Experiment title:

Structural Instability in L-Alanine ?

(CH-1339)

Experiment number:

CH-1339

Beamline:

ID10A

Shifts: 18

(1shift=8h)

Date of experiment:

from: 12 Décembre 2002 to:18 Décembre

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Report:

Crystallized L-Alanine , one of the simpler amino-acids, exhibits a panel of anomalous physical properties whose origin is unclear [1]. At low temperature, dynamic instabilities of some lattice phonons and internal vibrations [2] occur without any change in the $P2_12_12_1$ space group symmetry.

Our experiment on ID10A aimed to check - with the best available resolution - a possible existence of a splitting of some Bragg reflections, which should indicate a structural transition from the orthorhombic space group to a monoclinic one with a nearly 90° angle, not evident in a classical structural investigation.

So we have performed crystallographic measurements on L-Alanine single crystals, as a function of temperature with a displex cryostat. The incident photon energy was E = 8.0449 KeV , l = 1.54115 Angström, and the resolution DE/E = $1.4x10^{-5}$. An Eulerian cradle was also mounted for varying the crystalline scattering plane (first [010] and then [100]).

Due to the required high resolution,the first attempts to measure the Bragg profiles suffered from the microdisplacements of the sample holder when the temperature is changed, and from the mosaicity of the crystal. This problem was overcome when the impact of the beam on the crystal was watched by a videocamera, and kept on the same zone of the sample surface.

A series of experiments was performed between 11K and 300K, on a sample where the largest faces were the {120} ones. Careful measurements of position and profile of the (004) Bragg reflection have given the following results:

- No splitting of the (004) Bragg reflection could be detected at any temperature, in disagreement with our assumption of a two-domain structure in this geometry.

- Figure 1 shows the variation of the c lattice parameter as a function of temperature. It anomalously increases when decreasing the temperature; the anomalous expansion processes by discrete steps (at about 230K, 180K, 130K, 80K) looking like a "devil staircase" in incommmensurate structures.

A very weak hysteresis seems to appear also. These data are tentatively explained as a sequence of weak conformational micro-transitions progressively affecting the shape of the molecule (mainly the NH3+ tetrahedron, and the electric dipole moment [3]);

- The diffuse scattering, measured at 220K and 250k near the (004) reflection, is not intense, but stronger at the lower temperature, in disagreement with an expected thermally activated process. It may indicate the onset of some structural instability.

- A weak intensity was found at 250K on the (003) forbidden reflection.

- Preliminary measurements of position of the (040) Bragg reflection demonstrate that the temperature dependence of the b lattice parameter is normal (decreasing with decreasing temperature)

As a conclusion, important new insight have been brought by this high resolution measurement of the L-Alanine c lattice parameter: the crystal, submitted to the unequal distorsions of the three H-bond networks counteracting the other packing forces, or the varying dipolar interaction, is strongly frustrated and relaxes by discrete steps. These micro-transitions preserve the crystalline unit cell symmetry, but presumably affect the electric polarisation symmetry. The question arises now to check if the sequence of conformational micro-transitions persists at higher temperature, and if the c lattice parameter contraction persists on heating above room temperature.

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The answer is relevant not only for the complete understanding of the dynamics of this "simple" amino-acid, but as well for progressing in the knowledge of the interplay of breathers with structural instabilities, and may be also in the open debate about the part of the parity violation energy difference, or Salam hypothesis, to explain homochirality of biomolecules [4].

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[1] M. Barthes et al. - J. Phys. Chem. A - 2002,106, 5230-5241

[2]A. Vik et al. - Journées de Spectrométrie Raman - 6/7 Déc. 2001 - to be publ. in Journal de Physique IV- Proceedings.

[3] J. Zaccaro et al., to be publ.

[4] A. Salam, Phys. Lett. B, 288,153, 1992.

H. Zepik et al., Science, 295, 1266-1269, 2002.

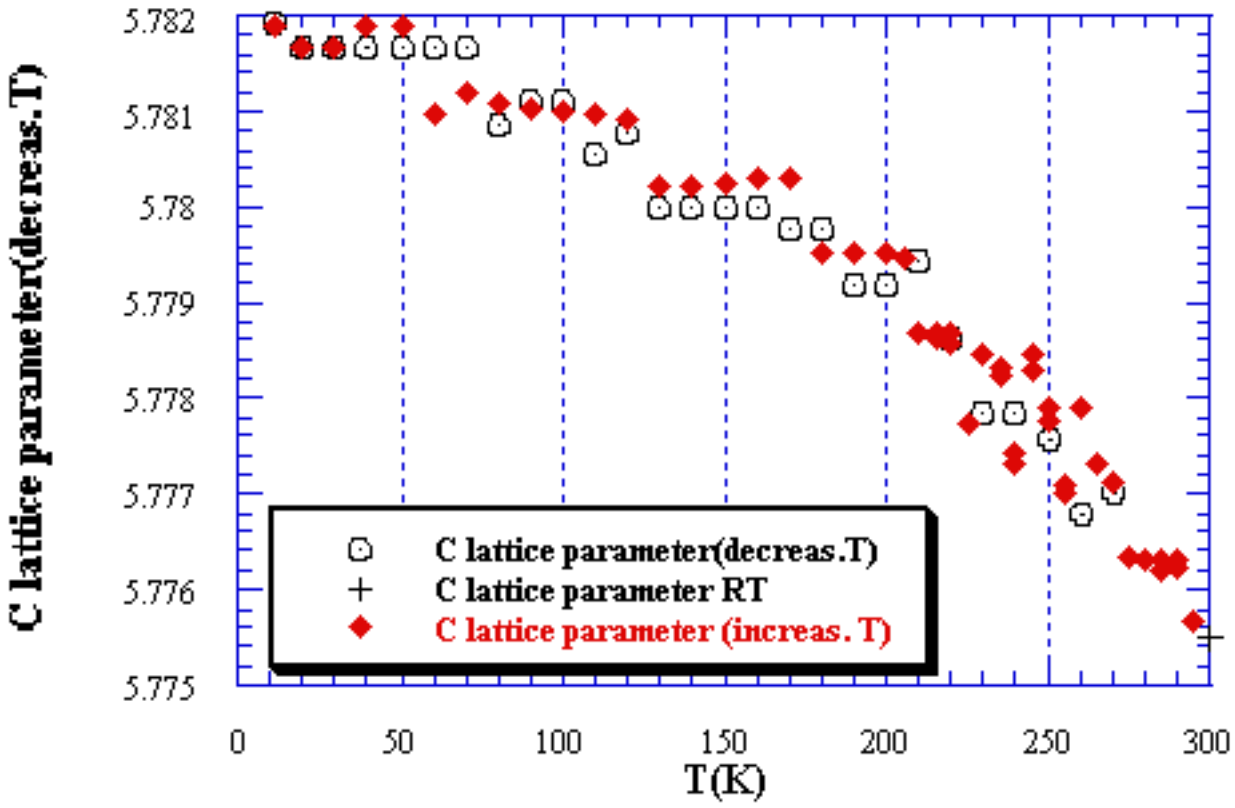

Fig. 1- c lattice parameter of crystallized L-Alanine (Angström)

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