

02-Methods for Structure Determination and Analysis,
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to propagate phase information from those reflexions where it is strongly indicated to those where it is essentially absent. Maximum-entropy extrapolation will perform this task in an optimal fashion.

MS-02.02.04 DETERMINATION OF THE STRUCTURE OF A LARGE PROTEIN BY MAD PHASING: GLUTAMINE PRPP AMIDOTRANSFERASE. by J.L.Smith*, E.J.Zaluzec, and J.-P.Wery, Dept. of Biological Sciences, Purdue Univ., West Lafayette, IN 47907 USA, and Y.Satow, Faculty of Pharmaceutical Science, University of Tokyo, Bunkyo-ku, Tokyo, Japan

Glutamine PRPP amidotransferase is a unusual FeS protein that catalyzes the first step of *de novo* purine biosynthesis. The enzyme is a tetramer or 50-kDa subunits; each subunit contains one Fe_4S_4 cluster. MAD phasing was based on K-edge anomalous scattering by Fe. Multiwavelength data to 3.0Å spacings were measured on imaging plates at beamline 14A at the Photon Factory. The asymmetric unit of the crystals contains one tetrameric molecule. Positions of the Fe_4 clusters were initially determined using data to 5.5Å spacings, and individual Fe atoms were located by analysis of partial-structure Fourier maps at 3.0Å resolution. Experimental phases to 3.0Å were derived from the multiple |Fobs| by a probability treatment similar to the Blow-Crick analysis of errors in isomorphous replacement (Pahker, Smith & Hendrickson(1990) Acta Cryst. A46, 537-540). Once the Fe partial structure was known, phase probability expressions were computed for all experimental observations. The resulting phase coefficients were combined for all observations of each unique reflection without regard to the crystal, asymmetric unit or time of the measurement. The final MAD phase set was used as a starting point for phase refinement by local symmetry averaging and solvent flattening. A procedure was developed for automatic mask generation and rapid, automatic phase refinement (J.T.Bolin, S.W.Muchmore & J.L.Smith, Unpublished), which allowed us to experiment with the phase refinement protocols until we found the most interpretable map. The final 3.0Å electron density was of excellent quality and was easily interpreted for the structure.

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PS-02.02.05 ANHARMONIC THERMAL VIBRATION OF RUTILE (TiO_2) DETERMINED FROM NUCLEAR DENSITY DISTRIBUTION OF MAXIMUM ENTROPY METHOD ANALYSIS

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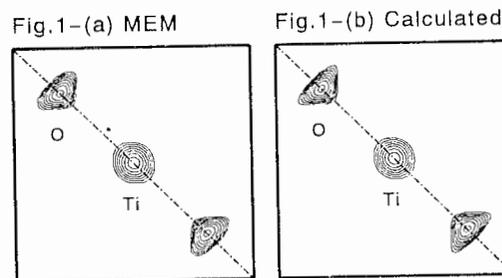
Maximum Entropy Method (MEM) analysis enables us to have an electron density distribution which is consistent with the observed structure factors and least biased with the not-observed structure factors when it is applied to X-ray diffraction data. By applying it to neutron diffraction data, a nuclear density distribution can be obtained, which is considered to describe the thermal

smearing of the nuclei. Such a thermal smearing must be influenced, by all kinds of thermal vibrations regardless harmonic and anharmonic vibrations. It is, therefore, possible to determine thermal parameters of the constituent atoms by the analysis of the nuclear density distributions obtained by the MEM analysis. In this work, the MEM nuclear density distribution of rutile (TiO_2) were analysed by least square refinement and thermal parameters for an effective one particle potential (OPP) were determined. This is a second example of determining the thermal parameters from the nuclear density distribution. First example was done by Takata, Sakata, Larsen, Kubota & Iversen; (1992) *Inaugural Conference, AsCA'92* in the case of Be. In this case, Be atom is located at a special position and it was not necessary to determine the atomic position beforehand. In rutile case, x-coordinate of oxygen has to be determined before the thermal parameters are analysed. In the present study, the atomic position was defined and determined as the position for which the first order moment of nuclear density becomes zero. The obtained x-coordinate was 0.30477, which shows excellent agreement with the previous result of Rietveld refinement by Howard, Sabime & Dickson; (1991) Acta Cryst. B47, 462-468, i.e. 0.30478 (6). The higher moments which are related to thermal behaviors are also calculated, which is very helpful to consider what kind of OPP model to be employed for thermal parameters analysis.

The least square refinement was successfully performed and thermal parameters are obtained as well as the harmonic ones. More specifically to say about anharmonicities of rutile, it was found that Ti atoms had the 4th order anharmonic terms and that O atoms had not only 4th order but also 3rd order anharmonicities, which cause substantial skewness of O atoms in rutile. In Fig.1. both (a) the MEM nuclear densities and (b) the calculated densities from the final thermal parameters determined by the present least square refinement are shown for (002) plane, which are beautifully agreed.

Fig. 1-(a) MEM

Fig. 1-(b) Calculated



PS-02.02.06 Determination of the Anharmonicity Constant of GaAs by Means of the Bijvoet-Relation of the weak (666) Reflection

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Due to the influence of anomalous dispersion the weak (h,h,h) and (-h,-h,-h) reflections of the zinc-blende structure differ from each other. At large scattering vectors this difference, scaled by the Bijvoet-relation

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$$B = \frac{F(h,k,l) * F(h,k,l)' - F(-h,-k,-l)*F(-h,-k,-l)'}{2 * [F(h,k,l) * F(h,k,l)' + F(-h,-k,-l)*F(-h,-k,-l)']} \quad (1)$$

depends solely on the amount of the anharmonic force constant β which is described in terms of an anharmonic one-particle potential expanded up to the third order (Dawson, Hurley & Maslen, 1967)

$$V(x,y,z) = V_{00} + \alpha_1/2 * (x^2+y^2+z^2) + \beta_1 xyz + ... \quad (2)$$

(α_1 describes the harmonic force constant). β can be determined by measuring B near the K-absorption edge of any constituent. This experiment was performed for the (6,6,6) and (-6,-6,-6) reflection of GaAs between $\lambda = 0.90$ and 0.97 \AA near the arsenic K- edge. The HUBER four circle goniometer at the HASYLAB beamline D3 was used. The wavelength was tuned by a silicon (111) double crystal monochromator to an accuracy better than $\delta \lambda = 0.001 \text{ \AA}$. The normalized scattering power was measured from $\langle 111 \rangle$ and $\langle -1, -1, -1 \rangle$ cut single-crystal wafers (A and B surface) having nearly the same thickness of about 0,350 mm. Within the angular limits of the diffractometer ($2\theta \leq 145^\circ$) the (6,6,6) was measureable up to $\lambda \leq 1.0 \text{ \AA}$. The range between $\lambda = 0,9 \text{ \AA}$ and $\lambda = 1.0 \text{ \AA}$ was chosen for measurement. For each wavelength ω -scans were performed for a range of ψ - values (PSI scan) in order to find regions free from Umweganregung. A nearly linear slope of $I(6,6,6)$ and $I(-6,-6,-6)$ was found between $\lambda = 0.9 \text{ \AA}$ and about $\lambda = 0.95 \text{ \AA}$ (Fig.1). Due to the influence of EXAFS oscillations the scattering power did not follow the expected behavior at larger wavelengths, thus the range above $0,95 \text{ \AA}$ was neglected in the further interpretation. The standard deviations of the measured $I(6,6,6)$ and $I(-6,-6,-6)$ are in the 1% region for each λ . In order to enhance the accuracy of the evaluated $B(\lambda)$ the $I(\lambda)$ for both reflections were approximated by straight lines. The evaluated B -values are determined using pairs of experimental $I(h,k,l, \lambda)$ and the value from the fitted straight line. The anharmonicity constant was evaluated to $\beta = -1.75 \pm 0.15 \text{ J/\AA}^3$. Its accuracy is much better than that given in previous publications (Bilderback 1976). The anharmonicity of GaAs is almost the same as that of Ge (Roberto, Battermann & Keating, 1974). This is not surprising taking the predominant covalent bonding character into account.

Bilderback, D.H. Thesis, Purdue University, West Lafayette 1976
Dawson B, Hurley, A.C. & Maslen V.W., (1967) Proc.Roy.Soc.(London) A298 289-306
Roberto J.B., Battermann B.W. & Keating D. (1974) Phys.Rev. B9,2590-2599

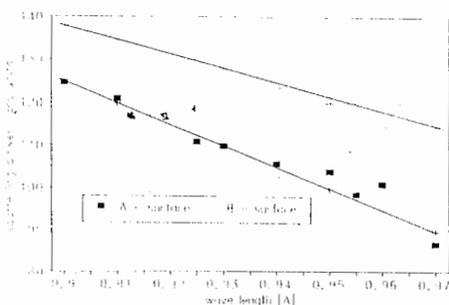


Fig.1: The intensities $I(6,6,6)$ and $I(-6,-6,-6)$ measured at regions free from Umweganregung between $\lambda=0,9 \text{ \AA}$ and $\lambda = 0.97 \text{ \AA}$. The straight lines were obtained by regression of the measured values.

PS-02.02.07 THE SUPERSTRUCTURE OF PbZrO_3 : INVESTIGATION AT Pb L_{III} AND Zr K ABSORPTION EDGES.
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It is demonstrated that a use of an effect of X-ray anomalous dispersion on superlattice diffraction is efficacious for the structure analysis. Intensity measurements on several superlattice diffractions from a PbZrO_3 single crystal have been made as a function of incident X-ray energy in the region of $\pm 0.1 \text{ keV}$ at Zr K and Pb L_{III} absorption edges at intervals of 0.008 keV . From the intensity, after the corrections for synchrotron orbit current, incident spectrum, Lorentz factor and absorption, $|F_{hk\ell}(\epsilon)|^2$, the squared structure factor as a function of incident X-ray energy, is calculated. Observed changes in $|F_{hk\ell}(\epsilon)|^2$ with ℓ even at the absorption edges directly indicate contributions of Pb and Zr atoms to the superstructure in the orthorhombic ab plane. This is consistent with the structure model in the literature. On the other hand, $|F_{hk\ell}(\epsilon)|^2$ with ℓ odd is expected to be independent of the incident energy on the basis of the model; in other words, Pb and Zr atoms have no contribution to the superstructure along the c axis. On the contrary, a significant intensity change in $|F_{hk\ell}(\epsilon)|^2$ at Zr K absorption edge is observed for the superlattice diffractions with ℓ odd; the results show the existence of displacement vector component of Zr atom along the c axis. The advantages of the present method are that elements to be examined can be selected by tuning incident X-ray energy, and that a relative intensity change due to a change in anomalous dispersion terms is quite large even if the superlattice diffraction is extremely weak.

PS-02.02.08 SOME NEW METHODS OF APPLYING MULTI-WAVELENGTH ANOMALOUS SCATTERING DATA.
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Two analytical methods of using multi-wavelength anomalous scattering data are described. The first of these, called AGREE, explores a range of values of $|F|$, the contribution of the non-anomalous scattering, and finds that value which gives the greatest consistency of the anomalous scattering contribution for the different wavelengths, given all the magnitudes $|F^+|$ and $|F^-|$. The information enables both the positions of the anomalous scatterers to be found and also the angle, θ , between F and the real part of the non anomalous scattering - and thus the phase of F .

The second method, called ROTATE, assumes that the positions of the anomalous scatterers are known. Starting with six possible angles θ , uniformly occupying the range 0 to 2π and a value of $|F|$ which is the average of all the values of $|F^+|$ and $|F^-|$ the values of θ and $|F|$ are refined by a least-squares technique which takes into account the standard deviations of the observations. The values giving the least residuals are accepted.

Where there is only one type of anomalous scatterer then for different wavelengths the values of $|F^+|$ and $|F^-|$ should be related by having