References:

[1] Empirical temperature-dependent intermolecular potentials determined by data mining from crystal data, DWM Hofmann, LN Kuleshova, Chemical Physics Letters 699, 115-124 (2018).
[2] Are Crystal Phase Diagrams Predictable with Force Fields? Case of Benzene Polymorphs. DWM Hofmann, LN Kuleshova, Crystal Growth & Design 14 (8), 3929-3934 (2014)
[3] Data Mining in Organic Crystallography, DWM Hofmann, Structure and Bonding 134 (Data Mining in Crystallography), 89--135, 19 (2009)

Keywords: Crystal Structure Predtion, Data Mining, Force Fields

MS33-O5

X-ray diffraction data as a source of information of vibrational contribution to enthalpy and entropy of polymorphic systems

Anna Hoser[1], Philip Miguel Kofoed[2], Anders Ø. Madsen[2]

1. Chemistry Department, University of Warsaw, Warsaw, Poland
2. Department of Chemistry, University of Copenhagen, Copenhagen, Denmark

email: annahoser@chem.uw.edu.pl

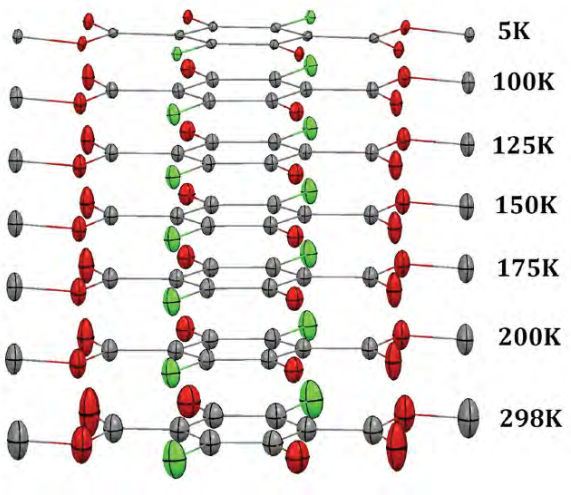
The stability of crystals at a given temperature is determined not by the lattice energy, but by Gibbs free energy. Thus, to compare stabilities of polymorphs at given temperature beside lattice energy, one should take into account contributions from vibrational enthalpy, entropy and zero point energy. Those contributions can be calculated by means of DFT methods, but, as they require supercell calculations, they have high computational costs.

An idea of estimating entropy from X-ray diffraction data is not new - in 1956 Cruickshank [1] estimated entropy of crystalline naphthalene by means of TLS analysis from ADPs from single crystal X-ray diffraction data. In 1989 Jack Dunitz and co-workers used a similar approach to estimate the entropy of conformational polymorphs of dimethyl-3,6-dichloro-2,5-dihydroxyterephthalate [2]. Dunitz et al was able to explain the mechanism of phase-transformation based on an analysis of the Debye-Waller factors, but their results contradicted the well-established thermodynamic order of stability of the systems. They write:

"Why has our intuition led us astray in expecting that the crystal with the larger atomic ADP's should have the greater entropy?"

We decided to reinvestigate this particular polymorphic system with normal mode refinement, which enables the refinement of frequencies of normal modes obtained from *ab-initio* periodic computations at Γ point, against single crystal diffraction data. Frequencies obtained from *NoMoRe* can be used to estimate thermodynamic properties – heat capacity and vibrational contributions to entropy and enthalpy [3].

In order to conduct *NoMoRe* refinements we collected new high-quality single crystal X-ray diffraction data for polymorphs and we conducted DFT theoretical calculations of frequencies at Γ point and a reference supercell calculations. Estimates of the frequencies of acoustic modes, obtained after *NoMoRe* are in very good agreement with those from supercell calculations. Based on the *NoMoRe* analysis, we can predict, that white form is stable at high temperature range, and yellow at low temperature range, which is in agreement with experimental results. By discussing contributions from low and from high frequency modes to vibrational entropy and enthalpy we are able to explain the important question which was raised by Dunitz et al.



References:

[1] Cruickshank, D. W. J. (1956). Acta Cryst. 9, 1010-1011
[2] Richardson, M. F., Yang, Q.-C. , Novotny-Bregger, E., Dunitz J. D. (1990). Acta Cryst. . B46, 653-660
[3] Hoser, A. A., & Madsen A. Ø. (2017). Acta Cryst. A73, 102-114

Keywords: polymorphism, lattice dynamics

MS34 Exploring structural dynamics in crystals

Chairs: Dr. Pance Naumov, Prof. Leonard Barbour

MS34-O1

From reactivity of solids to high-pressure crystallography and back: response of molecular crystals to mechanical stress

Elena Boldyreva[1]

1. Novosibirsk State University, Chair of Solid State Chemistry, Novosibirsk, Russia

email: eboldyreva@yahoo.com

The contribution gives a survey of the research that has been carried out through over several decades. Any reaction in a crystal is accompanied by generating stress. The manifestations of this stress are elastic and plastic strain and fragmentation. As a reaction proceeds, the mechanical stress that arises in the crystal can have a significant influence on the subsequent transformation. This phenomenon is termed as feed-back, which can be either positive, or negative. One can introduce the concept on “chemical pressure”, to describe the reaction in the crystal which is stressed by the reaction itself. In selected cases the mechanism of the reaction in relation to the mechanical response of crystals can be studied in detail. I illustrate this, using selected examples of reactions in molecular crystals. The effects of “chemical pressure” can be compared with those of strain imposed by hydrostatic compression. Modern high-pressure crystallography makes it possible to follow even subtle changes in molecular geometry and intermolecular interactions. I discuss structural distortion induced by high pressure and structural transformations, in a comparison with strain and structural transformations accompanying chemical reactions in the same crystal. Eventually, we consider the chemical reactions induced by irradiation or heating if occurring in the hydrostatically compressed crystals.

References:

Boldyreva E.V., Boldyrev V.V. (Eds.) Reactivity of Molecular Solids, Wiley: Chichester, 1999; Boldyreva E.V., Dera P. (Eds.) High-Pressure Crystallography, Springer: Dordrecht, 2010; Boldyreva E.V. Solid State Ionics. 1997, 101-103, 843-849; Boldyreva E.V. Coord. Chem., 2001, 27(5), 323-350; Boldyreva E.V. Acta Crystallogr. A, 2008, 64, 218-231; Naumov P., Sahoo S.C., Zakharov B.A., Boldyreva E.V. ACIE, 2013, 252 (38), 9990-9995; Naumov P., Chizhik S., Panda M., Nath Naba K., Boldyreva E. ChemRev, 2015, 115 (22), 12440-12490; Zakharov B.A., Marchuk A.S., Boldyreva E.V. CrystEngComm, 2015, 17 (46), 8812-8816; Sidelnikov A.A., Chizhik S.A., Zakharov B.A., Chupakhin A.P., Boldyreva E.V. CrystEngComm, 2016,18 (38), 7276-7283; Zakharov B.A., Gribov P.A., Matvienko A.A., Boldyreva E.V. Z. Krist., 2017, 232 (11), 751-757; Chizhik S., Sidelnikov A., Zakharov B., Naumov P. & Boldyreva E., Chem. Sci., 2018, 9, 2319-2335.Keywords: mechanical stress, pressure, reactivity of solids

Keywords: mechanical stress, pressure, reactivity of solids