Eur. Phys. J. B **37**, 375–382 (2004)
DOI: 10.1140/epjb/e2004-00069-1

THE EUROPEAN
PHYSICAL JOURNAL B

Micro-transitions or breathers in L-alanine?

M. Barthes[1,a], H.N. Bordallo[2], F. Dénoyer[3], J.-E. Lorenzo[4], J. Zaccaro[4], A. Robert[5], and F. Zontone[5]

[1] Groupe de Dynamique des Phases Condensées, Université Montpellier 2, 34095 Montpellier Cedex 05, France
[2] Hahn-Meitner Institut, Glienicker Str. 100, 14109 Berlin, Germany
[3] Laboratoire de Physique des Solides, UMR 8502, bâtiment 510, Université Paris-XI, 91405 Orsay Cedex, France
[4] CNRS, Laboratoire de Cristallographie, B.P. 166, 38042 Grenoble Cedex 09, France
[5] ESRF, B.P. 220, 38043 Grenoble Cedex, France

Received 29 July 2003 / Received in final form 19 December 2003

Abstract. The lattice dynamics of crystalline L-alanine shows unusual features tentatively assigned to a localization of vibrational energy. However, other properties alternatively suggest the existence of a second order phase transition undetected in previous crystallographic work. In this paper, we present the results of a high resolution X-ray diffraction study down to 10 K, together with new structure determinations at intermediate temperatures. The data rule out the hypothesis of a conventional structural phase transition. No change in the space group symmetry is observed and an anomalous decrease of the lattice parameter c in discrete steps is discovered when heating the crystal from 10 K to room temperature. It could be ascribed to a progressive conformational change of the NH_3^+ group of the zwitterionic molecule. An analysis of the physical properties of crystalline L-alanine suggests the existence of a strong dynamic Jahn-Teller-like effect owing to the NH_3^+ charge-lattice coupling. This would explain both the splitting of some vibrational states and properties related to a microscopic lattice instability like the onset of depolarization in the transmitted light below ∼250 K.

PACS. 61.10.Nz X-ray diffraction – 05.45.Yv Solitons – 64.70.Kb Solid-solid transitions

1 Introduction

L-alanine is the smallest chiral naturally occurring amino acid. Its crystal structure was determined by both X-ray (300 K and 23 K) and neutron (300 K) diffraction [1–3]. The system crystallizes in the $P2_12_12_1$, (or D_2^4) space group, with four ($^+H_3N\text{-}C_2H_4\text{-}COO^-$) zwitterionic molecules per unit cell, linked by three networks of hydrogen bonds of unequal strength. Earlier observations of the non-linear behavior of two Raman modes at 42 and 49 cm^{-1}, assigned to a dynamic localization of vibrational energy [4], have attracted an additional interest to this widely investigated compound, a building block for proteins and a model system for a large range of important processes in biochemistry.

The vibrational dynamics [5] has been studied by infrared spectroscopy [6], Raman scattering [7], CARS [8], coherent [9] and incoherent [10] inelastic neutron scattering. Investigations of thermal conductivity [11], phonon echo [12] and NMR spectra [13] have also been reported. Besides the anomalous intensity of the two low frequency Raman modes, some other unusual properties have been discovered, e.g. a negative thermal expansion along the **c**-axis [2,3], an unusual temperature dependence of the energy of the infrared band related to the torsion of the NH_3^+ group [6,7], very long lifetimes (>10 ps) of low-frequency librons [8], a large sound-wave velocity in the same direction **c** of the strongest chain of H-bonds, about twice the calculated value [9], the thermal conductivity not obeying the usual hyperbolic dependence on temperature [11], a structural transition at ∼170 K indicated by phonon-echo measurements [12], also found at approximately the same temperature in NMR data [13].

Therefore we undertook new spectroscopic investigations in L-alanine along the line of our studies of intrinsic localized modes (ILM, breathers, or vibrational polarons [14]) in strongly anharmonic molecular crystals. Our recent infrared measurements [15] reveal a splitting of the NH_3^+ torsional band below approximately 220 K, and an overtone of this band. The intensities of both bands are strongly dependent on temperature. These features are satisfactorily explained within the theory of vibrational polarons [16] by assuming a non-linear coupling of the NH_3^+ oscillator with lattice phonons.

However, light depolarization measurements revealed subtle symmetry breaking around and below ∼250 K [15], in disagreement with previous structural data which establish the same space group at 23 K and room temperature [1,2]. New Raman data from our group [17] confirm

---

[a] e-mail: `mariette@GDPC.univ-montp2.fr`

the anomalous behavior of the NH_3^+ torsional mode at about 220 K and the interplay between the two lowest frequency librons. In addition they show that most of the external modes have unusual intensity and frequency behaviors in this temperature range, suggesting some structural instability. These facts contradict the structural data but agree with light depolarization measurements [15] and previous phonon-echo [12] and T_1 NMR relaxation-time [13] measurements. Moreover, a new mode appears below ∼170 K in correspondence with the H-bond strains at ∼135 cm^{-1}, gaining intensity with decreasing temperatures [17].

The possibility of a structural transition attracts a new interest on alanine in connection with a fundamental debate, i.e. the hypothesis of a conformational change from D- to L-alanine driven by the parity-violation energy difference in a BCS-analog transition. This idea is at the origin of Abdus Salam's theory attempting to explain the homochirality of amino-acids in the terrestrial environment [18]. So far, a Salam transition has not yet been shown.

At this point, several hypotheses could be formulated to explain these contradictory properties, e.g. the breaking of one or two of the H-bond networks transforming the NH_3^+ group into a non-linear or chaotic oscillator [7], an increasing density of breathers creating a superlattice of domain walls (or discommensurations, or topological solitons), a slightly monoclinic structure with nearly 90° angles and two types of domains like in $BaMnF_4$ [19], a conformational phase transition affecting the shape of the molecule but not the space group as observed in networks of nanotubes under hydrostatic pressure [20].

To improve our understanding of these unexplained properties, we have undertaken new structural investigations using the high resolution setup of the ID10A beam line at the European Synchrotron Radiation Facility in Grenoble, France. The aims were to look for the possible splitting of some Bragg peaks which could result from two kinds of domains, or for new satellites arising from a hypothetic new phase, commensurate or not, or for diffuse scattering that would signal some dynamic disorder. The results are presented hereafter.

We also determined the crystallographic structure with a conventional setup (an ENRAF NONIUS four-circle diffractometer, at the Laboratoire de Cristallographie of the CNRS, Grenoble) at four different temperatures (293, 220, 170, and 120 K).

2 Experimental details

The ID10A beam line is equipped with an energy-tunable Si(111) single-bounce monochromator in the horizontal scattering geometry providing a resolution $\Delta E/E = 1.4 \times 10^{-4}$. For our experiment we used the X-ray wavelength $\lambda = 1.54001$ Å ($E = 8.05088$ keV). The station is equipped with a horizontal four-circle diffractometer having an Eulerian cradle to allow for a large freedom in sample orientation. The samples were mounted in a standard Displex cryostat ($10 < T < 293$ K). The X-ray spot size was about 0.1×0.1 mm^2.

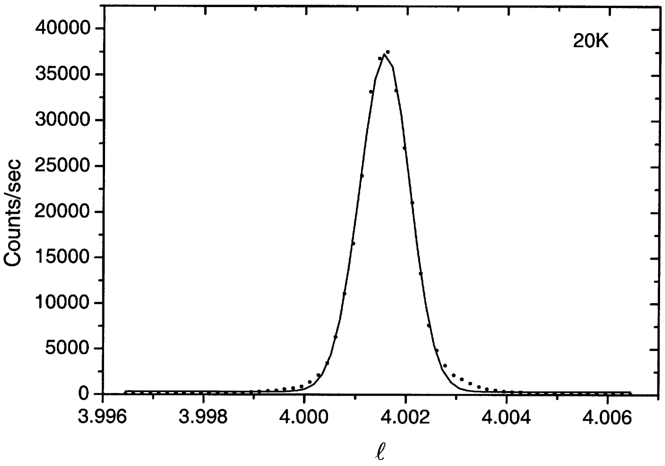
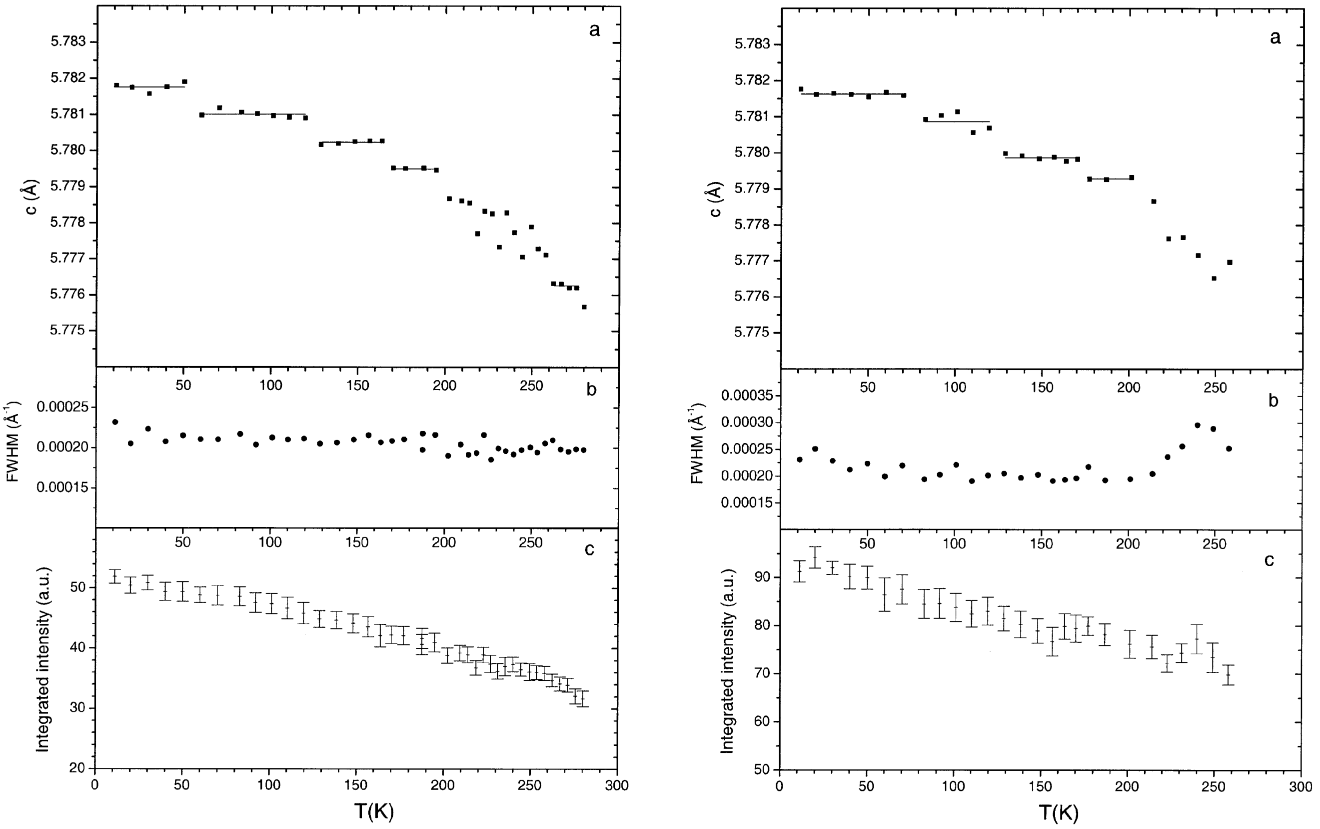


Fig. 1. Scan of the (0 0 4) reflection along the **c***-direction (dots) at 20 K. The curve is a Gaussian fit of the data.

For the crystallographic structure determinations, the intensity data were collected on a Nonius four-circle diffractometer equipped with a bidimensional detector, using monochromatic silver Kα radiation ($\lambda = 0.5608$ Å). The sample was cooled by a nitrogen stream using a 600 series Cryostream cooler from Oxford Cryosystems.

Differential Scanning Calorimetry (DSC) measurements have been performed with a 2920-T.A. Instruments calorimeter at the *Institut Européen des Membranes in Montpellier, France.*

The L-alanine needle single crystal used at ID10A was grown in water solution, at GDPC, Montpellier, France. The selected sample ($1 \times 1.5 \times 6$ mm^3) was glued at one extremity of its largest (1 2 0) face on the cold finger of the cryostat, so that the horizontal scattering plane contained the (h $2h$ ℓ) reflections. By tilting the cryostat around the **c**-direction it was possible to bring in the horizontal plane the scattering plane containing the (0 k ℓ) reflections. The instrumental resolution $\Delta\omega$ in these experiments is about 0.002° so that the weak mosaic spread of the sample resulted in a "splitting" of the Bragg peaks. Careful exploration of the crystal, and the small beam size, finally allowed for the selection of *a single crystallite.* Owing to the required high resolution, the first attempts to measure the Bragg profiles suffered from micro-displacements of the sample holder during temperature changes. To overcome this problem, the position of the beam on the crystal was permanently monitored by a video camera and kept fixed on the same zone on the sample surface. At each temperature, the Bragg reflections were centered by a series of scans (vertical translation scan Z_S and angular ω, ϕ, χ, and 2θ scans) and finally the reflections were measured by a ω-2θ scan. For the structure determinations, a small crystal ($0.42 \times 0.5 \times 0.83$ mm^3) with natural {100} faces was used.



(1) (2)

Fig. 2. Left side (1): (a) Temperature dependence of the lattice parameter c on heating from 11 K to 280 K. The error bars are typically 1.5×10^{-4} Å. One notices that c decreases in a succession of steps and plateaus. (b) Temperature dependence of the full width at half maximum (FWHM) of the (0 0 4) reflection. (c) Temperature dependence of the integrated intensity of the (0 0 4) reflection. The error bars take into account both the error on the fit parameters and the statistical counting. Right side (2): Similar as (1), but on cooling from 260 K to 11 K.

3 Experiments and results

3.1 ID10A results

In a first series of measurements we followed the (0 0 4) reflection in function of T. Figure 1 shows the (0 0 4) intensity profile along the $\mathbf{c}^*$ direction at 20 K. At each T-value the intensity profile was adjusted to a Gaussian. The c lattice parameter is deduced from the position ℓ_0 of the center of the Gaussian by the relation $c(\text{Å}) = 4 \times 5.784/\ell_0$ (where 5.784 is the value of the lattice constant c according to Ref. [1]). The temperature dependence of c is shown in Figure 2-1a for T increasing from 11 to 280 K. Figures 2-1b and 2-1c show the other parameters of the fits, i.e. the full width at half maximum (FWHM) and the integrated intensity, respectively. The FWHM is almost constant over this temperature range while one observes a regular decrease for the integrated intensity on heating. Figures 2-2a to 2-2c show the T-dependence of the same parameters on cooling.

The negative thermal expansion of c is confirmed and it is found to occur in a sequence of discrete steps at about 50–60 K, 120–130 K, 165–170 K, 195–200 K, separated by small plateaus (Fig. 2-1-a on heating and Fig. 2-2a on cooling). The discrete evolution of c, in steps of about 7.5×10^{-4} Å, is obvious. No anomaly in Figures 2b and 2c can be observed in relation to the steps observed in Figure 2a. The behavior of c between 218 and 258 K (scattering in the c-values much larger than the error bar of 1.5×10^{-4} Å) is not understood. One might ask whether this behavior is related to the anomalies in the same T-region that are listed in the introduction. To address this question we have measured the diffuse scattering at 214 K and 241 K by doing ℓ scans near the (0 0 4) reflection, ℓ varying between 3.75 and 4.25. The diffuse scattering is not intense, though stronger at lower T, in disagreement with an expected thermally activated process. This fact may indicate the onset of some structural instability.

In a second series of measurements, we have studied the (0 4 0) reflection as a function of T. We only report here the lattice parameter b as a function of T between 90 and 250 K owing to problems with the temperature controller (see the T error bar in Fig. 3). The data analysis was performed in the same way as for the (0 0 4) reflection. The lattice parameter b has a standard behavior, increasing with increasing T (Fig. 3) and no anomaly can be observed in $b(T)$.

Table 1. Crystal data and structure refinement data.

Formula	$C_3H_7NO_2$
Formula weight (g mol^{-1})	89.094
Wavelength (Å)	0.56087
Crystal System	Orthorhombic
Space group	$P2_12_12_1$
Z	4

Temperature	120 K	170 K	220 K	300 K
Unit cell dimensions :				
c (Å)	5.7877(2)	5.7872(2)	5.7871(2)	5.7821(2)
a (Å)	5.9506(2)	5.9709(2)	5.9904(2)	6.0272(2)
b (Å)	12.2700(5)	12.2856(6)	12.3064(6)	12.3412(6)
Volume (Å^3)	422.58(3)	424.53(3)	426.63(3)	430.09(3)
D_{calc} (g cm^{-3})	1.400	1.394	1.387	1.376
Absorption coefficient (mm^{-1})	0.07	0.07	0.07	0.07
F(000)	192	192	192	192
θ range for data collection (deg.)	2.70 – 21.34	2.69 – 21.36	1.31 – 21.35	2.97 – 21.32
Limiting indices	$-7 \to 7$, $-7 \to 7$, $-15 \to 15$	$-7 \to 7$, $-7 \to 7$, $-15 \to 15$	$-7 \to 7$, $-7 \to 7$, $-15 \to 15$	$-7 \to 7$, $-7 \to 7$, $-15 \to 16$
Reflections collected	965	970	979	992
Independent reflections	583 (559 with $I > 3\sigma(I)$)	587 (560 with $I > 3\sigma(I)$)	592 (566 with $I > 3\sigma(I)$)	597 (568 with $I > 3\sigma(I)$)
Data/parameters ratio	10.2	10.2	10.3	10.3
Goodness-of-fit on F^2	0.717	0.621	0.819	0.699
Final R indices	$R = 0.035$ $wR = 0.116$	$R = 0.031$ $wR = 0.074$	$R = 0.038$ $wR = 0.131$	$R = 0.038$ $wR = 0.136$
Largest peak and hole in the last Diff. Fourier synthesis (e Å^{-3})	0.23, –0.27	0.20, –0.18	0.23, –0.22	0.18, –0.21

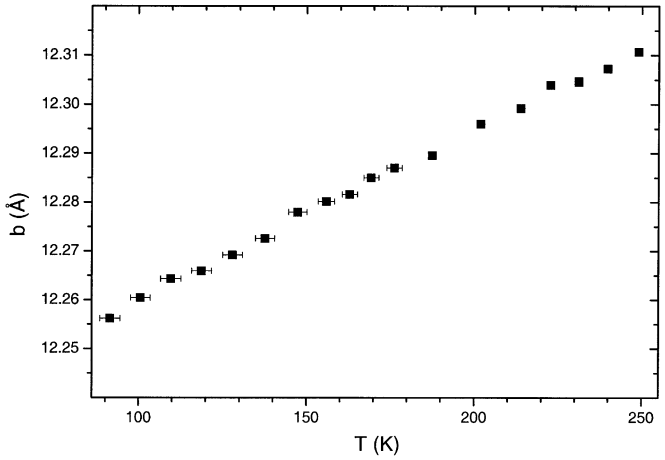


Fig. 3. Temperature dependence of the lattice parameter b on heating.

A small discrepancy (of about 2‰) is noticed between the c-values determined on ID10A and those reported in the literature for room temperature $\{c = 5.784$ Å [1], $c = 5.782$ Å (see Tab. 1 of this paper)$\}$ and for 23 K ($c = 5.794$ Å [2]). This difference, also observed in preliminary tests on the (0 0 2) reflection with another single crystal, is not clearly understood. It may be due to slight structural differences (vacancies concentration, dislocation rates, etc.) in crystals grown by different methods. However, the values of b determined on ID10A are in good agreement with other measurements (compare the values of b in Tab. 1 and the values of b reported in Fig. 3 at 120, 170 and 220 K, or compare also the values at room temperature between Tab. 1 and Ref. [1]).

3.2 Structure determinations

Four crystallographic structure determinations were undertaken at ~293, 220, 170, and 120 K using a Nonius Kappa CCD diffractometer. For each temperature, 960 to

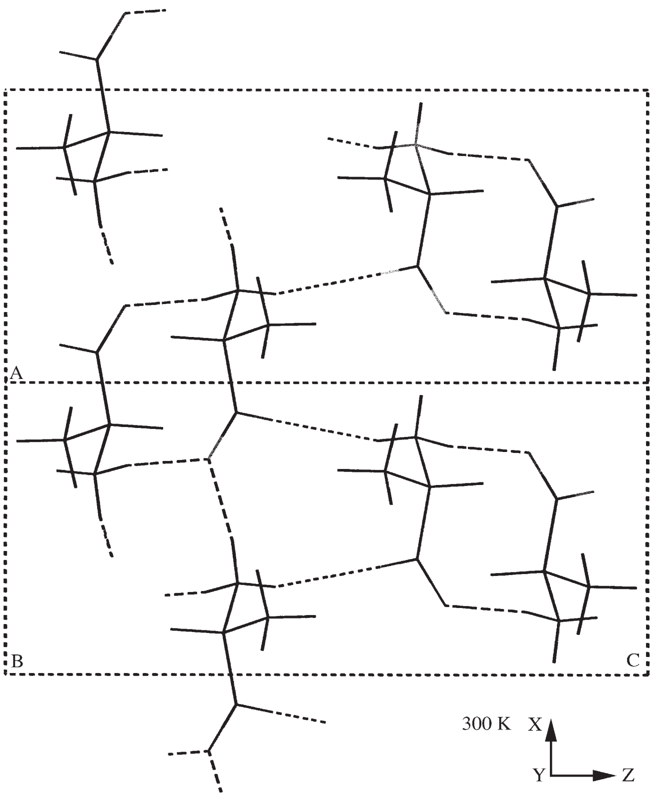


Fig. 4. Projection on the (**b**, **c**)-plane of two unit cells of the L-alanine crystal. No significant changes with temperature are observed, except for these shown in Figure 5.

995 reflections were collected. In each case, the best refinement was obtained with space group $P2_12_12_1$. Space group $P2_1cn$ gave a similar though slightly lesser agreement, but one notes that the chirality of the molecules excludes the reflections symmetries across glide planes that occur in $P2_1cn$. Hence, the $P2_1cn$ space group can be ruled out. Crystal data and details are presented in Table 1. Owing to the very weak absorption of the crystal ($\mu = 0.07$ mm^{-1}) no absorption corrections were applied. The structures were solved by direct methods with the SIR97 program and refined by full matrix least squares, based on F^2, using the Maxus software [21]. The final reliability factors R converged to values of 0.031 to 0.038 for 559 to 568 reflections with $I > 3\sigma(I)$.

Clearly the previously determined space group $P2_12_12_1$, at room temperature and at 23 K remains valid at our intermediate temperatures, and it represents the average symmetry of the structure. Two unit cells are drawn in Figure 4. No significant changes with temperature could be detected, except for slight variations of the C-N-H$_i$ angles, which are shown in Figure 5 in which the structures of the molecules at the four temperatures are superimposed. The conformation of the electrically charged NH_3^+ tetrahedron is modified below ∼220 K: the average proton displacements, though very small, produce a change in the molecular electric dipole moment.

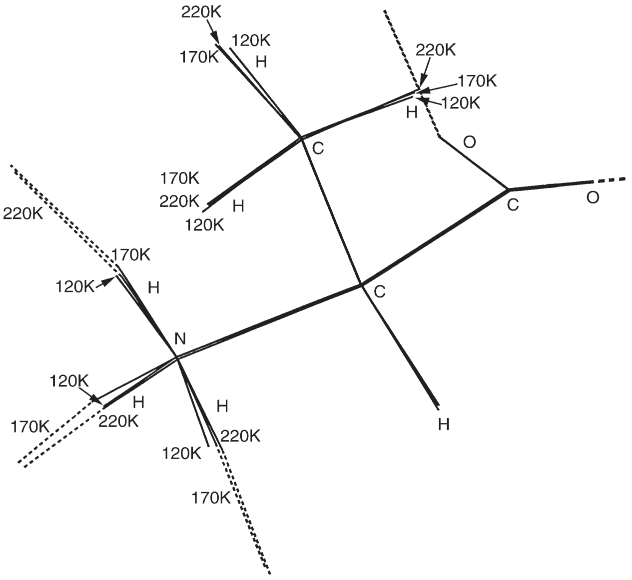


Fig. 5. Structure of the L-alanine molecule at 293, 220, 170, and 120 K. The average conformations at 293 K and 220 K coincide.

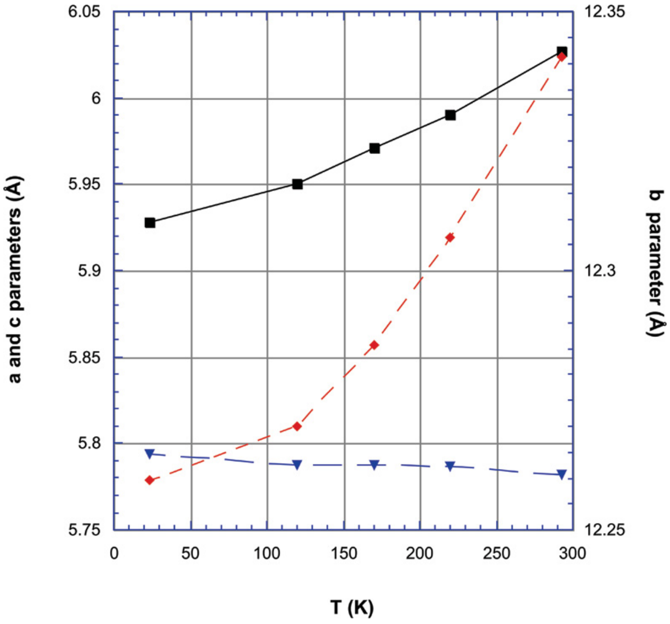


Fig. 6. The a, b, and c lattice parameters (squares, lozenges, and triangles, respectively) as determined with the Nonius Kappa diffractometer. The points at 23 K are taken from [2].

The lattice parameters measured at each temperature are plotted in Figure 6. The characteristic distances and angles of the three hydrogen bonds have been deduced as well and they are given in Table 2.

3.3 DSC study

Our calorimetric study reveals a very small step in the specific heat (less than 0.01 W/g) around 243–246 K, as seen in Figure 7. Such a behavior would be characteristic

Table 2. Lengths and angles of the three hydrogen-bonds.

T (K)	N-H1...O1	N-H2...O2	N-H3...O2
298 K *from [2]	2.853(1) Å 160.9°	2.832(2) Å 163.7°	2.813(1) Å 168.1°
293 K	2.852(2) Å 163.7°	2.827(2) Å 166.9°	2.809(2) Å 167.7°
220 K	2.842 Å 161.81°	2.825 Å 167.05°	2.799 Å 174.33°
170 K	2.836 Å 163.2°	2.821 Å 170.0°	2.797 Å 169.5°
120 K	2.832 Å 161.2°	2.817 Å 171.9°	2.792 Å 175.7°
23 K *from [3]	2.835 Å 161°	2.814 Å 161.2°	2.792 Å 169.5°

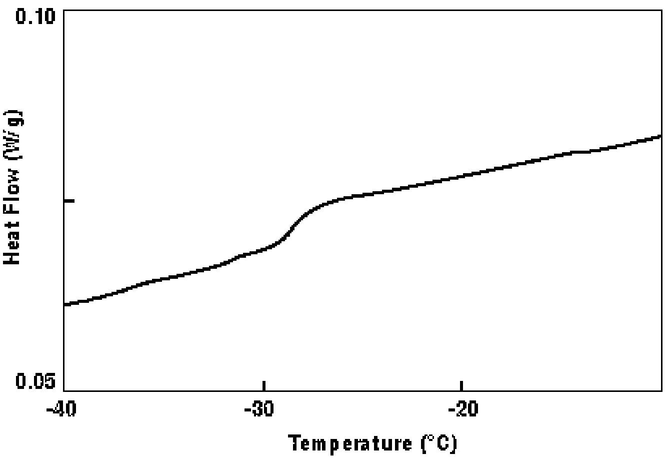


Fig. 7. DSC-curve of L-alanine showing a step smaller than 0.01 W/g between 243 and 246 K.

of a second order structural phase transition. Unfortunately, the temperature accuracy is not very good because of the speed of heating (5°/min). However, this curve confirms that some kind of slight structural instability occurs around this temperature. It is worth remarking that previous experiments performed two years ago with a less precise instrument failed to detect such a small anomaly. Additional measurements, extended towards lower temperatures are being considered now.

4 Discussion

In summary, the new physical observations are as follows:

- a stepwise anomalous decrease of the lattice parameter c on heating from 11 K to 280 K, reversible on cooling;
- very slight changes in molecular conformations, mainly affecting the charged NH_3^+ group below ~220 K and the methyl group below 170 K;
- no change in the average space-group symmetry in the range 300–120 K, in agreement with previous room temperature and 23 K data;
- no splitting observed on scans of the (0 0 2), (0 0 4), and (0 4 0) reflections at any temperatures;
- an anomalous weak diffuse scattering below ~250 K.

Thus, many open questions subsist: Do structural phase transitions exist? If so, what is the order parameter? What is the driving mechanism? Is this instability consistent with the lack of space-group change at any temperature? Why does the c variation occur in discrete jumps? Does each jump correspond to a microscopic conformational transition?

From another point of view, does a self-trapping of vibrational energy exist, as suggested by the dynamics of the low frequency librons [4], by their long lifetime [8], by the properties of the "cold" sideband appearing near the IR band of the NH_3^+ torsion (and near the corresponding Raman peak, in $b[ca]b$ scattering geometry [22]), and by the new mode at ~135 cm^{-1} appearing below ~170 K [17]?

Our assumption of a monoclinic structure with nearly 90°-angle and two types of domains is not confirmed because neither broadening nor splitting of any of the studied Bragg peaks could be observed. However, the (h 0 0) reflections have not yet been examined.

On the other hand, the crystal could undergo an antiferroelectric-ferroelectric transition driven by small distortions of the NH_3^+ group below ~220 K. This deformation does affect the polarisability tensor and the amplitude and direction of the dipole moment $\mu \sim 12$ debyes [9] of each molecule. However, such a transition would affect the $P2_12_12_1$ crystalline symmetry. On the contrary, a small variation $\delta\mu$ (less than ~1%) would be allowed by symmetry and it would not be the order parameter of a conventional transition, though it could be at the origin of the interplay of eigenvectors in the Raman 42 and 48 cm^{-1} librons.

The stepwise increase of c below ~220 K is not understood. Different observations may be related to this stepwise behavior:

- the anomaly in the optical activity begins around ~250 K [15];
- an anomaly in the frequency (and intensity) of most low frequency Raman modes is seen also around ~250 K [17];
- moreover, the pathological Raman modes at 42 and 48 cm^{-1} show also small singularities in their frequency and intensity at ~220 K [17];
- the splitting of the NH_3^+ torsional mode is observed at ~220 K [15];
- a structural transition was reported at ~170 K by phonon-echo and dielectric permittivity measurements [12];
- a structural transition was also reported at ~170 K by the observation of the change in slope of the

T_1relaxation time in ^{1}H NMR measurements. Different activation energies for the methyl and amine group reorientations have been measured [13]. The onset of the random hopping of the methyl protons takes place at a lower temperature than that of the NH_3^+ protons bounded by the H-bonds;

- below ∼170 K, we observe a new Raman mode at ∼135 cm^{-1} [17].

The small jump in the DSC curve (Fig. 7) reflects also some instability in the 240–250 K temperature range. It was recently confirmed by the observation of a large anomaly of the ultrasound attenuation at ∼247 K [23]. In the range ∼220–260 K, the scattering in the c-values is much larger than the error bars. Presumably, the lattice fluctuates under opposite strains.

Hence, a singular behavior of some properties successively occurs at several temperatures. The anomalies observed in the vicinity of 170 K may be related to the presence of the small jump in c between 165 K and 170 K. These jumps suggest attempts to relax some frustration.

What could be the interaction competing with the crystal packing forces on cooling? The self-trapping of vibrational energy [4], or "vibrational polaron" or "breather" [14], involves a "dressing" of one vibration by lattice phonons, creating a local distortion of the surrounding lattice. The density of such defects increases with decreasing temperature. This microscopic modification of the structure which is not a phase transition is called a "polaron glass" [24].

However, the L-alanine molecule is zwitterionic, so the coupling mechanism may be a charge-lattice coupling, formally analog to a breather. According to the Jahn-Teller theorem [25], any non-linear molecular system in a degenerate electronic state (except for Kramers degeneracy) is unstable and will undergo a distortion to form a system of lower symmetry and lower energy, thereby lifting the degeneracy. This process results from a coupling of the electronic state with non-totally symmetric vibrations. In the dynamic Jahn-Teller effect, the coupling is smaller and the complex resonates between two or more equivalent modes of distortion, the degeneracy is lifted, but the average symmetry is preserved [26].

In the L-alanine molecule, the charged NH_3^+rotator is of C_{3v} symmetry, with a degenerate fundamental level. Two types of eigenfunctions are found, a state with nuclear spin 3/2, and E-states with nuclear spin 1/2. In analogy with a dynamic Jahn-Teller interaction, the E-states of NH_3^+may couple with some lattice vibrations of appropriate symmetry, for example belonging to one of the B(i) representations. In this assumption, the NH_3^+ group could undergo simultaneously a dynamic distortion and a lifting of the degeneracy of its ground and excited states, producing the splitting of the IR and Raman torsional modes. An oscillating distortion of the H_3^+ triangles would affect the electric dipole moment, and could explain the observed light depolarization below ∼250 K [15]. The observed diffuse scattering may result as well from a pretransitional regime or from a dynamic Jahn-Teller-like coupling in which the lattice fluctuates between different distortions [27].

Hence, the L-Alanine structure could become frustrated on cooling, under the opposite influence of competing interactions: the crystal packing forces on the one hand, and the "Jahn-Teller-like" charge-phonon coupling on the other hand. The increase of c on cooling is then an attempt to relax the increasing opposite stresses. As listed above, other effects happen in the same range of temperature. However, the stepwise character of the anomalous c increase on cooling is not fully explained. A new systematic study of diffuse scattering at low temperatures is also underway.

This work has been performed within the EC Network LOCNET (HPRN-CT-1999-00163). We acknowledge Gerhard Gruebel for helpful discussions and advice for the ID10A experiments. We are also very grateful to Henri Gleyzolle from ESRF and Marcel Lopez from I.E.M. Montpellier for technical assistance.

References

1. H.J. Simpson Jr., R.E. Marsh, Acta Cryst. **20**, 550 (1966)
2. R. Destro, R.E. Marsh, R. Bianchi, J. Phys. Chem. **92**, 966, (1988)
3. M.S. Lehman, T.F. Koetzle, W.C. Hamilton, J. Am. Chem. Soc. **94**, 2657 (1972)
4. A. Migliori, P.M. Maxton, A.M. Clogston, E. Zirngiebl, M. Lowe, Phys. Rev. B **38**, 13464 (1988)
5. E. Loh, J. Chem. Phys. **63**, 3192 (1975)
6. J. Bandekar, L. Genzel, F. Kremer, L. Santo, Spectrochim. Acta A **39**, 357 (1983)
7. C.H. Wang, R.D. Storms, J. Chem. Phys. **55**, 3291 (1971); K. Machida, A. Kagayama, Y. Saito, T. Uno, Spectrochim. Acta A **34**, 909 (1978)
8. T. Kosic, R.J. Cline, D.D. Dlott, J. Chem. Phys. **241**, 1138 (1984)
9. A. Micu, D. Durand, M. Quilichini, M.J. Field, J.C. Smith, J. Phys. Chem. **99**, 5645 (1995)
10. H.N. Bordallo, M. Barthes, J. Eckert, Physica B **241**, 1138 (1998)
11. R.S. Kwok, P. Maxton, A. Migliori, Solid State Commun. **74**, 1193 (1990)
12. V.V. Lemanov, S.N. Popov, Phys. Sol. State **40**, 1921 (1998)
13. K. Beshah, E. Olejniczak, R. Griffin, J. Chem. Phys. **86**, 4730, (1987); P. Jackson, R.K. Harris, J. Chem. Soc. Faraday Trans. **91**, 805, (1995)
14. A.C. Scott, *Nonlinear Science* (Oxford University Press, Oxford, 1999)
15. M. Barthes, A.F. Vik, A. Spire, H.N. Bordallo, J. Eckert, J. Phys. Chem. A **106**, 5230, (2002)
16. A. Scott, I. Bigio, C. Johnston, Phys. Rev. B **39**, 12883, (1989)
17. A.F. Vik, Y.I. Yuzyuk, M. Barthes, J.L. Sauvajol, *Comm. at "Journées Françaises de Diffusion Raman"* (6/8 Dec. 2001, Montpellier), proceeding available on request to M. Barthes
18. A. Salam, Phys. Lett. B **288**, 153 (1992); H. Zepik et al., Science **295**, 1266 (2002)

19. P. Saint-Grégoire, R. Almairac, A. Freund, J.Y. Gesland, Ferroelectrics **67**, 15 (1986)
20. R. Almairac, private communication
21. S. Mackay, C.J. Gilmore, C. Edwards, N. Stewart, K. Shankland, (1999) maXus Computer Program for the Solution and Refinement of Crystal Structures, Bruker Nonius, The Netherlands, MacScience, Japan and The University of Glasgow
22. A.F. Vik, Y.I. Yuzyuk, M. Barthes, J.L. Sauvajol, unpublished
23. W. Wang, W. Min, C. Zhu, F. Yi, Phys. Chem. Chem. Phys. **5**, 4000 (2003)
24. G. Kalosakas, G. Tsironis, S. Aubry, Phys. Rev. B **58**, 3094 (1998)
25. C. Kittel, *Introduction to Solid State Physics*, 3rd edn. (John Wiley, N.Y., 1968), p. 630.
26. F.S. Ham, Phys. Rev. **138**, A 1727(1965).
27. D.N. Argyriou, H.N. Bordallo, J.F. Mitchell, J.D. Jorgensen, G.F. Strouse, Phys. Rev. B **60**, 6200 (1999)