MS.55.3

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Using phonon measurements to study electrons in superconductors

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Recent inelastic neutron and x-ray scattering measurements of lattice vibrations in superconductors revealed exceptionally strong electron-phonon coupling in many materials. In the cases of conventional superconductors, it is well described by standard theory; in copper oxides it is entirely unexpected. One can take advantage of this strong electron-phonon coupling to investigate electronic charge degrees of freedom by measuring phonon spectral functions. One can obtain detailed information of the superconducting gap as well as the competition between charge density wave and superconductivity. The talk will survey recent results beginning with conventional strong-coupling superconductors YNi_2B_2C and $NbSe_2$, then moving on to unusual charge fluctuations that renormalize bond stretching phonons in cuprate superconductors.

Keywords: phonon, superconductor, dynamics

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Time-resolved X-ray diffraction study of $LiNbO_3$ under pulsed external electric field

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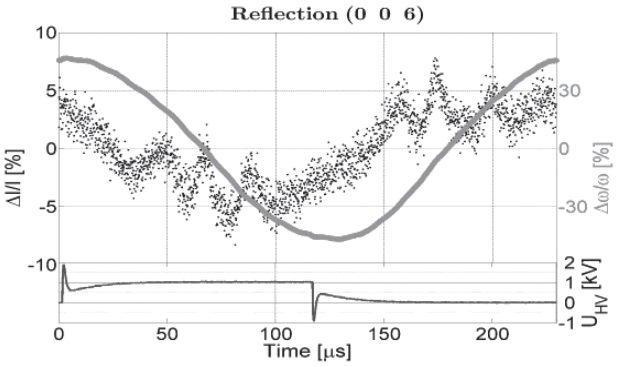
Interaction of a crystal with a permanent external electric field is well known in form of macroscopic phenomena, such as elastic deformation and converse piezoelectric effect. The atomistic origin of the corresponding physical properties of solids (elasticity and piezoelectricity) may be understood on the basis of precise investigations of the atomic movements induced by an applied electric perturbation. In our studies we investigated the response of ferroelectric $LiNbO_3$ single crystals to a perturbation caused by a pulsed external electric field. Using a stroboscopic like (modulation-demodulation) technique, involving periodic switching of the amplitude and direction of the applied field, which is described elsewhere [1]. For the periodic modulation we switched a high voltage (HV) with U ~ 1kV. To measure at the resonance frequency of the crystal system, the modulation frequency of the applied voltage is in the wide range of 1Hz - 10kHz. The time-dependent crystal response was studied by measuring ω-rocking curves of a few Bragg reflections. Sufficient statistics where collected by summing up over about 10^6 succeeding HV cycles for each ω-angle of a rocking curve.

We performed our experiment using a home lab X-ray source, with a high resolution four-circle diffractometer and an open point detector with a high counting rate. The samples were produced in a sandwich like structure with a 0.65mm thick z-cut $LiNbO_3$ crystal plate covered by thin Gold contacts on both sights. Macroscopic bending mode vibrations of the specimen could be excited and visualised using Resonant Ultrasonic Spectroscopy (RUS) calculations. These bending modes are detected by time resolved X-ray diffraction from periodic oscillations of peak positions of near surface Bragg reflections. Due to the [001] orientation of the crystal plate we probed two symmetric (00L) reflections quantitative but a few (H0L) (with L>H) reflections qualitative accessible in Bragg geometry. In addition, significant periodic variations of relative Bragg peak intensities could be resolved if the cycle frequency of external perturbation coincides with an eigenmode of macroscopic mechanical vibration of specimen.

Changes in the order of 5% have been observed if the external E-field of 2kV/mm is switched within 200ns at cycle frequencies of 4.45kHz. Figure shows resonance case with the switching below. It is not clear yet what caused this intensity changes and the finding might be explained by several effects. The experiment opens the chance to detect the atomic response to an external elastic perturbation of a crystal.



[1] S. Gorfman, O. Schmidt, M. Ziolkowski, M. von Kozierowski, U. Pietsch, *J.Appl. Phys.* **2010**, *108.*

Keywords: ferroelectricity, charge_density_oszillation, time resolved_X-ray_diffraction

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Phonons observed by Laue diffraction on a continuous neutron source

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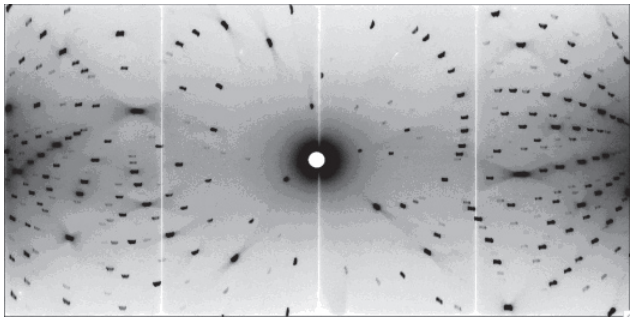
After languishing for many decades as a technique mainly for aligning single crystals, neutron Laue diffraction has been reborn thanks to the success of X-ray Laue diffraction for protein crystallography at synchrotrons and to the development of efficient large-area image-plate detectors. The Laue technique with thermal neutrons is proving very successful for small-molecule crystallography on crystals frequently no larger than 0.1 mm^3, first on VIVALDI at the ILL in France [1], and now on KOALA at ANSTO in Australia [2], and is opening neutron diffraction to fields of structural chemistry previously deemed impossible. The volumetric view of reciprocal space, such a strength in the detection of phase changes, incommensurability and twinning, does come at a price though: all scattering, inelastic as well as elastic, contributes to the observed Laue patterns. Can we turn this to our advantage?

The geometry of the projection of the four-dimensional dispersion surfaces of coherent inelastic neutron scattering [3] onto the two dimensions observed by neutron Laue diffraction is derived. The scattering from low-energy acoustic phonons dominates, resulting in a 'bow-tie' of thermal diffuse scattering symmetric about the plane of diffraction for each Laue spot. Simple analysis of the shapes of the 'bow ties' for different Laue spots permits direct and rapid determination of the sound velocities, with no need for particular alignment of the crystal on modern Laue diffractometers with large-solid-angle detectors. Experimental Laue patterns for Al_2O_3 from VIVALDI illustrate several

geometrical aspects of the manifestation of thermal diffuse scattering, and yield values of the sound velocities in good accord with values obtained by ultrasound attenuation measurements.



A typical long-exposure neutron Laue pattern for Al_2O_3

[1] G.J. McIntyre, M.-H. Lemée-Cailleau, C. Wilkinson *Physica B* **2006**, *385-386*, 1055-1058. [2] P.D.W. Boyd, A.J. Edwards, M.G. Gardiner, C.C. Ho, M.-H. Lemée-Cailleau, D.S. McGuinness, A. Riapanitra, J.W. Steed, D.N. Stringer, B.F. Yates *Angew. Chem.* **2010**, *49*, 6315-6318. [3] C.J. Carlile, B.T.M. Willis *Acta Cryst. A* **1989,** *45*, 708-715.

Keywords: neutron_Laue_diffraction, image-plate_detectors thermal_diffuse_scattering

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Structural identification and antiproliferative activity of metallodrugs

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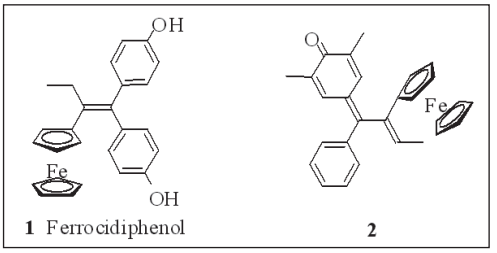
The first line drug used to combat hormone-dependent breast cancers is tamoxifen, the archetypal selective estrogen receptor modulator (SERM). Since tamoxifen is active only against tumours that are estrogen receptor positive (ER+), and frequently gives rise to resistance after prolonged use, the search for related but different agents has intensified considerably over the last few years.

We have designed novel therapeutic agents which are based on organometallic compounds that express high antiproliferative activity against breast cancer cells [1], [2]. We found that ferrocidiphenol **1** is characterized in vitro by a strong antiproliferative effect on both hormone-dependent (MCF-7) and hormone-independent (MDA-MB-231) breast cancer cells (IC_{50} values around 0.5 μM), whereas OH-Tam has an effect only on hormone-dependent cells.

Many complexes have been synthesized, allowing the study of the structure-activity relationship. Electrochemical experiments have suggested that the active metabolite of these compounds is a quinone methide. This hypothesis is now supported by isolation and X-ray structural determination of the quinone methide **2** [3].

The structural requirements for activity seem to be 1) the presence of a ferrocene group, 2) a conjugated linker, 3) aromatic para-substitution by a protic function and 4) an ethyl group residing on the same carbon as the ferrocene group. X-ray absorption spectroscopy has been used to obtain addition information on these compounds.



1 Ferrocidiphenol **2**

XANES spectra of ferrocidiphenol and its diphenyl analogue (2-ferrocenyl-1,1-diphenyl-but-1-ene) have been compared to XANES of ferrocene. Spectra indicate that the iron electronic properties are affected by the group that replaces a hydrogen of the unsubstituted Cp ring [4].

[1] S. Top, A. Vessières, G. Leclercq, J. Quivy, J. Tang, J. Vaissermann, M. Huché, G. Jaouen, *Chem. Eur. J.* **2003**, 9, 5223-5236. [2] A. Vessières, S. Top, P. Pigeon, E. Hillard, L. Boubeker, D. Spera, G. Jaouen *J. Med. Chem.* **2005**, *48*, 3937-3940. [3] D. Hamels, P. Dansette, E. A. Hillard, S. Top, A. Vessières, P. Herson, G. Jaouen, D. Mansuy *Angew. Chem. Ed. Int.* **2009**, *48*, 9124-9126 [4] I. Ascone, D. Hamels, P. Pigeon, M. Salome, Y Joly, T. Prange, A. Vessières, S. Top, G. Jaouen. Manuscript in preparation.

Keywords: organometallic, anticancer, XANES

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XANES spectroscopy for determination of the 3D nanoscale atomic structure

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The status of modern theoretical analysis of the experimental x-ray absorption spectra to extract structural parameters will be presented. Novel method for extracting of 3D structural information on the basis of advanced quantitative analysis of X-ray absorption near edge structure (XANES) realized in "FitIt" software [1] is described. The approach is based on the fitting of experimental XANES data using multidimensional interpolation of spectra as a function of structural parameters and adva nced "ab-initio" XANES simulations. Small number of required ab-initio calculations is the main advantage of the approach, which allows one to use computationally time-expensive non-muffin-tin methods. The possibility to extract information on bond angles and bond-lengths is demonstrated and it opens new perspectives of quantitative XANES analysis as a 3D local structure probe. As XANES spectrum can be measured simultaneously, one can use XANES to study the local structure in time-dependent experiments within a time domain of 100 picoseconds and less.

Advanced theoretical analysis based either on self-consistent muffin-tin model or full potential (non-muffin-tin) theory, coupled with DFT geometry optimization have been applied to extract structural information from experimental XANES data. The status of modern research shows that XANES spectroscopy and its "ab initio" theoretical analysis can be a useful tool for the investigation of both local structure and electronic subsystem of many advanced materials without long range order. The present approach can provide a subatomic level (i.e., 0.01- 0.03 angstrom) of accuracy in the determination of the interatomic distances and several of degrees in the determination of the bonding angles at specific atomic site of nanostructured materials without long range order.