Oral presentation

Anahrmonic oscillations in the structure of NTE material 1,3-diacetylpyrene

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The anharmonic effects in the description of the atomic/molecular vibrations in the crystal are crucial when predicting various properties of a material from experimental charge density analysis, through precise IR or Raman spectra to thermodynamic characteristics including relative polymorph stability. The presence of vibrations with a non-negligible anharmonic component are one of the major causes of Negative Thermal Expansion (NTE) in certain materials [1], a property much sought after in modern mateirals. On the other hand, anharmonic effects as manifested in experimental X-ray data can be small and hence elusive, hard to deconvolute from other effects and easily neglected. In order to be unequivocally identified and interpreted, they require high-quality and suitable-resolution diffraction data collected at several temperatures and aspherical atomic scattering factors to interpret them. According to a recent study based on CSD search, systematic structural studies, based on larger series of complete and reliable diffraction datasets remain rare [2].

Here I present a systematic study of a purely organic, moderately scattering material: a new polymorph of 1,3-diacetylpyrene obtained from melt, which turned out to display a spectacular uni-axial NTE (contraction coefficient of -200(7) MK $^{-1}$) behavior at RT conditions [3]. Complete and reliable X-ray diffraction datasets were collected for a wide temperature range as well as at increased pressure, allowing to pinpoint the onset of anharmonic behavior with increasing temperature and its quenching with increased pressure. The structures were obtained based on HAR refinements and the anharmonic corrections in Gram-Charlier formalism were introduced within Olex2 framework [4]. The NTE behavior could be explained by anharmonic oscillations of the carbonyl O atoms in a framework of weak C – H · · · O hydrogen bonds (**Figure 1)**. The presence of anharmonic effects explains why thermodynamic properties of this relatively simple organic compound proved challenging when predicting relative polymorph stability.

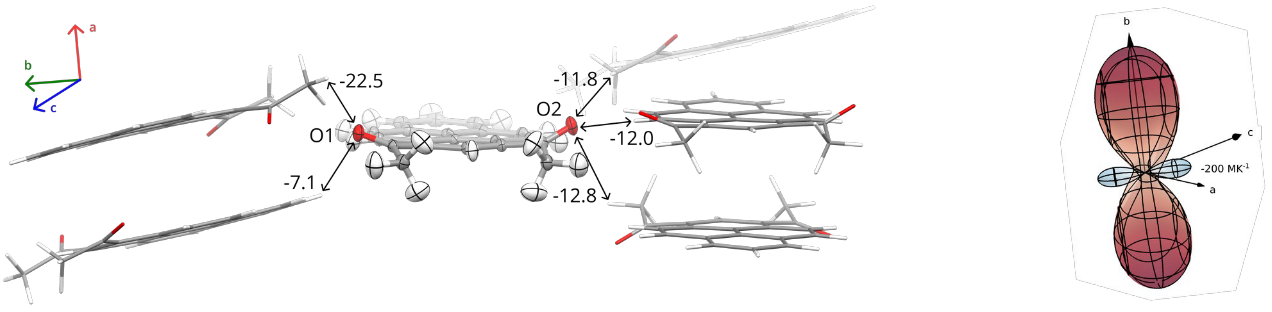

Figure 1. Left: framework of weak C – H · · · O hydrogen bonds in the analyzed material. Right: thermal expansivity indicatrix [5].

[1] Miller, W., Smith, C. W., Mackenzie, D. S., Evans, K. E. (2009). *J. Mater .Sci.* **44**, 5441.

[2] Bond, A. D., (2021). *Acta Cryst.* **B77**, 357.

[3] Zwolenik, A., Tchoń, D., Makal, A. (2024). *IUCrJ* **11**, https://doi.org/10.1107/S2052252524003634

[4] Kleemiss, F. V., Dolomanov, O., Bodensteiner, M., Peyerimhoff, N., Midgley, L. J., Bourhis, L., Genoni, A. A., Malaspina, L., Jayatilaka, D. L., Spencer, J., White, F., Grundkötter-Stock, B., Steinhauer, S.,Lentz, D., Puschmann, H. & Grabowsky, S. (2021). Chem. Sci. 12, 1675.

[5] Cliffe, M.J., Goodwin, A.L. (2012). *J. Appl. Cryst.* **45**, 1321.

We acknowledge SOLEIL for providing access to the CRISTAL beamline and Dr Pierre Fertey for his invaluable assistance. Daniel Tchoń is acknowledged for collecting high-pressure X-ray diffraction data. This study was in part financially supported by the NCN grant No. DEC-2015/17/B/ST4/04216. Theoretical periodic DFT calculations were performed using resources provided by PLGrid (grant Nos. plgamakalhp6–plgamakalhp8a).