

SNBL (SWISS-NORWEGIAN BEAMLINE) ON BM1



From left to right:
P. Pattison,
K. Knudsen,
H. Emerich,
W. Van Beek;
in the car: H.P.
Weber.

The Swiss-Norwegian facility is split into two branch lines: one dedicated to single-crystal diffraction (2.5 mrad fan of radiation, focused beam, high-resolution monochromator) and the other to powder diffraction, EXAFS and topography (1 mrad fan of radiation, unfocused, channel-cut monochromator). To illustrate the kind of research carried out on the two beamlines, we present and discuss one recent investigation from each branch line.

A NEW TECHNIQUE: PHYSICALLY ESTIMATED TRIPLET PHASES

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Information on phase is lost in the general diffraction experiment with hard x-rays, a fact which gives rise to the so-called phase problem in crystallography. This is in contrast to diffraction of visible light or electrons, where the scattered beams can be collected by suitable lenses, to provide directly a reconstruction of the scattering object. However, even with hard x-rays, phase information can be retrieved from specially designed experiments.

Electron diffractionists have known for about 50 years that phase information is available as interference effects between several beams diffracted simultaneously in *perfect crystals* (n-beam diffraction) [1, 2].

Experimental evidence was obtained later with x-rays [3]. This direct, physical approach to structure-factor phase acquisition became of much greater practical importance when several groups [4, 5, 6] in the early 1980's found that phase effects can be significant also with truly *mosaic crystals*. Mosaic, or non-perfect crystals are vastly more abundant than the perfect specimens.

STATUS

Theoretical descriptions of n-beam x-ray diffraction have been developed by several authors on different levels of approximation; for a review see Weckert and Hümmel [7]. In a recent contribution Thorkildsen and Larsen have considered the influence of various parameters describing the radiation and its interaction with a finite, non-perfect diffracting crystal, on the solution of the Takagi equations for three-beam diffraction [8]. The experimental side has grown very strongly over the past decade, first and foremost through the diligent work of

Weckert, Hümmel and collaborators in developing highly sophisticated instrumentation and measurement techniques. Triplet phases can now be estimated physically even for crystals of macromolecules. At present, phases have been acquired successfully for at least 5-6 different proteins.

EXPERIMENT

The n-beam experiment in its simplest form comprises three beams ($n = 3$), one incoming and two diffracted beams. A very simple representation is shown in Figure 1. In the crystal the incident beam \mathbf{K}_0 can be scattered into the \mathbf{K}_H direction by two different pathways, either by the direct wave diffracted at the lattice planes H, or by the *Umweg* wave diffracted first at lattice planes L, and then at the H-L planes. In analogy with holography experiments the total wavefield in direction \mathbf{K}_H will depend both on the amplitudes of the component waves - F_H , F_L and F_{H-L} - and the phase difference $D = (f_L + f_{H-L}) - f_H$. The latter quantity can be rewritten as a phase sum $F_3 = f_{-H} + f_L + f_{H-L}$, a so-called three-

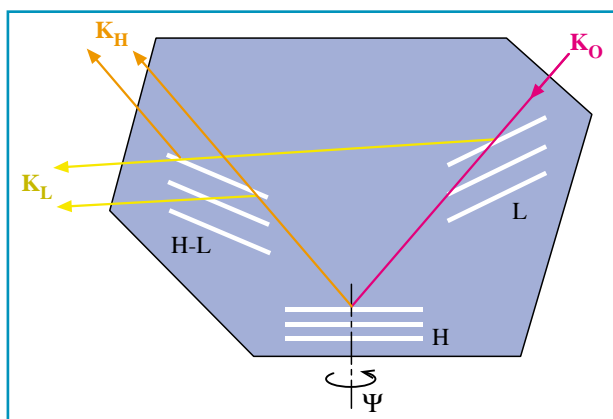


Fig. 1: A three-beam diffraction case illustrated in real space. K_0 is the incoming beam, K_H and K_L are the primary and the secondary diffracted beams, respectively.

phase structure invariant, which is a physically unique quantity of the crystal. In the experiment the crystal is rotated about the normal to lattice planes H, such that the planes L are brought successively into and out of the diffraction position, while reflection H remains fully excited. During this rotation, called a Y-scan, the primary diffracted intensity I_H is recorded. The interference between the diffracted beams which contains information about the triplet phase F_3 , is projected out as a characteristic modulation of the intensity profile. In addition to this phase dependent «signature», the primary diffracted intensity may be enhanced (*Umweganregung*) or depleted (*Aufhellung*) by phase independent contributions from the other beams.

APPLICATIONS

Physically estimated triplet phases (PETP) have several interesting applications, of which only a few have been realized so far. An obvious application is to initiate the determination of molecular structures. Apparently, only one unknown small structure has been solved from PETP [9]. Feasibility studies have shown that solution of macromolecular structures is within reach. Other applications include determination of absolute structure and studies of quasicrystals [7].

A NEW APPLICATION

Phases are much more sensitive to small changes in structure than are the structure-factor amplitudes that can be derived from the intensities measured in the standard diffraction experiment. Therefore, PETP could presumably be used as well to discriminate between several possible and closely-related models of a structure. This novel application was explored in a study of

the complex α -D-glucose Σ NaCl Σ H₂O (6:3:3) in space group $P3_1$, with unit-cell volume $V = 4180 \text{ \AA}^3$. A structure of the complex has been published (Model CA) [10]. However, there exists one alternative solution (Model GE) [11]. We found from refinements that the primary difference in structure is an interchange of the Cl and water O positions, which is accompanied by smaller, mainly translatory displacements of glucose rings, and a reorientation of water molecules and one of the glucose OH groups. This leads to a reversal of the polarity in chains of H-bonds along the polar c axis. The changes in structure imply significant changes in phase for about 50% of the structure factors. In contrast, triplet phases being sensitive to the model are extremely scarce. Thus, only about 0.05% of the calculated three-phase invariants with amplitudes suitable for phase measurement had a triplet-phase difference $|\Delta F_3| > 30^\circ$. By measuring several *model-sensitive* three-phase invariants and comparing with those calculated for the refined models CA and GE we expected initially to be able to

identify one correct model of the pair.

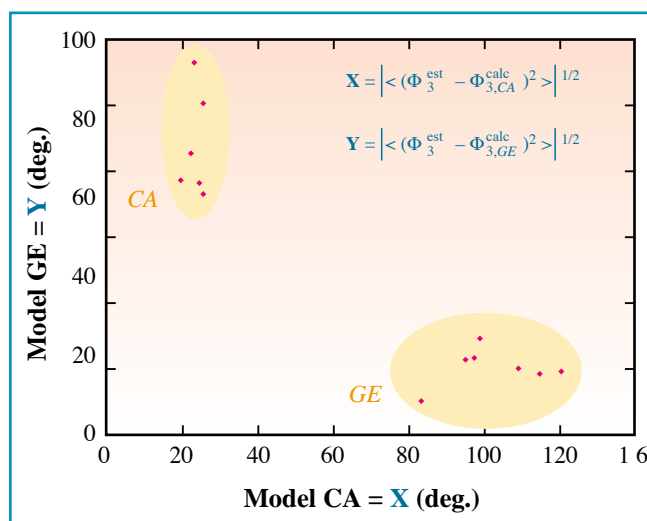
EXPERIMENTAL

Thirteen crystals, all cut from one large single crystal of the complex were subjected to physical phase estimation which involved studies of model-sensitive triplet phases. Each phase assignment was based on the intensity profiles mapped out in Y-scans of the pair of triplets -H/L/H-L and H/-L/-H+L, corresponding to phases $+F_3$ and $-F_3$, respectively. Two distinct right-handed cell matrices are possible in this space group. It was ascertained that the choice of unit cell of the crystals was internally consistent and in agreement with the indexing of the native data sets CA and GE. In total 309 pairs of three-beam interference profiles were collected for the thirteen crystals. The measurements included 89 different triplets.

RESULTS

The estimated triplet phases have been compared with the parent values calculated for the refined structure models CA and GE. A statistical analysis provides highly significant evidence that two structures are present, but do not coexist in the same crystal. Six crystals are in agreement with model CA, seven crystals fit the GE model. The estimated random error in the phase assignment is 19.7° ; for all crystals the model with the largest mean variance can be rejected at a significance level $p \ll 0.001$. The results are presented in Figure 2. The cell parameters of the two structures are equal within 1 esd., as determined with synchrotron radiation, $\lambda = 1.0000 \text{ \AA}$.

Fig. 2: Classification regions given for the mean errors calculated relative to the two models.





As an example, the intensity profiles for two triplets, one model insensitive with $|\text{IDF}_3| \sim 20^\circ$ (a), and one model sensitive with $|\text{IDF}_3| \sim 170^\circ$ (b), are shown in Figure 3 for both structure models. In each pair, the upper profile corresponds to the triplet -H/L/H-L. The modified intensity is plotted relative to the intensity at the two-beam level, $I_H = 1.0$, as a function of Ψ . Note the inverted asymmetry and the reversal of high/low amplitude from top to bottom profile between the two triplet pairs of Figure 3(b), in accord with phase assignments differing by about 160° . A full account of this work will be published [12].

The Y-scans were carried out on a 6-circle diffractometer (Prof. Hümmer, Univ. of Karlsruhe) located on the Swiss-Norwegian Beamline. ■

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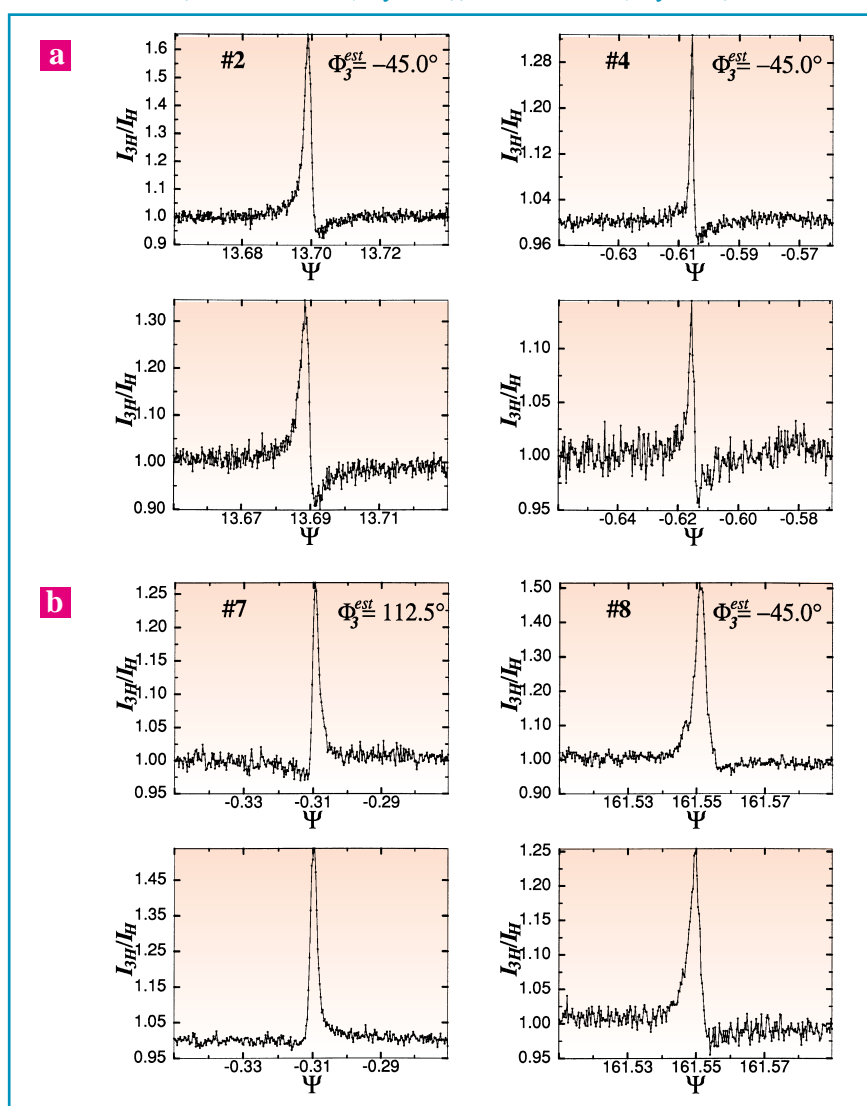
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Fig. 3: Y-scan profiles of four triplet pairs. Estimated triplet phase, F_3^{est} , and crystal serial no. are given in the upper profile of each pair. (a) Triplet 3 0 -4/ -2 4 -1/ -1 -4 5, $F_3CA = -48o$ (Cryst. #2), $F_3GE = -65o$ (Cryst. #4). (b) Triplet -2 -2 -3/ 1 4 -7/ 1 -2 10, $F_3CA = 105o$ (Cryst. #7), $F_3GE = -66o$ (Cryst. #8).



EXAFS: HYDRIDE TREATMENT CATALYSTS

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EXAFS is the only method suitable to determine the local structures of bulk, non-crystalline materials under arbitrary atmosphere temperature and pressure conditions. From an experimental point of view, EXAFS is a particularly simple technique; essentially, one measures x-ray absorption spectra of the samples of interest as a function of energy; the skill is mostly in the analysis of the spectra, and progress has come mostly from computer-intensive modelling. The technique has been widely used to investigate the structure of supported catalysts. Up to recently, only the contribution from the first shell of atoms (mostly M-O) to the EXAFS spectra was analyzed; this yielded the coordination number of the absorber atom. However, with the recent development of multiple scattering theory, the analysis of the contribution from the higher shells (mostly M-M interaction) has become possible; it

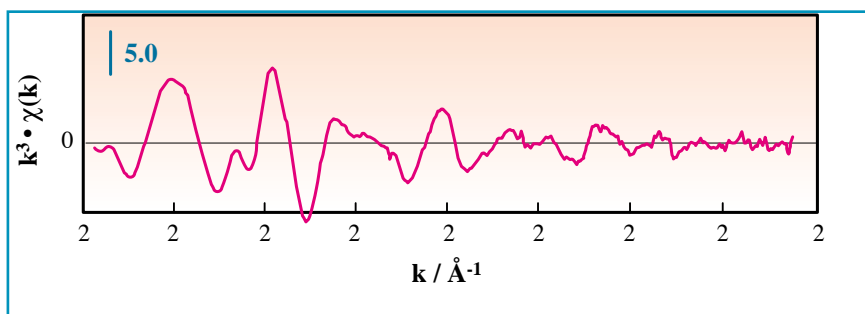
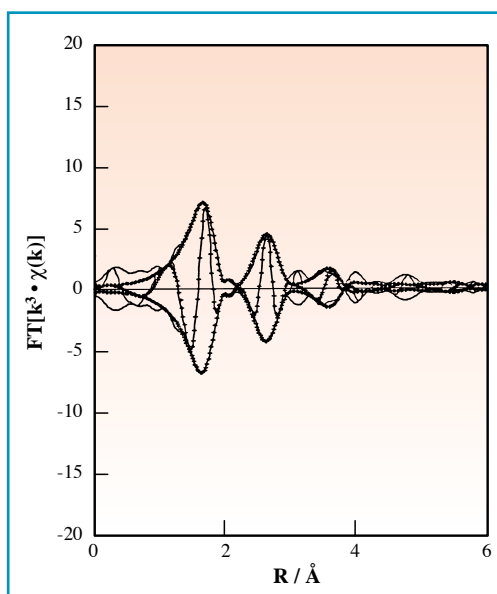


Fig. 1: k^3 -weighed EXAFS function of HTC-1.9 catalyst in the oxidic state. Obtained from the raw absorption data by subtracting background and normalizing to one absorber atom.

Fig. 2: Fourier-transformed k^3 -weighed EXAFS function. This radial distribution function reveals the number of atoms located at distance R from absorber atom (coordination number); the distance displayed is about 0.2 - 0.5 Å shorter than the actual distances due to a phase factor.



yields information about the shape and sizes of catalytic particles adsorbed on surfaces as well as on the interaction between particle and support surfaces. Prins and his group (ETH-Z) have recently characterized Hydride Treatment Catalysts (HTC), using EXAFS amongst other methods. The salient features of these catalysts are their high specific nickel surface area, together with their high reducibility. This uncommon combination of high nickel dispersion with low (but effective) interaction of metal with support raised questions as to how the Al_2O_3 support stabilizes the metal particles. Absorption spectra were collected in the oxidic, reduced and passivated states. Figure 1 and Figure 2 show the results obtained for the oxidic state. The Ni cations in the NiO particles are surrounded by 6 oxygen anions as in bulk NiO; the Ni-O distance (2.04 Å) inferred is close to the distance found in

bulk NiO (2.09 Å). As Ni loading of HTC was reduced, the coordination number due to the Ni-Ni contribution decreased dramatically. This small coordination number for Ni-Ni suggests that the NiO particles on the Al_2O_3 support are small. From a comparison with various NiO particle models of varying size and configuration (ranging from Ni (111) layer to cubic NiO (100) particles) it was concluded that the NiO particles in the oxidic catalysts were built up of successive (111) layers. This shape of the NiO particles implies that they interact strongly with their Al_2O_3 support. This was confirmed by the observation of a Ni-Al contribution at low Ni loading. A possible model for such a particle is shown in Figure 3. ■

SOME HISTORY

The Swiss-Norwegian collaboration was born at a workshop hosted by the ESRF in Frankfurt, Germany, in February 1989. On this occasion, in a hallside encounter, C. Riekel (ESRF) suggested to H.-P. Weber, University of Lausanne (UNIL), and F. Mo, University of Trondheim (UNIT), that they pool their resources and construct a bi-national beamline at the ESRF. On the Norwegian side, this idea was quickly given form by F. Mo and D. Nicholson in a proposal that involved additional commitment from UNIT to basic and applied research in physics, chemistry and materials science. The then Rector, Prof. R. Lenschow, and Director H. Skaar enthusiastically supported the proposal and submitted it for approval to the Collegium of the University. On 5 February 1990, UNIT, as the first institution, allocated 2 mill. NOK towards the construction of the Swiss-Norwegian beamline.

The Swiss side (next to H.-P. Weber, G. Chapuis and M. Fehlmann) was at first surprised by the alacrity with which their partners-to-be had converted a good yet vague idea into a fully-fledged project. However, when the Swiss counterparts (at first UNIL and the Swiss Federal Institute of Technology in Zurich) realized how modest the beam time fraction, to which Switzerland, as a full member of the ESRF, was entitled, they quickly moved into action and started raising funds. The ensuing Swiss-Norwegian Beam Lines Consortium was approved and fully funded by the respective national research councils and universities by the autumn of 1990. The universities of Oslo, Berne, Geneva, Stavanger College and the Swiss pharmaceutical industry (Hoffmann-LaRoche, Novartis) joined as full consortial members at a later date.

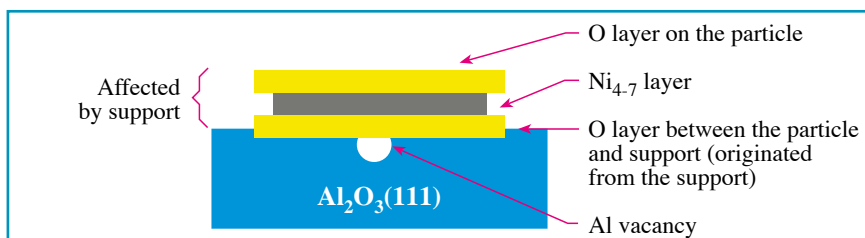


Fig. 3: Possible structure of the NiO particles.