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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  $\beta$  which is described in terms of an anharmonic one-particle potential expanded up to the third order (Dawson, Hurley & Maslen, 1967)

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

( $\alpha_1$  describes the harmonic force constant).  $\beta$  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  $0.97 \text{ \AA}$  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  $0,350 \text{ mm}$ . Within the angular limits of the diffractometer ( $2\theta \leq 145^\circ$ ) the (6,6,6) was measurable 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  $\omega$ -scans were performed for a range of  $\psi$ -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  $\lambda$ . 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

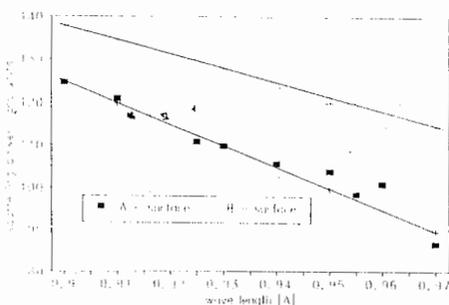


Fig.1: The intensities  $I(6,6,6)$  and  $I(-6,-6,-6)$  measured at regions free from Umweganregung between  $\lambda=0,9 \text{ \AA}$  and  $\lambda = 0.97 \text{ \AA}$ . The straight lines were obtained by regression of the measured values.

PS-02.02.07 THE SUPERSTRUCTURE OF  $\text{PbZrO}_3$ : INVESTIGATION AT Pb L<sub>III</sub> 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  $\text{PbZrO}_3$  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<sub>III</sub> absorption edges at intervals of  $0.008 \text{ keV}$ . 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  $\ell$  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  $\ell$  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  $\ell$  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.  
By Fan Hai-fu, Institute of Physics, Beijing, China and M M Woolfson and Yao Jia-xing\*, Department of Physics, University of York, UK.

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,  $\theta$ , 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  $\theta$ , uniformly occupying the range  $0$  to  $2\pi$  and a value of  $|F|$  which is the average of all the values of  $|F^+|$  and  $|F^-|$  the values of  $\theta$  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

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$$\frac{|F^+|^2 - |F^-|^2}{r''}$$

the same for all wavelengths (Karle, J, 1984, *Acta Cryst* A40, 1-4). In a process called REVISE observed anomalous intensities are modified, taking into account their standard deviations, so that the relationship is obeyed. Pre-processing the data with REVISE improves the results obtained with AGREE and ROTATE.

Using three-wavelength Photon Factory data with the structure of core streptavidin (Hendrickson, W A, Pähler, A, Smith, J L, Satow, Y, Merritt, E A and Phizackerley, R P, 1989, *Proc Nat Acad Sci* 86, 2190-2194) the best results gave a mean phase error of 54.3° for 4,018 reflections with a map correlation coefficient of 0.549.

Finally, criteria are suggested for the selection of suitable wavelengths for multi-wavelength anomalous scattering to give the best conditions for defining phases.

### 02.03 – Strategies for *ab initio* Structure Determination from Powder Data

**MS-02.03.01 DIRECT DETERMINATION OF POWDER STRUCTURES BY ENTROPY MAXIMISATION AND LIKELIHOOD RANKING.** By G. Bricogne, Department of Molecular Biology, Biomedical Centre, Box 590, 751 24 Uppsala, Sweden; and LURE, Bâtiment 209D, 91405 Orsay, France.

Classical direct methods for structure determination from single-crystal data are based on the derivation of intensity statistics and of probabilistic relations between structure factors. The three-dimensional indexing of the observed data is deeply embedded both in the formal structure of these relations and in their computer implementations.

The hallmark of the powder diffraction field, on the other hand, is the phenomenon of intensity overlap which spoils this indexing scheme to a considerable and irreparable extent. The direct determination of powder structures therefore requires a new formal framework in which the internal book-keeping of the statistical relations between structure factors would be decoupled from the mode of presentation of the data. The method of phase determination based on entropy maximisation and likelihood ranking [Bricogne (1984), *Acta Cryst.* A40, 410-445; Bricogne & Gilmore (1990), *Acta Cryst.* A46, 284-297] does fulfill this criterion, in that phase relations result from maximising entropy while the data are consulted by likelihood evaluation. Extending this method to powder data – and to data from other disordered specimens such as fibres – is then simply a matter of deriving the likelihood criterion adapted to the pattern of intensity overlap corresponding to each type of specimen disorder.

This lecture will describe the mathematical techniques by which this goal was achieved [Bricogne (1991), *Acta Cryst.* A47, 803-829]. It will be shown that the loss of information caused by intensity overlap in powder diagrams may be put on the same footing as the usual loss of phase for single-crystal data by a judicious use of a multiplicity-weighted metric and of the *n*-dimensional spherical geometry associated with that metric. Structure determination from powder diffraction data is thus cast in the form of a *Hyper-Phase Problem* in which the dimensionality varies from one data item to another. This geometric picture enables probability distributions for overlapped intensities to be derived not only under the standard assumption of a uniform distribution of random atoms – thus extending Wilson's statistics to powder data – but also for non-uniform distributions such as those occurring in maximum-entropy phase determination. The corresponding conditional probability distributions and likelihood functions are then derived. The possible presence of known fragments is also considered.

Besides yielding the desired extension of the aforementioned direct method, and thus enabling the *ab initio* determination of crystal structures from powder data, these new distributions and likelihood functions will be shown to lead to new methods of data normalisation; to new statistical tests for space-group assignment; to a generalisation of the partial-structure recycling method; and to a new criterion for conducting crystal structure refinement against powder data.

This analysis was implemented as part of a long-standing collaboration with Chris Gilmore and coworkers [Gilmore, K. Henderson & Bricogne (1991), *Acta Cryst.* A47, 830-841] and has been the basis of a rapidly growing number of *ab initio* determinations of inorganic and organic crystal structures from X-ray powder diffraction data [Tremayne, Lightfoot, Mehta, Bruce, Harris, Shankland, Gilmore & Bricogne (1992), *J. Solid State Chem.* 100, 191-196; Tremayne, Lightfoot, Glidewell, Harris, Shankland, Gilmore, Bricogne & Bruce (1992), *J. Mater. Chem.* 2, 1301-1302; Shankland, Gilmore, Bricogne & Hashizume (1993), *Acta Cryst.* A49, in the press; Lightfoot, Tremayne, Harris, Glidewell, Shankland, Gilmore & Bruce (1993), *Material Science Forum*, in the press].

Current developments are directed towards the application of the multichannel maximum-entropy formalism [Bricogne (1988), *Acta Cryst.* A44, 517-545] which will enable the method to deal more