



Session VI - Tuesday, September 1 - late afternoon

PL6

FERECRYSTALS (TURBOSTRATICALLY DISORDERED MISFIT LAYER CHALCOGENIDES)

David.C. Johnson

Department of Chemistry, University of Oregon, Eugene, Eugene OR 97401-3753 USA
davej@uoregon.edu

Ferecrystals are misfit layer compounds with extensive rotational disorder between the constituent layers described by the general formula $[(MX)_{1+x}]_m[TX_2]_n$, where X = Se or Te, M = Sn, Bi, Pb, or a rare earth metal, and T = Ta, W, Nb, V, Mo and Ti. The modulated elemental reactant has enabled us to prepare series of compounds with targeted m and n values and specific nanoarchitectures. When n is larger than one, turbostratic disorder also can occur between the X-T-X trilayers. The individual MX and TX_2 layers are crystalline within the planes with grain sizes on the order of 10 to 100 nm. There are structurally abrupt interfaces between the two structures but layer-to-layer miss-orientation prevents long-range order. In general,

ferecrystals are poised between the crystalline and amorphous state consisting of independent layers, but there are several examples where long range order in small regions has been observed.

The talk will present our current understanding of the mechanism of formation and a summary of the structural data collected on these compounds using both x-ray and electron microscopy techniques. The connection between the unusual structure, electronic structure and physical properties will also be summarized.

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S6-L1

STRUCTURE ANALYSIS OF FERECRYSTALS BY ADVANCED METHODS OF TRANSMISSION ELECTRON MICROSCOPY: POSSIBILITIES AND LIMITATIONS

W. Neumann^{1,3}, C. Grosse¹, I. Häusler², R. Atkins³, D. B. Moore³, J. Ditto,
M. Beekman⁴, D.C. Johnson³

¹Institute of Physics, Humboldt University Berlin, Newtonstr. 15, 12489 Berlin, Germany

²BAM Federal Institute for Material Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany

³Department of Chemistry, University of Oregon, Eugene, Eugene OR 97401-3753 USA

⁴Department of Natural Sciences, Oregon Institute of Technology, Klamath Falls, OR 97601 USA
wolfgang.neumann@physik.hu-berlin.de, wsn@uoregon.edu

Ferecrystals (FCs) [1] are a special class of misfit layer compounds (MLCs) [2] described by the general formula $[(MX)_{1+x}]_m[TX_2]_n$, where X = Se or Te, M = Sn, Bi, Pb, or a rare earth metal, and T = Ta, W, Nb, V, Mo and Ti. FCs are a state of matter between crystalline and amorphous having incommensurate intergrowth structures with in-plane crystallinity, abrupt interfaces, layer-to-layer misorientation, and turbostratic disorder. The Modulated Elemental Reactants (MER) method [3] enables the preparation of FCs for arbitrary n and m.

We will illustrate the possibilities and limitations of high-resolution transmission electron microscopy (HRTEM) and high-resolution scanning transmission electron microscopy (HRSTEM) for the analysis of the crystal structure and crystal imperfections of various FC-systems on the atomic scale. For the interpretation of the HRTEM images, computer simulations as a function of the microscope and specimen parameters are necessary [4]. An important task of the structure analysis of FCs is the measurement of the misorientation of the individual grains

within the layers. It will be demonstrated how precession transmission electron diffraction (PED), nanobeam transmission electron diffraction (NBED) and scanning NBED (SNBED) can be applied for the automatic phase and orientation analysis of the crystallites in the layers [5-7].

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7. I. Häusler, R. Atkins, M. Falmbigl, S.P. Rudin, W. Neumann, D.C. Johnson, *Z. Kristallogr.* **230** (1), (2015), 45.

S6-L2

DIFFUSE SCATTERING AND ATOMISTIC SIMULATIONS IN PROTOTYPE ANTIFERROELECTRIC MATERIAL PbZrO_3

M. Paściak¹, T. R. Welberry², J. Hlinka¹

¹*Institute of Physics, Czech Acad. Sci., Na Slovance 2, 18221 Prague 8, Czech Republic*

²*Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia*
pasciak@fzu.cz

Lead ziconate (PZO) has recently regained attention with new ideas revolving around the mechanism of antiferroelectric (AFE) phase transition (PT) observed for this compound. Since there is no direct link between the paraelectric cubic and orthorhombic phases, the explanation of the emergence of low-temperature AFE order is not straightforward. To solve a puzzle one has to find a relationship between three lattice instabilities observed across the PT – antiparallel displacements of Pb atoms and two rotation (tilting) modes of oxygen octahedra.

Results of X-ray inelastic as well as Brillouin scattering experiments has directed Tagantsev et al. to propose a flexoelectric coupling to be the main physical mechanism behind the AFE PT [1]. In this picture the dominating instability is of the ferroelectric type and it is ‘transformed into an antiferroelectric phase transition’ due to strain-gradient – polarization coupling. Octahedra rotations are induced by lead displacements. It is pointed out that the AFE phase can be treated as a ‘missed incommensurate phase’ as in the absence of the fourth-order anharmonic terms, the flexoelectric coupling would induce an incommensurate instability.

On the other hand, Hlinka et al. on the basis of infra-red, Raman and THz spectroscopy as well as group theory considerations proposed an alternative picture of the PT mechanism where soft ferroelectric branch is coupled by a trilinear term to two oxygen octahedra tilt modes [2]. Importantly in this picture the flexoelectric coupling is not a necessary condition for the antiferroelectricity, but it is the coupling to octahedra tilts that is essential for the transition mechanism.

We enter this discussion with extended diffuse scattering (DS) experimental results (see Fig. 1) and atomistic molecular dynamics simulations. The shell model that we are using was already proven to give very good agreement between modeled and experimental DS intensities (coming mostly from phonons) [3]. This assures that the model correctly describes dynamics of the system (includes all im-

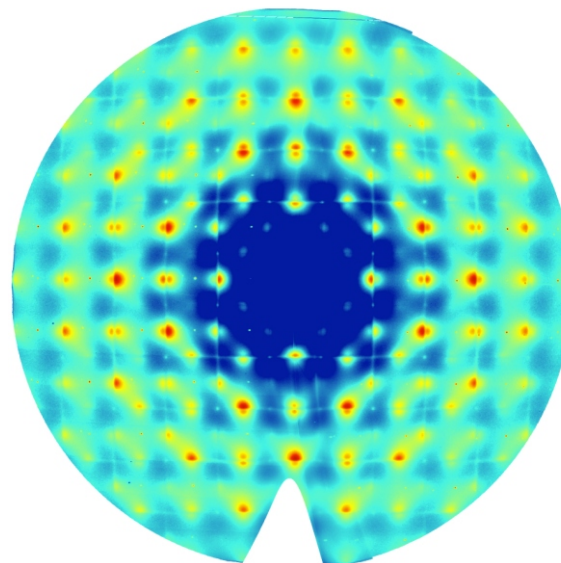


Figure 1. Experimental X-ray diffuse scattering from cubic PbZrO_3 on $hk0.5$ plane.

portant instabilities). We trace temperature changes of the reciprocal space features related to polar correlations and octahedra rotations. According to our model the latter ones are observed at temperatures well above the PT.

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S6-L3

3D- PDF ANALYSIS OF DIFFUSE SCATTERING FROM UREA-ALKANE INCLUSION COMPOUNDS

A. Simonov^{1,2}, C. Mariette², A. Bosak³, L. Guerin², B. Toudic², P. Rabiller²

¹*Inorganic Chemistry Laboratory, University of Oxford, South Parks Road
Oxford, UK*

²*Institut de Physique de Rennes, University of Rennes 1, 263 av. Général Leclerc
35042 Rennes, France*

³*European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble, France
arkadiy.simonov@alumni.ethz.ch*

Diffuse scattering analysis presents a unique tool which allows to investigate various types of non periodic crystals, including crystals ordered in less three dimensions. In the current contribution the one-dimensional para-crystalline sublattice of alkane in urea-inclusion compound is investigated using 3D- PDF approach.

Urea inclusion compounds are host-guest composite materials. Urea forms a well-ordered host sublattice with hexagonal channels which can be occupied by linear alkane molecules. The periodicity of inclusion molecules is not compatible with the host, and also the host and the guest are connected only through weak Van-der-Waals interaction, which gives rise to extremely complicated behaviour manifested e.g. in a wide variety of phase transitions to three- four- and five-dimensional phases as a function of temperature and alkane length [1].

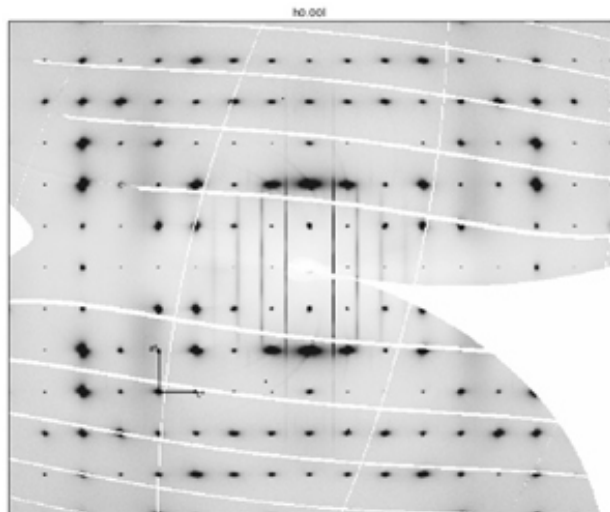


Figure 1. Urea-alkane inclusion compound, h0lm layer

In the present study we report the 3D- PDF analysis of diffuse scattering presented in the hexagonal three dimensional phase of urea inclusion compounds. It is shown that the diffuse scattering can be explained by a simple model of one-dimensional para-crystal. The alkane molecules in one channel show only very small interaction with the host lattice around them and also with the molecules in the next channel. The relation between local order and the ordered lower phases is discussed.

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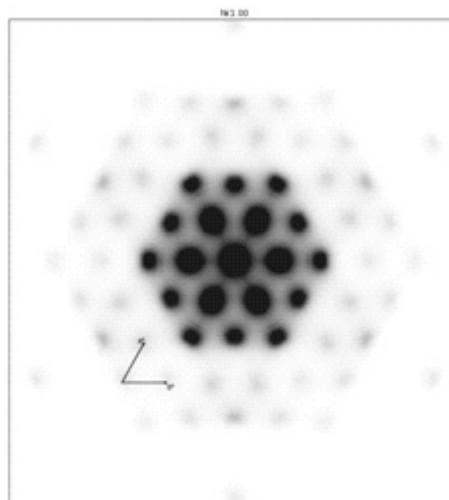


Figure 2. Urea-alkane inclusion compound, hk01 layer

S6-L4

ELECTRON PROPAGATION IN PERIODIC AND QUASI LATTICES VIA OPTICAL SPECTROSCOPY IN THE RARE-EARTH CADMIUM BINARY ALLOYS

N. M. R. Armstrong¹, K. Mortimer¹, T. Kong², S. Budko², P. Canfield², T. Timusk¹

¹Department of Physics and Astronomy, McMaster University, Hamilton, ON, Canada

²Iowa State University, Ames Laboratory and Department of Physics and Astronomy, Ames, IA, USA
armstrong@mcmaster.ca

Quasicrystals and their approximants have traditionally shown quite similar optical conductivities. In early work, the optical conductivities did not have a Drude peak and have shown, with photon energies up to 1 eV, a linear rise from near zero to several thousand $(\Omega \text{ cm})^{-1}$ [1]. In our study of the quasicrystal $i\text{-GdCd}_{7.98}$ and the approximants GdCd_6 and YCd_6 , we do not see this rigid linear conductivity and, in fact, we see a dramatic difference between a quasicrystal and its approximants.

GdCd_6 and YCd_6 are both good approximants to $i\text{-GdCd}_{7.98}$ as their stoichiometries and atomic clusters are similar to the quasicrystal. Further, they also have large unit cells and pseudo 10-fold diffraction patterns as required of a quasicrystal approximant [2]. Thus, these approximants are expected to have similar optical conductivities to the quasicrystal. The quasicrystal $i\text{-GdCd}_{7.98}$, like other quasicrystals, does not have a Drude peak, but instead of a linear optical conductivity, it starts at a small plateau and then monotonically rises to what appears to be an

interband transition above 1 eV. The approximants surprisingly show Drude-like peaks, below 200 meV, which are unexpected given the behaviour in the previous types of quasicrystals approximants (Fig. 1).

Fitting the conductivities using Mayou's generalized Drude model [3], which accounts for electrons traveling diffusively according to $L(t) \sim t^{-\nu}$, we put bounds on the diffusion exponent ν . We find that electron propagation in a quasilattice and a crystalline lattice are significantly different in this system. Specifically, electron wave packets are travelling sub-ballistically in the approximant and are travelling sub-diffusively in the quasilattice.

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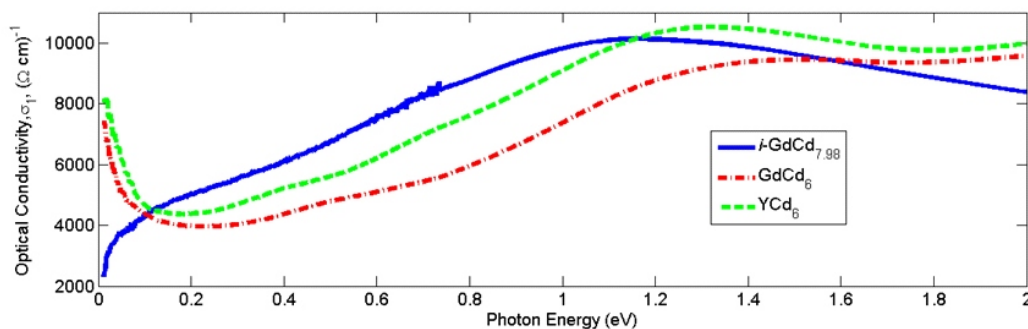


Figure 1. Optical conductivity of $i\text{-GdCd}_{7.98}$, GdCd_6 , and YCd_6 from reflectance measurements.