1. freezing of one type of AO_4 libration
2. ordering of the two-dimensional hydrogen bridge system
3. AO_4 dimer switching
4. proton ordering within a hydrogen bridge

    A complete survey of all known transitions will be presented and examples of the different ordering mechanisms will be analysed in view of experiment and theory.

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MS11.05b.06 STRUCTURE DETERMINATION AT HIGH PRESSURES FROM MOLECULAR DYNAMICS SIMULATIONS. S. K. Sikka, Surinder M. Sharma, R. Chidambaram, High Pressure Physics Division, Bhabha Atomic Research Center Bombay - 400 085

    We describe the use of molecular dynamics (MD) simulations to determine the structures of some high pressure phases which give only a few Bragg peaks in their diffraction patterns. In α-quartz, Kingma et al[1] had reported the diffraction pattern of a new phase before amorphization at 21 GPa. Using the coordinates derived from MD simulations, employing the pair potentials of Tsuneyuki et al[2], we got x-ray patterns in excellent agreement with experimental results - indicative of a tripling of the α-quartz unit cell in its basal plane. A monoclinic cell could then be derived.[3]

    In $LiCsSO_4$, there has been a controversy about the number and nature of pressure induced phases. We have carried out x-ray diffraction studies on this and have detected two c-c transitions at 4 and 7 GPa and amorphization at ~ 19 GPa[4]. Our data rule out the earlier conjecture that the 4 GPa transition is the orthorhombic to monoclinic (a low temperature phase) one. Instead the x-ray pattern here strongly resembles the one calculated from the coordinates of 9.8 GPa phase of $LiKSO_4$ as computed by an earlier MD simulation[5]. This new structure is related to the ambient one through the softening of the (1/3,1/2,0) mode and has higher oxygen coordination for Li atoms.

    Another application to solve the intermediate structure between fcc and hcp structures of Xe in the pressure range 12-75 GPa will also be described.

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Analysis of Atomic Displacement Parameters

MS11.06.01 NORMAL MODE ANALYSIS FROM ELASTIC DIFFRACTION DATA IS POSSIBLE! WHY AND HOW? H. B. Bürgi, Labor für Kristallographie, Freiestr. 3, Universität, CH-3012, Bern, Switzerland

    It is generally believed that atomic mean square displacement parameters (ADP) obtained from an elastic diffraction experiment provide information on the motion of individual atoms, but cannot say anything on the cooperative displacements of groups of atoms unless assumptions of questionable validity are made. This opinion is correct with respect to ADP's pertaining to a single temperature; it is untenable, however, when ADP's at several temperatures are available. Why is this so?

    ADP's can be considered as a superposition of the contributions from many normal modes. The absolute atomic displacements of a mode depend on its energy (v), its effective or reduced mass (μ), on temperature (T) and on relative displacement (A) according to $A*h/(8*\pi^2*\mu*v)*coth$ [$h*v/(2*k*T/$]. At sufficiently low temperatures this expression can be approximated by $A*h/(8*\pi^2*\mu*v)$. At sufficiently high temperatures the corresponding approximation is $A*k*T/(4*\pi^2*\mu*v^2)$.

    Now, suppose that a mean squared displacement U is the result of a superposition of two normal modes only and that it has been measured at a low and at a high temperature; then
U(lowT) $=A1*h/(8*\pi^2*\mu1*v1) + A2*h/(8*\pi^2*\mu2*v2)$
U(high T) $= A1*k*T/(4*\pi^2*\mu1*v1^2)+A2*k*T/(4*\pi^2*\mu2*v2^2)$.

    From the two independent observations the two normal frequencies can be determined, provided A1 and A2 are known. This simple argument can be generalized to more than two frequencies and to the corresponding relative displacements if the coth-dependence and the three-dimensional information contained in the ADP's are taken into account. In practice, ADP's need to be measured at a sufficient number of appropriate temperatures.

MS11.06.02 MODELLING THE THERMAL MOTION OF FREELY ROTATING MOLECULES. R. T. Downs and L. W. Finger, Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. N.W., Washington D.C. 20015, phone: (202) 686-2410 x 2469, e-mail: downs@gl.ciw.edu

    All molecular gas-phases become crystalline when subjected to sufficient pressure. Spectroscopic studies show that the molecules are freely rotating while near the freezing point for many of these phases. As pressure increases the motion is constrained and a lowering of symmetry occurs. In order to model the freely rotating molecule we calculated molecular electron-density wave functions using the *Gaussian92* program for energy-optimized model molecules. The electron-density was then spherically averaged in order to mimic the rotations. The Fourier transform of this spherically averaged electron density provides the scattering factor for the rotating molecule. The displacement parameters obtained from the structure refinement then provide estimates of translational motion.

MS11.06.03 LATTICE-DYNAMICAL CALCULATION OF ATOMIC DISPLACEMENT PARAMETERS (ADPs). Carlo M. Gramaccioli and Francesco Demartin, Università degli Studi, Via Botticelli 23, I-20133, Milano, Italy, Tullio Pilati, CNR-CSRSRC, Via Golgi 19, I-20133 Milano, Italy

    ADPs comparable with the corresponding values obtained from crystal structure refinement can be derived from Born-von Karman lattice dynamics. A rigid ion model has been assumed, where atomic charges and VFF parameters have been deduced from best fit to the vibrational frequencies of a series of similar compounds, either molecular crystals or even ionic, non-molecular

inorganic compounds, such as most minerals.

Besides confirming the physical meaning of ADPs, a detailed interpretation of atomic motion is allowed, also in terms of internal degrees of freedom of atomic groups and their correlated motion. The possibility of correcting bond lengths for thermal motion in the most general case is also provided, since the correlation tensors between the displacement of different atoms can be obtained as by-products; particularly interesting is the link to spectroscopic and thermodynamic properties, and the possibility of checking if empirical potentials are transferable.

In comparison with the parallel interpretation of motion which can be obtained by fitting the individual ADPs, a way which is presently preferred by most crystallographers, the main difficulties of our theoretical calculations are the need of adequate knowledge of empirical potentials, which still have to be developed for many groups of substances, and the harmonic approximation, since no satisfactory model of this kind has yet been developed for anharmonic motion.

However, at least in some problematic instances (pyrope, almandine), where anharmonic behaviour has long been claimed, joint examination of crystallographic and thermodynamic properties compared with the theoretical model has provided a consistent explanation based on harmonic motion and order-disorder transformations.

MS11.06.04 ANALYSIS OF ANISOTROPIC DISPLACEMENT PARAMETERS IN A SERINE PROTEASE Th.R. Schneider, European Molecular Biology Laboratory (EMBL), c/o DESY, Notkestr. 85, 22607 Hamburg, F. Parak, Faculty of Physics, E17 of the Technical University Munich, 85748 Garching

Based on X-ray diffraction data to atomic resolution the structure of a serine protease has been determined at 90, 120, 180 and 300 K. Refinements were performed employing restrained anisotropic displacement parameters (ADP's) as implemented in the program SHELXL93[1]. After convergence several cycles of block-matrix least-squares refinement were run to determine estimated standard deviations for coordinates and displacement parameters. Graphical inspection of vibrational ellipsoids revealed that significant anisotropy in atomic displacements can frequently be found for solvent exposed sidechains and carbonyl oxygens. Numerical analysis of the ADP's originated from the evaluation of the rigid-body test[2] whereby extended parts of the polypeptide backbone were detected as 'potentially rigid'. Fits of physically constrained TLS-models to these regions allow the explanation of parts of the individual atomic displacements in the protein molecule by a temperature dependent disorder of the molecule as a whole. It must be emphasized that, since internal normal modes are not considered in a pure TLS-analysis, the derived magnitudes for the TLS-terms only represent upper limits to the real values[3]. The remaining contributions to the ADP's can be linked to conformational substates, internal dynamics and zero-point motions.

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MS11.06.05 ANISOTROPIC VIBRATIONAL ANALYSIS OF THE SMALL PROTEIN CRAMBIN. Martha M. Teeter* and Boguslaw Stec. Department of Chemistry, Boston College, Chestnut Hill, MA 02167. *Sabbatical address: Max Planck Institute for Biophysics, 60528 Frankfurt/Main, Germany.

Full Matrix Least Squares refinement of the small protein crambin (4.7 kDa, 46 residues) at 0.83 resolution and 130K permits full anisotropic refinement of most atoms in the protein (Stec, Zhou and Teeter, (1995) Acta Cryst. D51, 663-681). With the program RFINE, the protein can be refined by the small molecule

vibrational method of TLS refinement (Schomaker, V. and Trueblood, K. (1968) Acta Cryst. B24, 63-76). This refinement can show how well the atomic displacement for the protein atoms are modeled by rigid body movement. It can also indicate non-rigid body motion, such as disorder, and aid in determination of external or lattice contributions to the anisotropic vibration factors.

Better agreement with individual B value refinement is found with three-rigid bodies rather than with two or one. However, the deviations in single rigid body B values from the individual B values are found to occur at disordered residues. This means that such a plot can be useful to indicate disorder, modeled or unmodeled.

We have used TLS to estimate the percentage of the B values that is due to external vibration. In this approach, we modeled the protein as one rigid body, two rigid bodies and three rigid body. We hypothesized that the common parts of the tensors for these three descriptions would represent the external or lattice contribution to the vibrational factors. This leads to the conclusion that 60% of the motion is external. This is in agreement with Diamond's refinement of a protein using by normal modes (Diamond, R. (1990) Acta Cryst. A46, 425-435), where external vibration was found to dominate the B value.

MS11.06.06 RECOMMENDATIONS ON ADP NOMENCLATURE AND USAGE. Kenneth N. Trueblood, Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569, USA

Modern x-ray and neutron diffraction techniques can give precise parameters that describe dynamic or static displacements of atoms in crystals. However, confusing and inconsistent terms and symbols for these quantities occur in the crystallographic literature. The recommendations of a subcommittee appointed by the IUCr Commission on Crystallographic Nomenclature concerning these quantities will be described. The report of this subcommittee is now under consideration by the IUCr Executive Committee. We anticipate that the entire report will be published in 1996, in *Acta Cryst.* A52.

The chief focus is on anisotropic atomic displacement parameters (ADPs) in the Gaussian approximation. The principal recommendations will be presented, with examples to illustrate their implications. These include:

— With the common Gaussian approximation, use either the quantities U^{ij}, which have dimension (length)^2, or the dimensionless β^{ij} (each of which will be defined). Avoid using those now usually symbolized as B^{ij} which are directly proportional to the U^{ij}, the ratio being $8\pi^2$.

— Avoid using the term "temperature factor", because the phenomenon represented may not be due entirely to thermal motion and because that phrase has been used in several distinct senses.

— Published values of U_{eq} should always be accompanied by their standard uncertainties. The ratio of the minimum to maximum eigenvalues of the corresponding anisotropic displacement tensors should also be published, either in the primary publication itself, or in the secondary (deposition) publication.

Authors of crystallographic software are encouraged to introduce the minor modifications needed to implement the subcommittee's recommendations.