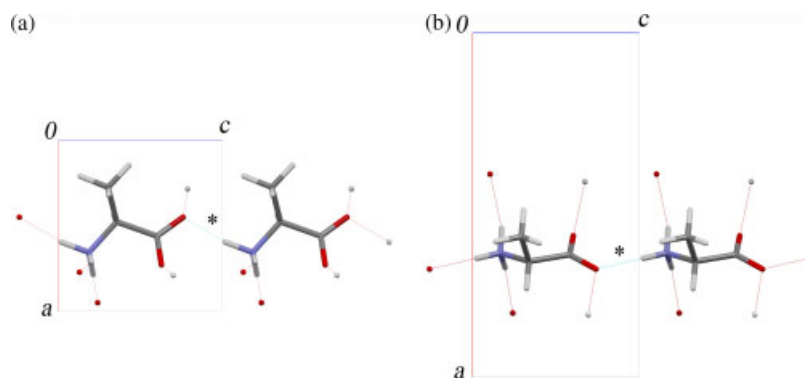
Figure 2. The fragments of the crystal structures of L- (a) and DL- (b) alanine. The head-to-tail chains formed by zwitterions are shown, hydrogen bonds are represented by dashed lines, the shortest hydrogen bonds N*–H*···O* are marked with an asterisk.
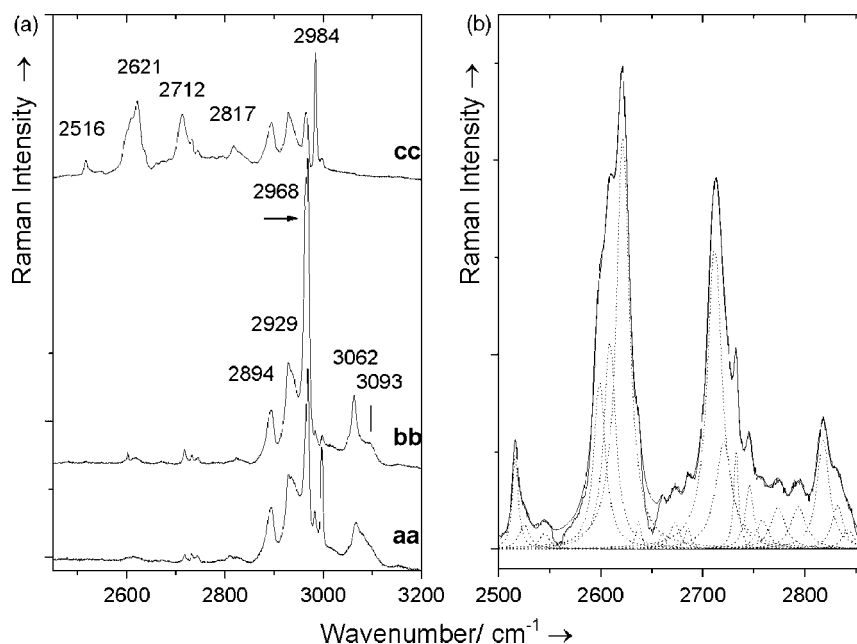

Figure 3. Polarized Raman spectra of the L-alanine oriented single crystal at 3 K in the range of N–H stretching vibrations (a) and deconvolution of the **cc**-spectrum into Lorentz components (b). The definitions **aa**, **bb** and **cc** imply the directions of polarization vector of incident (first symbol) and scattered (last symbol) light with respect to crystal axes.

Table 1.	Hydrogen bond geometry (in Å and °) in L-alanine at 60 K[53]				
	D–H	H···A	D–H–A	D···A	
N1–H6	1.040(3)	1.808(4)	162.5(3)	2.818(1)	O2[x + 1/2, −y + 1/2, −z − 1]
N1–H4	1.059(3)	1.751(3)	169.0(2)	2.799(1)	O2[x, y, z − 1]
N1–H1	1.045(3)	1.828(4)	161.3(3)	2.838(2)	O1[−x − 1/2, −y, z − 1/2]

The author's notations for atom numbering and symmetry operations are preserved. H4 atom is the one involved in the N*–H*···O* hydrogen bond. Similar values have been reported by other authors.[19,31]

but was not interpreted and no assignment was suggested (Table 1 in Ref. [27]). The strong temperature dependence of the intensities of these bands can also be noticed from the published spectra (Fig. 1 in Ref. [27]), but it was not discussed by the authors of Ref. [27]. In the IR-spectra of the polymorphs of glycine, a broad envelope of NH_{str} vibrations and CH_{str} vibrations in the range of 2500–3000 cm^{-1} was observed, which looks as if it were formed by multiple sharp equidistant overlapping temperature-dependent peaks, the origin of which was not discussed.[22] The main feature of the observed nonassigned vibration bands in the 2500–3000 cm^{-1} spectral range is a strong temperature dependence of their intensity, which makes them noticeably different from all the other bands in the spectrum. The regular spacing between the band packets in the vibrational spectra of all the studied crystals (∼100 cm^{-1}) is equal to the wavenumber of an optical phonon in the lattice. One can term the band packets as 'zero-phonon' (2510–2550 cm^{-1}), 'one-phonon' (2580–2650 cm^{-1}), 'two-phonon' (2680–2750 cm^{-1}) and 'three-phonon' (2800–2850 cm^{-1}) bands.

Intensity of the zero-phonon band (i.e. the band in the range of 2510–2550 cm^{-1}) can be fitted quite well by the exponential function const + exp($-\alpha - \beta_{DW}T^2$) (Fig. 5(a)) with fitted parameters $\alpha = 0.6$ and $\beta_{DW} = 3 \times 10^{-5}$. The one-phonon
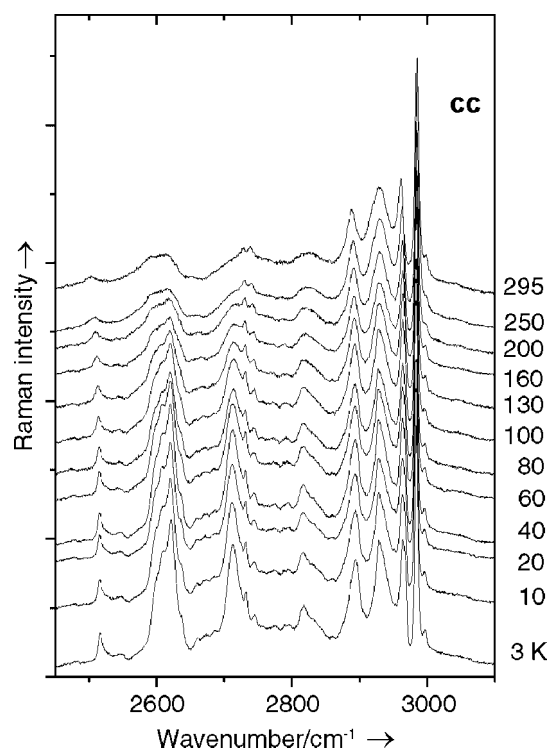
Figure 4. The **cc**-Raman spectra of L-alanine at different temperatures.

band is accompanied by emitting a single phonon with the wavenumber $\omega_0 \approx 100 \, cm^{-1}$. To take into account the thermal optical phonon population, one can try to fit the temperature dependence of its integral intensity by the product of the zero-phonon fitting function and a typical factor for intensity of Stokes Raman scattering, $(n + 1)$, where

$$n = \frac{1}{e^{\hbar\omega_0/k_B T} - 1} \tag{1}$$

Temperature dependence of the integral intensity of one-, two- and three-phonon bands are shown in Fig. 5(b)–(d). The three dependencies are almost identical. Each set of the experimental data, that is the intensity of one-, two- and three-phonon bands, is fitted well by const $+ \exp(-\alpha - \beta_{DW}T^2) \times (n + 1)$ with slightly different parameters α and β. This result implies that the two- and three-phonon bands are accompanied by emitting two and three phonons, respectively, with equal or almost equal wavenumbers. Most likely, the phonons with $k \neq 0$ are emitted.

The polarized spectra of α-, β-, γ-glycine are shown in Figs S2–S4 (supporting information), respectively. As in the case of alanine, a few groups of the overlapping bands spaced at approximately 100 cm^{-1} from each other, corresponding to the polarization in one crystallographic direction only could be observed. The spectra of α-, β- and γ-glycine at different temperatures [Figs S2–S4 (supporting information)], and the changes in the integral intensity of the band packets *versus* temperature [Fig. S5 (supporting information)] are also similar to those of L and DL-alanine.

Discussion

The observed phenomenon resembles very much the one, which has been previously studied in several systems[36–43] – namely, the

formation of 'self-trapped states.' The temperature dependence of the intensity (Figs 5(a)–(d), S2(b)–S4(b) and S5 (Supporting Information)) suggests that all the four observed groups of bands are related to self-trapped (ground and excited) states of the N–H···O vibration (Fig. 1 in Ref. [40]).

The energy of the internal D–H stretching vibration (D – donor) of a D–H bond linked to an acceptor A, D–H···A (hereafter: free exciton) depends directly on the D···A distance. By this reason, there is a strong anharmonic coupling between the internal D–H and the external D···A (i.e. lattice phonons) vibrations. As a result of this coupling, some lattice phonons can be excited during the D–H stretching vibration. To prevent the decay of the exciton, the wave packet arising from the excited lattice phonons should meet at least two requirements: (1) the wave packet and the exciton should be located at the same place and (2) the wave packet should distort the lattice in such a way that the D···A distance becomes shorter, than that of a free exciton, i.e. the lattice should contract around the exciton.

Davydov and Kislukha[44] and Davydov[45] proposed that the coupled exciton–phonon(s) state can arise in the chain of molecules linked by hydrogen bonds, and that this state should be characterized by a shorter intermolecular distance and a lower vibrational energy, as compared with the energy of a free exciton. This state can move along the chain slowly without a loss of energy forming a so-called Davydov's soliton or self-trapped (self-localized) state. The theory of Davydov was later extensively examined by Scott.[39] Alexander[36] and Alexander and Krumhansl[37] suggested to consider a self-trapped state as a small or large vibrational polaron.

Careri *et al.*[46,47] were the first to relate the appearance of an additional C=O internal mode (amide I band) in the spectra of a small-molecule organic crystal, acetanilide (ACN), to the formation of a self-trapped state. Since that time, ACN seems to remain as the main model system for the theoretical and experimental studies of the self-trapped states, which are based to a large extent on the analysis of the FT-IR spectra, especially of the amide I band, of this compound (see for reviews Refs. [39,43]). Already in Davydov's articles, the formation of the self-trapped states was discussed in relation to the transport of vibrational energy along a protein chain,[45,48,49] and the biological objects remain central when the problem of the self-trapped states is discussed.[42,50] To the best of our knowledge, the self-trapped states have never been discussed in relation to the crystals of amino acids.

A theoretical consideration of a self-trapped state usually starts with the introduction of the chain of hydrogen bonds, like the C=O···H–N chain in ACN. However, in most real systems there are several different types of N–H···O bonds, and, respectively, several different chains of hydrogen bonds in the lattice. In a recent article on the formation of self-trapped states or phonons caused by the interaction of excitons with lattice vibrations in α-helices, the α-helix consisting of a helical sequence of amino acids was treated as if the three quasi-one-dimensional chains of hydrogen bonds were independent.[42] However, the different H-bond chains can interact, and this can influence on the formation of the self-trapped states. It remains unclear, if each of the several types of the N–H bonds can form a soliton state. Crystalline amino acids can serve as a good model system, when studying the systems with several types of intermolecular hydrogen bonds, and, as a result, several chains of hydrogen bonds (see Figs 1 and 2 as examples). This can be illustrated using the data obtained in this study.

The difference Δ in the energy between a free and a self-trapped exciton is the binding energy of the latter. Alexander
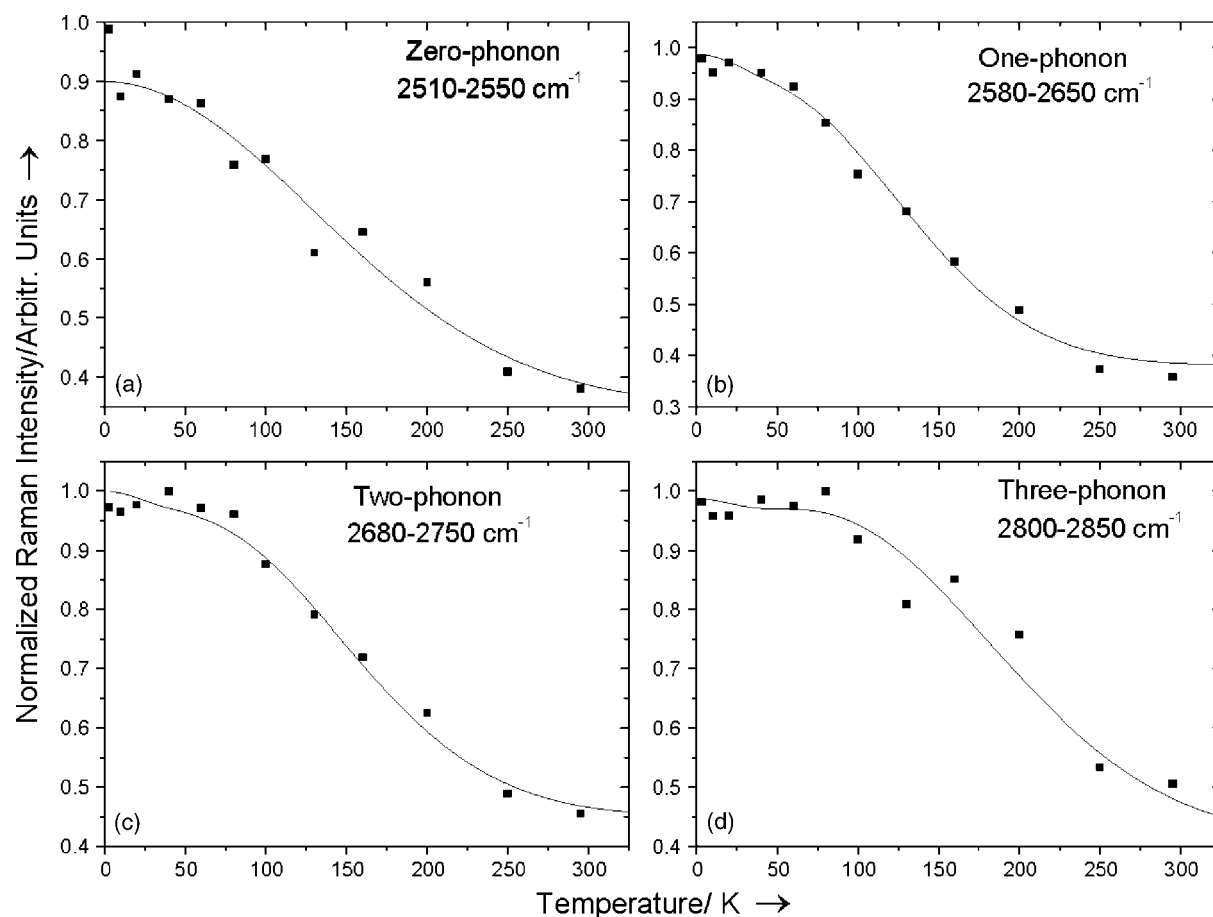
Figure 5. Normalized to unity integral intensity of zero, one, two and three-phonon bands (see text) *versus* temperature. The experimental data for each band are fitted by const $+ \exp(-\alpha - \beta_{DW}T^2) \times (n+1)$, where $\alpha = 0.6$, $\beta = 3 \times 10^{-5}$ for zero-phonon band (a), $\alpha = 0.5$, $\beta = 6.5 \times 10^{-5}$ for one-phonon band (b), $\alpha = 0.6$, $\beta = 5 \times 10^{-5}$ for two-phonon band (c) and $\alpha = 0.55$, $\beta = 3.5 \times 10^{-5}$ for three-phonon band (d); $n = 0$ for zero-phonon band and $n = 1/[\exp(144/T)-1]$ for one-, two- and three-phonon bands.

and Krumhansl[37] showed that the binding energy of the self-trapped C=O vibration in ACN, i.e. 23 cm^{-1},[39] agrees well with the value predicted by a theoretical calculation, if the interaction of a free exciton with acoustic and optic phonons is considered. However, the binding energy of the N–H self-trapped state in ACN is much larger, about 500 cm^{-1}.[51] Taking into account the known exciton–phonon coupling parameter for N–H···O hydrogen bonding,[52] the observed value Δ for N–H self-trapped state in ACN can hardly be explained by the same theoretical considerations as were mentioned above in relation to the C=O vibration.

Along with the self-trapped states, Raman spectra of alanine (Fig. 3(a)) should contain a band of the free N–H exciton corresponding to the self-trapped states. The bands at 3062 and 3093 cm^{-1} are assigned unambiguously to N–H vibrations, but they are observed in the **aa** and **bb**-spectra and cannot be related to those vibrations, which can form the self-trapped states directed along the **c**-axis. There is no appropriate vibrational band in the Raman **cc**-spectrum, which could be assigned to the vibration of a free exciton. However, the required information can be found in IR-spectra of L-alanine. Rozenberg *et al*.[27] have published the IR-spectra of pure N–H and isotopically substituted (10 and 90% doped ND/NH) polycrystalline L-alanine recorded at different temperatures (10–300 K). In addition to the two bands observed in the Raman spectra (Fig. 3(a)), the IR-spectra contain a third band at ∼3035 cm^{-1}, which should be assigned to an

N–H stretching mode (Fig. 1 in Ref. [27]). Therefore, the mode at ∼3035 cm^{-1} is the vibration of a free N–H exciton, which couples with lattice distortions and forms the self-trapped states. Raman intensity of the free exciton is too small to be detected in the Raman spectra. Thus, the binding energy of the ground self-trapped state is

$$\Delta = 3035 \text{ (free exciton)} - 2520 \text{ (zero-phonon)} = 515 \text{ cm}^{-1} \quad (2)$$

Molecules of amino acids exist in the crystals as zwitterions linked in the head-to-tail chains, that is the proton of the carboxy-group – COOH of one molecule goes to the amino-group –NH$_2$ of the neighboring molecule, owing to a larger proton affinity of the latter. The process, however, is complete only in the crystalline state, because the additional hydrogen bonds directed from the surrounding molecules in the crystal to the oxygen atom of the carboxy-group damp the proton affinity of the latter, and the additional hydrogen bonds of the NH$_3$ group (i.e. the bonds of primary NH$_2$ group) strengthen the proton affinity of the nitrogen atom. The COO$^-$···H–N$^+$ hydrogen bond linking the zwitterions within a head-to-tail chain (hereafter – the N*–H*···O*) is the shortest and the strongest one, as compared with other N–H···O bonds in the crystal. See as examples of the geometric parameters the values reported for L-alanine (Table 1),[53] in which the N*–H* stretching wavenumber is ∼3035 cm^{-1}, instead of 3062 and 3093 cm^{-1} for the other two N–H···O hydrogen bonds.

The analysis of the polarized spectra shows, that, similar to the case of ʟ-alanine, in all the crystal structures, considered in this study, the only hydrogen bond N–H⋅⋅⋅O, which causes the formation of the self-trapped states, is the shortest N*–H*⋅⋅⋅O* bond linking zwitterions within a head-to-tail chain.

Calculating the binding energy Δ from the theoretical models and comparing it with the experimental value can shed light on the nature of the self-trapped states in the crystalline amino acids considered in this study. When optical phonons mediate self-trapping in ACN, where molecules are in the nonionized (not zwitterionic) state, the binding energy is:[37,39,45]

$$\Delta_{op} = -\frac{\chi^2}{2K} = -\frac{2\chi^2}{M\omega_{op}^2} \qquad (3)$$

Where $\chi = dE/dR$ is the exciton–phonon coupling parameter (characterizing the N–H stretching wavenumber with the N⋅⋅⋅O distance), R – donor-acceptor distance, K – force constant of the hydrogen bond, M – molecular mass and ω_{op} – the characteristic optical phonon wavenumber (for the one-dimensional chain of identical molecules ($\omega_{op} = 2\sqrt{K/M}$).

The coupling with acoustic phonons in ACN gives:[37]

$$\Delta_{ac} = -\frac{\chi^2 q_D}{8\pi^2 M N_0 \omega_{ac}^2 l^2} f(q_D) \qquad (4)$$

Where N_0 is the number of primitive cells per unit volume, $q_D \equiv (6\pi^2 N_0)^{1/3}$ is the Debye momentum, $l \equiv (a + b + c)/3$ is the mean value of the unit cell parameters, ω_{ac} is the characteristic wavenumber of acoustic phonons, and parameter $f(q_D) \approx 0.23$ for alanine (see expression D13 in Ref. [37]). Acoustic phonons, which modulate effectively the intermolecular distance a in the chain, are the zone-boundary ($k = \pi/a$) phonons. For the one-dimensional chain consisting of identical molecules, optical and zone-boundary acoustic phonons are close to each other in wavenumber. For this reason, we have chosen the value of $100\,cm^{-1}$ as an estimate for the wavenumber of acoustic phonons in alanine. The values of $50–70\,cm^{-1}$ found in Refs. [37–40] for the wavenumber of phonons mediating the self-trapping in ACN are also close to optical or zone-boundary acoustic phonons, and are lower, than the estimate for alanine, because the mass of an ACN molecule is larger, and the force constant seems to be smaller than those of alanine.

The dynamical properties of the N*–H*⋅⋅⋅O* hydrogen bond in crystalline amino acids may be different from those of the C=O⋅⋅⋅H–N bond in ACN. For this reason, the accepted theory of the self-trapped states suggested by Davydov,[45] Scott[39] and Alexander and Krumhansl[37] may be not necessarily valid for the self-trapped states related to this bond. In this case, one can estimate the binding energy as follows: as the distortion of the crystal lattice on self-trapping should be the same order of magnitude, as the amplitude of the lattice vibration, the binding energy Δ_{dist} is:

$$\Delta_{dist} = \frac{dE}{dR}\overline{\Delta x_i} = \chi \overline{\Delta x_i} \qquad (5)$$

Where $\overline{\Delta x_i}$ is a mean square of the amplitude of the lattice vibration of quantum number i:

$$\overline{\Delta x_i} = \frac{\Delta x_i}{\sqrt{2}} = \sqrt{\frac{2\hbar(i + 1/2)}{\sqrt{KM}}} \qquad (6)$$

(the latter follows immediately from an equality of a full $(1/2)K\Delta x_i^2$ and a quantum-mechanical $\hbar\omega_{op}(i + 1/2)$ energy of a harmonic oscillator). Force constant K for a typical N–H⋅⋅⋅O hydrogen bond is 13.1 N/m (this value is derived also from the wavenumber of the optical phonon $\omega_{op} = 100\,cm^{-1}$ in alanine and the molecular mass of alanine is 89 a.u.m. $= 1.477 \times 10^{-25}$ kg). According to Nakamoto et al.,[52] χ is around 2.78×10^{-10} N ($1400\,cm^{-1}\,Å^{-1}$). The problem, however, is that this value is defined for the N–H⋅⋅⋅O wavenumber range of $3090–3450\,cm^{-1}$.[52] The observed wavenumber of the self-trapped states is about $2500\,cm^{-1}$ and is far away from the region characterized by Nakamoto et al.,[52] corresponding to very strong hydrogen bonding. Recently Gilli et al.[54] have extended noticeably the range of the ν_{N-H} frequencies and the N⋅⋅⋅O distances in the N–H⋅⋅⋅O hydrogen bonds. They have shown that $\chi = 330\,cm^{-1}\,Å^{-1}$ for the high-wavenumber range (i.e. $\nu_{N-H} = 3200–3400\,cm^{-1}$, $d_{N\cdots O} = 2.6–3.2$ Å) and $\chi = 6800\,cm^{-1}\,Å^{-1}$ for the low-wavenumber range (i.e. $\nu_{N-H} = 2350–3100\,cm^{-1}$, $d_{N\cdots O} = 2.48–2.58$ Å). We used these χ values to calculate the binding energy Δ using the three different approaches described above (Table 2).

One can see, that the amplitude of the zero-point quantum motion ($i = 0$) and the exciton–phonon coupling parameter $\chi = 6800\,cm^{-1}\,Å^{-1}$ give an estimate of the binding energy, which is in a good agreement with the experimental data. It is interesting to note, that using the approach based on considering the zero-point quantum motion, one can estimate the binding energy for amide I vibration in ACN as $22\,cm^{-1}$ (the experimentally observed value is $23\,cm^{-1}$), supposing $\chi_{C=O} = 5 \times 10^{-11}$ N, the mean value of $3.5–6.2 \times 10^{-11}$ N.[39]

The assumption, that zero-point quantum motions mediate the self-trapping, suggests a very clear and transparent explanation of the observed temperature dependence of the Raman intensity of the self-trapped states: the intensity decreases as the thermal population of lattice vibrations increases and thus the zero-point quantum motions disappear. The process is controlled by the Debye-Waller factor e^{-2W}, and at low temperatures (at $T < \theta_D$, θ_D is Debye temperature) the temperature dependence of $2W$ can be approximated[55] by $(-\alpha - \beta_{DW}T^2)$ (Fig. 5). In addition, there is no 'temperature delay' in the temperature dependence of zero-phonon band intensity, i.e. the decrease in its intensity on heating is observed immediately from the lowest temperature, $4–20$ K, whereas the intensities of the one-, two- and three-phonon bands start decreasing on heating only after $50–100$ K (Fig. 5). It implies, that the lattice phonons of wavenumber $\omega > 10\,cm^{-1}$ do not contribute to this band. Low-wavenumber acoustic phonons ($k \approx 0$) do not change an intermolecular distance and, therefore, do not couple with the free N–H vibration. Debye-Waller approximation used here for fitting the experimental data is valid only for low temperatures; in addition, the accuracy of the Raman intensity measurements is not sufficiently high. Both these factors and complicated spectral structure of the observed one-, two- and three-phonon bands make it difficult to obtain a more detailed information on the population of the phonon states.

The size of a soliton σ_0 is:[45,39]

$$\sigma_0 = 7aKJ/\chi^2 \qquad (7)$$

where J is the dipole–dipole interaction energy between adjacent vibrational dipoles. Substituting $K = 13.1$ N/m, $\chi = 1.35 \times 10^{-9}$ N ($6800\,cm^{-1}\,Å^{-1}$), and $J = 1.55 \times 10^{-22}$ J ($\sim 8\,cm^{-1}$),[39] we would get:

$$\sigma_0 = 8 \times 10^{-3}a \qquad (8)$$

That is much less than the characteristic length of a lattice phonon or a phonon wave packet. Of course, the obtained result is not

Table 2. Binding energy Δ (cm^{-1}) for N–H self-trapped states in alanine calculated with different values of the exciton–phonon coupling parameter χ and different approaches (1–3)

Approach	$\chi = 6.55 \times 10^{-11}$ N (330 cm^{-1} Å^{-1})	$\chi = 2.78 \times 10^{-10}$ N (1400 cm^{-1} Å^{-1})	$\chi = 1.35 \times 10^{-9}$ N (6800 cm^{-1} Å^{-1})
(3) – Δ_{op}, optical phonons	8.3	149	3500
(4) – Δ_{ac}, acoustic phonons	0.4	7	171
(5) – Δ_{dist}, ($i = 0$)	29	122	592
(5) – Δ_{dist}, ($i = 1$)	50	211	1027

The experimental value of Δ is 515 cm^{-1}.

realistic and the theoretical considerations used,[39,45] seem to be not applicable to the case of the self-trapped states in the crystalline alanine or glycine.

As was already mentioned above, the strength of the N*–H*···O* hydrogen bond depends substantially on the additional hydrogen bonds from the surrounding molecules to N* and O* atoms. The latter are directed almost normal to the N*–H*···O* bond. In the other words, the strength of the N*–H*···O* hydrogen bond depends on the intermolecular distances both along the N*–H*···O* chain and normal to it. Phonons propagating in mutually orthogonal directions are not able to form a phonon wave packet. For this reason, the role of the zero-point quantum motions rises considerably.

Finally, zero-point quantum motions are not periodic (harmonic) oscillations; for this reason, no restrictions on the lifetime of a self-trapped state related to a frequency and a phase of phonon vibrations are imposed.

A specific feature of the N*–H*···O* bond is that the displacement of the surrounding molecules affects the proton affinity of the O* and N* ions and thus the position of the H* atom in the bond. In the extreme case, when all the hydrogen bonds from surrounding molecules disappear, the H* proton should move from N* back to the O* atom. One can imagine, that in the crystal the H* atom can change its position between the N* and O* atoms in the N*–H*···O* bond due to the external vibrations of the surrounding molecules and the hydrogen bond can become very strong, when the N–H and the H–O distances approach each other, thus favoring the formation of the self-trapped states with a large binding energy. Of course, this phenomenon is dynamic and becomes possible only through a strong coupling of N*···O* and N···O distance changes. It cannot lead to a static hardening of a zwitterionic hydrogen bond, but can result in the N*–H*···O* bond becoming strong at some conditions (as evidenced by the low, 2520 cm^{-1}, wavenumber of the zero-phonon band), although the average N–O distance in the N*–H*···O* bond given by diffraction data (about 2.8 Å) is longer, than the limits (2.55 Å) considered for very strong H–bonds in Ref. [54]. Such an interpretation is at the present moment speculative and requires some more support by computations, which are now in progress. The model suggested, although speculative at this stage, helps to interpret the fine structure of the one-, two- and three-phonon bands. These bands consist of the two to three sub-bands of high intensity and a few sub-bands of weak intensity (Fig. 3(b)). One can suppose, that the intensive sub-bands arise due to the coupling of the self-trapped (zero-phonon) state with the longitudinal optical and acoustic ($k = \pi/a$) phonons of the crystal chain involving N*–H*···O* bond, whereas the sub-bands of weak intensity can be assigned to the coupling of the zero-phonon self-trapped state to the external vibrations of the surrounding molecules, which

modify the strength of the additional N–H···O* and N*–H···O hydrogen bonds.

Thus, we propose, that the self-trapping in alanine and glycine crystals occurs most likely due to the interaction of the N*–H* exciton with zero-point quantum motions of the neighboring atoms. It results in the local distortion of the lattice (i.e. mainly in the distortion of the additional hydrogen bonds) and creates a potential well with the energy minimum corresponding to stronger N*–H*···O* hydrogen bonding and lower N*–H* vibrational wavenumber as compared with those of a free exciton. The N*–H* exciton 'digs' a potential well around itself, just as an electron does, when this electron polarizes the crystal lattice and forms a polaron state. From this point of view, N–H self-trapped states in alanine and glycine are rather vibrational polarons (in terms of Alexander[36,37]), than solitons (in terms of Davydov[44,45] and Scott[39]).

Conclusion

In contrast to the crystal of ACN formed by noncharged molecules, the crystals of alanine and glycine are built from zwitterions. This may account for the formation of very strong N*–H*···O* hydrogen bonds and the well-localized N–H self-trapped states with a large binding energy. In general, self-trapping in ACN is considered as nonlinear interaction of a vibrational exciton with longitudinal phonons propagating along a chain of hydrogen-bonded molecules. The novel mechanism proposed in this article assumes, that all the molecules surrounding the N*–H*···O* hydrogen bond within a head-to-tail chain of zwitterions can participate efficiently in the self-trapping. Zero-point quantum motions were supposed to be involved in the self-trapping, and this model, in our opinion, is advantageous, as compared with that based on considering the phonon medium, at least in relation to the systems considered in this study.

Supporting information

Supporting information may be found in the online version of this article.

References

[1] E. V. Boldyreva, Crystalline amino acids – a link between chemistry, materials sciences and biology, in *Models, Mysteries, and Magic of Molecules* (Ed.: J.C.A. Boeyens, J.F. Ogilvie), Springer Verlag: **2007**, pp 169.

[2] S. N. Vinogradov, *Int. J. Pept. Protein Res.* **1979**, *14*, 281.

[3] C. G. Suresh, M. Vijayan, *Int. J. Pept. Protein Res.* **1983**, *22*, 129.

[4] E. V. Boldyreva, *Phase Transitions* **2009**, *82*, 303.

[5] H. N. Bordallo, B. A. Kolesov, E. V. Boldyreva, F. J. Juranyi, *J. Am. Chem. Soc.* **2007**, *129*, 10984.

[6] B. A. Kolesov, E. V. Boldyreva, *J. Phys. Chem. B* **2007**, *111*, 14387.

[7] B. A. Kolesov, V. S. Minkov, E. V. Boldyreva, T. N. Drebushchak, *J. Phys. Chem. B* **2008**, *112*, 12827.

[8] V. S. Minkov, N. A. Tumanov, B. A. Kolesov, E. V. Boldyreva, S. N. Bizyaev, *J. Phys. Chem. B.* **2009**, *113*, 5262.

[9] E. N. Kolesnik, S. V. Goryainov, E. V. Boldyreva, *Doklady Chem.* **2005**, *404*, 61 (Rus.), or 169 (Engl).

[10] S. A. Moggach, D. R. Allan, C. A. Morrison, S. Parsons, L. Sawyer, *Acta Crystallogr.* **2005**, *B61*, 58.

[11] E. V. Boldyreva, H. Sowa, Yu. V. Seryotkin, T. N. Drebushchak, H. Ahsbahs, V. V. Chernyshev, V. P. Dmitriev, *Chem. Phys. Lett.* **2006**, *429*, 474.

[12] T. N. Drebushchak, H. Sowa, Yu. V. Seryotkin, E. V. Boldyreva, H. Ahsbahs, *Acta Crystallogr.* **2006**, *E62*, 4052.

[13] S. A. Moggach, D. R. Allan, S. J. Clark, M. J. Gutmann, S. Parsons, C. R. Pulham, L. Sawyer, *Acta Crystallogr.* **2006**, *B62*, 296.

[14] V. S. Minkov, A. S. Krylov, E. V. Boldyreva, S. V. Goryainov, S. N. Bizyaev, A. N. Vtyurin, *J. Phys. Chem. B.* **2008**, *112*, 8851.

[15] R. E. Marsh, *Acta Crystallogr.* **1958**, *11*, 654.

[16] Y. Iitaka, *Acta Crystallogr.* **1960**, *13*, 35.

[17] Y. Iitaka, *Acta Crystallogr.* **1960**, *14*, 1.

[18] H. J. Simpson Jr, R. E. Marsh, *Acta Crystallogr.* **1966**, *20*, 550.

[19] R. Destro, R. E. Marsh, R. Bianchi, *J. Phys. Chem.* **1988**, *92*, 966.

[20] M. S. Nandhini, R. V. Krishnakumar, S. Natarajan, *Acta Crystallogr. C* **2001**, *57*, 614.

[21] C. Murli, S. Thomas, S. Venkateswaran, S. Sharma, *Phys. B Condens. Matter* **2005**, *364*, 233.

[22] G. B. Chernoby, Yu. A. Chesalov, E. B. Burgina, T. N. Drebushchak, E. V. Boldyreva, *J. Struct. Chem.* **2007**, *48*, 339 and references therein.

[23] H. N. Bordallo, M. Barthes, J. Eckert, *Phys. B Condens. Matter* **1997**, *241–243*, 1138.

[24] S. Forss, *J. Raman Spectr.* **1982**, *12*, 266.

[25] A. F. Vik, Yu. I. Yuzyuk, M. Barthes, J.-L. Sauvajol, *J. Raman Spectr.* **2005**, *36*, 749.

[26] C. H. Wang, R. D. Storms, *J. Chem. Phys.* **1971**, *55*, 5110.

[27] M. Rozenberg, G. Shoham, I. Reva, R. Fausto, *Spectrochim. Acta A: Mol. Biomol. Spectrsc.* **2003**, *59*, 3253.

[28] A. Migliori, P. M. Maxton, A. M. Clogston, E. Zirngiebl, M. Lowe, *Phys. Rev. B* **1988**, *38*, 13464.

[29] J. M. De Souza, P. T. C. Freire, H. N. Bordallo, D. N. Argyriou, *J. Phys. Chem. B* **2007**, *111*, 5034.

[30] M. Barthes, A. Fahre Vik, A. Spire, H. N. Bordallo, J. Eckert, *J. Phys. Chem. A* **2002**, *106*, 5230.

[31] M. Barthes, H. N. Bordallo, F. De'noyer, J.-E. Lorenzo, J. Zaccaro, A. Robert, F. Zontone, *Eur. Phys. J. B* **2004**, *37*, 375.

[32] Y. Gong, W.-Q. Wang, *Guang Pu Xue Yu Guang Pu Fen Xi/Spectrosc. Spectral Anal.* **2006**, *26*, 90.

[33] E. V. Boldyreva, V. A. Drebushchak, T. N. Drebushchak, E. S. Shutova *J. Cryst. Growth* **2002**, *241*, 266.

[34] E. V. Boldyreva, T. N. Drebushchak, E. S. Shutova, *Z. Kristallogr.* **2003**, *218*, 366.

[35] *X-SHAPE*. STOE & Cie GmbH: Darmstadt, Germany, **2003**.

[36] D. M. Alexander, *Phys. Rev. Lett.* **1985**, *54*, 138.

[37] D. M. Alexander, J. A. Krumhansl, *Phys. Rev. B* **1986**, *33*, 7172.

[38] A. C. Scott, I. J. Bigio, C. T. Johnston, *Phys. Rev. B* **1989**, *39*, 12883.

[39] A. Scott, *Phys. Rep.* **1992**, *217*, 1.

[40] J. Edler, P. Hamm, A. C. Scott, *Phys. Rev. Lett.* **2002**, *88*, 067403–1.

[41] J. Edler, P. Hamm, *Phys. Rev. B* **2004**, *69*, 214301–1.

[42] J. Edler, R. Pfister, V. Pouthier, C. Falvo, P. Hamm, *Phys. Rev. Lett.* **2004**, *93*, 106405–1.

[43] P. Hamm, G. P. Tsironis, *Eur. Phys. J. Special Topics* **2007**, *147*, 303.

[44] A. S. Davydov, N. I. Kislukha, *JETP (Russian J. Exper. Theor. Phys.)* **1976**, *71*, 1090.

[45] A. S. Davydov, *Phys. Scr.* **1979**, *20*, 387.

[46] G. Careri, U. Buontempo, F. Carta, E. Gratton, A. C. Scott, *Phys. Rev. Lett.* **1983**, *51*, 304.

[47] G. Careri, U. Buontempo, F. Galluzzi, A. C. Scott, E. Gratton, E. Shyamsunder, *Phys. Rev. B* **1984**, *30*, 4689.

[48] A. S. Davydov, *J. Theor. Biol.* **1977**, *66*, 379.

[49] A. S. Davydov, *Solitons in Molecular Systems*. Reidel: Dordrecht, **1985**.

[50] A. Xie, L. Van Der Meer, W. Hoff, R. H. Austin, *Phys. Rev. Lett.* **2000**, *84*, 5435.

[51] G. B. Blanchet, C. R. Fincher Jr, *Phys. Rev. Lett.* **1985**, *54*, 1310.

[52] K. Nakamoto, M. Margoshes, R. E. Rundle, *J. Am. Chem. Soc.* **1955**, *77*, 6480.

[53] Ch. C. Wilson, D. Myles, M. Ghosh, L. N. Johnson, W. Wang, *New J. Chem.* **2005**, *29*, 1318.

[54] P. Gilli, V. Bertolasi, V. Ferretti, G. Gilli, *J. Am. Chem. Soc.* **2000**, *122*, 10405.

[55] C. Kittel, *Quantum Theory of Solids*. John Wiley & Sons: New York, **1963**.

Copyright © 2009 John Wiley & Sons, Ltd.
www.interscience.wiley.com/journal/jrs