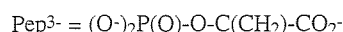


**MS11.06.07 NEUTRON SCATTERING STUDIES OF THE DISTRIBUTION AND ANHARMONIC VIBRATION OF Ag<sup>+</sup> AND Cu<sup>+</sup> IN FAST-ION CONDUCTORS.** Bernhardt J. Wuensch, Department of Materials Science and Engineering, Massachusetts Institute of Technology Cambridge, MA 02139

The Ag<sup>+</sup> and Cu<sup>+</sup> halides and chalcogenides are the prototype cation-disordered fast-ion conductors. The distribution of mobile ions in their structures long remained enigmatic despite the fact that the anion arrangements are based on simple bcc, hcp, or fcc packing. Disruptive phase transformations hindered the preparation of singlecrystal specimens and powder diffraction patterns, as a consequence of disorder and very large thermal vibration amplitudes, provide too few intensities to permit specification of a satisfactory structural model. Methods for the preparation of a single crystal, coupled with neutron scattering measurements (performed at the HFBR at Brookhaven National Laboratory) has enabled us to obtain precise descriptions of a number of these structures:  $\alpha$ -AgI, Ag<sub>2</sub>S,  $\beta$ -Ag<sub>2</sub>Se,  $\beta$ -Cu<sub>2</sub>S,  $\alpha$ -Cu<sub>2</sub>S,  $\alpha$ -Cu<sub>2</sub>Se,  $\beta$ -AgCuS,  $\alpha$ -Ag<sub>3</sub>SI, and  $\beta$ -Ag<sub>3</sub>SI. Fast-ion conduction is a consequence of the cations residing in shallow potential wells at sites that form a continuous pathway through the structure. All of the structures display cations that are delocalized by positional disorder and highly-anharmonic thermal vibrations. To distinguish dynamic anharmonic vibration from positional disorder over closely-spaced equilibrium sites (i.e., "split atoms"), all of our structure analyses were performed as a function of temperature to insure that the "thermal" parameters extrapolate to zero at 0K. Anharmonic vibration, "split atoms" and, sometimes, both were found in the structures. The distribution of cation scattering density is not solely a function of the geometry of the anion arrangement, but depends on the concentration and bonding characteristics of the mobile cations as well.

**PS11.06.08 CRYSTALLOGRAPHIC ANALYSES OF THE FLEXIBILITY OF THE P-O-C ESTER LINK IN PHOSPHOENOLPYRUVATES.** Thomas P. O'Connor, Jr.<sup>1,2</sup>, Robert H. Blessing<sup>1</sup>, <sup>1</sup>Hauptman-Woodward Medical Research Institute, 73 High Street, Buffalo, New York 14203-1196 USA, <sup>2</sup>Graduate Studies Program in Natural Sciences, Roswell Park Cancer Institute, Elm and Carlton Streets, Buffalo, New York 14263 USA

Analyses of soft modes of internal torsional vibrations about the P-O and O-C bonds and P-O-C valence angle bending vibrations in phosphoenolpyruvate species in crystals will be described. A database of room-temperature anisotropic mean-square atomic displacement parameters for 19 crystallographic occurrences of H<sub>3</sub>Pep, H<sub>2</sub>Pep<sup>-</sup>, HPep<sup>2-</sup>, and Pep<sup>3-</sup> phosphoenolpyruvate species has been analyzed to complement a recent analysis of the corresponding valence and conformational geometries [M. Souhassou, P. M. Schaber, and R. H. Blessing (1996), *Acta Cryst.*, Part B, submitted].



Phosphoenolpyruvates are of interest because, among the various species involved in the ATP cycle of bioenergetics, phosphoenolpyruvate has the highest free energy of hydrolysis or phosphate group transfer potential.

We are grateful to several colleagues for indispensable help with this work: Prof. Tadeusz Lis and his co-workers at the University of Wrocław determined or refined most of the phosphoenolpyruvate crystal structures that formed the basis of our studies, and they kindly provided parameter files in machine-readable form. Prof. Kenneth Trueblood of UCLA provided his THMA14 program. Prof. Bryan Craven of the University of Pittsburgh provided his and Dr. Xiao-Min He's EKRT program, and Professor Hans-Beat Buergi and Dr. Juerg Hauser of the University of Bern provided their PEANUT program. We also acknowledge with gratitude research support from NIH Grant No. PO1 GM46733.

**PS11.06.09 EINSTEIN VERSUS DEBYE SOLID IN THE MODELLING OF THE Pa3 PHASE OF ACETYLENE.** A.T.H. Lenstra, K. Verhulst & C. Van Alsenoy, Department of Chemistry, University of Antwerp (UIA), Belgium

Minimum-energy geometries of acetylene were obtained using standard ab initio methods as well as the electrostatic crystal field (ECF) approach. The calculated difference in C-C bond length between gas phase and solid state is 0.002Å. An experimental verification is therefore practically impossible. Neutron and X-ray studies produced not only a solid-state geometry, but also ADP's. For acetylene in its cubic phase the displacements along and perpendicular to [1,1,1] are given by:  $\langle U^2 \rangle_{\parallel} = T$  and  $\langle U^2 \rangle_{\perp} = T + 3Lr^2$ . For the molecular translation (T) and libration (L) we calculated the relevant energy profiles. Via Boltzmann statistics we reconstructed U<sub>||</sub> and U<sub>⊥</sub> within the Einsteinian ECF approximation. Since U<sub>⊥</sub> is too small the librational analysis appears to be inadequate. To incorporate intermolecular interactions caused by electron overlap we extended our wavefunctional unit to a supermolecule which contains the reference molecule and its two nearest-neighbour coordinating shells. The potential governing the axial length is practically harmonic:  $E(a-\langle a \rangle) = f(a-\langle a \rangle)^2$  with  $\langle a \rangle = 6.10\text{Å}$  (observed 6.094Å at 131K) and  $f = 43\text{kJ/molÅ}^2$ . This leads to an axial rms of 0.095Å at 131K. The translational displacement of the central molecule is also harmonic with a force constant of 38kJ/molÅ<sup>2</sup>, giving a rms amplitude of 0.120Å at 131K. To reproduce U<sub>||</sub> we need to sum the two individual rms-values, which means that translational disturbance and lattice relaxation operate in phase. Elasticity links these oscillators via an action/reaction mechanism preserving the minimum-energy unit cell. Molecular libration within this supermolecule approach boils down to a rms of 6.5° which is smaller than the ECF-value of 8.5°. Assuming that the libration provokes an equi-important lattice relaxation, the combined librational oscillator has a rms-angle of 13°. This academic construction is factual, because it explains not only the C-C shrinkage (1.212(2)Å gas versus 1.177(6)Å solid) but also the observed U<sub>⊥</sub>-values.

### Intermolecular Interactions

**MS11.07.01 TOWARDS A COMPREHENSIVE MODEL OF HYDROGEN BONDING INTERACTIONS: PAST RESULTS AND FUTURE RESEARCH PROJECTS.** Gastone Gilli, Dipartimento di Chimica and Centro di Strutturistica Diffraattometrica, Università di Ferrara, via L. Borsari 46, I-44100 Ferrara, Italy

In a series of previous papers (Gilli et al., *J. Am. Chem. Soc.* 1989, *111*, 1023; 1994, *116*, 909; *Acta Cryst.* 1993, *B49*, 564; Bertolasi et al., *J. Am. Chem. Soc.* 1991, *113*, 4917; *Acta Cryst.* 1994, *B50*, 617) it has been shown that (a) *very strong homonuclear XH...X H-bonds* are to be conceived as *totally delocalized X...H...X <=> X...H...X three-centre-four-electron covalent bonds*; (b) their occurrence is limited to the three chemical classes where the H-bond can be assisted by positive or negative charges, or by  $\pi$ -resonance; (c) they are the stronger the more similar are the proton affinities of the two H-bond donor and acceptor atoms and, accordingly, (d) heteronuclear X-H...Y bonds can only give weak H-bonds of mostly electrostatic nature.

In this lecture the results of such previous investigations are briefly reviewed and the general problem addressed of whether or not a comprehensive model accounting for both homo- and heteronuclear

H-bond can be conceived. It will be shown that a tentative solution can be inferred by comparing a number of crystal structures where strong or very strong O-H...N, N-H...O and N-H...O interactions are known to occur.