P.11.01.1

Acta Cryst. (2005). A**61**, C385

Structure/Properties Relationships in doped MgB_2 Single Crystals

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MgB_2 is a two electronic-bands, two energy gaps superconductor with a high T_c of 39K and unusual properties such as temperature and field dependent anisotropy.

Superconducting hexagonal single crystals of pure and Al, C, Mn and Fe doped MgB_2 phase have been grown at a pressure of 30 kbar using cubic anvil technique [1-2] to study the intrinsic properties of MgB_2. The superconducting transition of doped MgB_2 single crystals can be tuned in a wide temperature range between 10 and 39 K by adjustment of the nominal composition. Al [1], Mn and Fe are substituted on the Mg position of MgB_2 and C [2] on the B position. Introduction of disorder by substitution is partly observed.

In order to elucidate structure/properties relationships we have carried out x-ray single crystal measurements on doped MgB_2 single crystals (the composition varies between 1 and 15 % doping material). Additional temperature dependent measurements on pure MgB_2 and Mn doped MgB_2 has been carried out.

[1] Karpinski J., Zhigadlo N. D., Schuck G., Kazakov S. M., Batlogg B., Rogacki K., Puzniak R., Jun J., Muller E., Wagli P., Gonnelli R., Daghero D., Ummarino G. A., Stepanov V. A., *Phys. Rev. B*, *submitted*, cond mat/0411449.
[2] Kazakov S. M., Puzniak R., Rogacki K., Mironov A. V., Zhigadlo N. D., Jun J., Soltmann Ch., Batlogg B., Karpinski J., *Phys. Rev. B*, 2005, **71**, 024533.

Keywords: high-Tc superconductivity, structure-physical properties relationships, X-ray crystal structure analysis

P.11.01.2

Acta Cryst. (2005). A**61**, C385

The Investigation of Crack Propagation in Cleavage Directions on the Surface of SiC by Sclerometry

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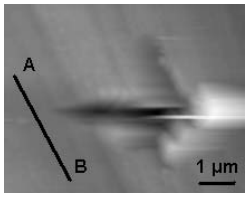
The SiC crystals have been scratched using SPM-Nanoindenter Nanoscan [1]. The studied samples represent thin hexagonal plates with the natural grown surface The values of hardness have been measured for "Si" (23±3 GPa) and "C" (34±4 GPa) sides of the H6-SiC samples with nitrogen impurity of $1x10^{18}$ cm^{-3}. The effect of microcracks along the cleavage direction {1 $\bar{1}$00} (marked AB) occurs with the load about 10 mN, that is shown on the image. Secondary microcracks propagate from the cracks in direction of secondary cleavage {11 $\bar{2}$0}. The width of cracks is in range of 300-600 nm, depth up to 60 nm. The cracks are developed during the scratching with the "face forward" indenter arrangement. The direction "edge forward" does not develop scratches with cracks, but the effect of periodic pile-up's is present. The period is in range of 300-600 nm for given loads. The samples have been turned to achieve various direction of scratching. The differences found between the behaviours of cracks around the scratches made in various directions and different indenter orientations.



[1] Blank V., Popov M., Lvova N., Gogolinsky K., Reshetov V., *J. Mater. Res*., 1997, **12**, 3109.

Keywords: scanning probe microscopy, hardness, structure defects

P.11.01.3

Acta Cryst. (2005). A**61**, C385

Superstructures of Pb-free and Pb-doped $Bi_2Sr_2Ca_2Cu_3O_{10}$ Superconducting Phases

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The structures of Bi-2223 and Bi,Pb-2223 were studied by single-crystal XRD. The structures are characterized by incommensurate modulations, however, they can be conveniently described in 5-fold supercells. An additional O atom was found to be inserted in the Bi-O chains, at the level of approximately every 10^{th} cation, which defines the translation unit of the modulation wave. A partial substitution of Ca by Bi was also observed in both crystals, and the actual compositions of the crystals were $Bi_{2.16}Sr_2Ca_{1.84}Cu_3O_{10.17}$ (*P*222, $a = 27.105(4)$, $b = 5.4133(6)$, $c = 37.010(7)$ Å) and $(Bi_{1.89}Pb_{0.22})Sr_2Ca_{1.89}Cu_3O_{10.18}$ (*Pnnn*, $a = 26.976(7)$, $b = 5.4130(10)$, $c = 37.042(11)$ Å), respectively. The structures of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+\delta}$ series have a strong 2D character with weak interactions between the BiO layers. In the orthorhombic superstructure of Bi-2223 (n = 3), the longitudinal displacement waves of the Bi atoms in two neighboring BiO layers are in phase and, consequently, the transverse waves are out of phase (shifted by 180°). For the monoclinic superstructures of Bi-2212 (n = 2) and Bi-2201 (n = 1), the phase differences between the transverse waves of the Bi atoms in consecutive slabs are 160 and 72°, respectively. The amplitude of the transverse displacement wave increases with decreasing thickness of the slabs (0.139(7) Å in Bi-2223, 0.156(6) Å in Bi-2212, and 0.310(7) Å in Bi-2201).

Keywords: high-T_c superconductor, modulated structure, supercell

P.11.01.4

Acta Cryst. (2005). A**61**, C385

Presence of an Ionic Charge ordering at the Verwey Transition in Fe_3O_4: A Resonant X-ray Diffraction Study

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Magnetite, Fe_3O_4, is a mixed valence system that exhibits many interesting properties, some of them known since the early times. Moreover, magnetite is also on the spot of physicists because of the lack of consensus as to the nature of the metal-insulator transition occurring at T_V=120K (Verwey transition). The real question that remains largely open is the amount of charge, δ, that is going to localize at the octahedral metal sites giving rise to iron charge states of the type $Fe^{2.5\pm\delta}$. To this end we have carried out a series of resonant X-ray diffraction (RXD) experiments in the neighborhood of the Fe K-edge that have revealed distinct signatures of a small charge ordering (CO) compatible with the symmetry of the low temperature structure. The magnitude of the charges, $\delta \approx 0.15$ e^-, has been determined through a refinement of the energy dependence around the of the Fe K-edge of the line shape of 30 selected reflections of the low temperature structure. Our results, in agreement with bond valence sums calculations, are in striking contradiction with previous RXD experiments that have concluded on the absence of any CO in magnetite. This small value of the charge is of fundamental importance and strengthen the argument that covalency effects play a major role in the physics of these strongly correlated compounds. In this paper the strength and limitations of RXD will be discussed as well as, hinting why CO was not observed in previous experiments.

Keywords: charge transfer, iron oxides, DAFS

P.11.01.5

Acta Cryst. (2005). A**61**, C385-C386

Crystal Chemistry and Crystallography of the $Ba_2RCu_3O_{6+x}$ - $SrTiO_3$ System

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Continued world-wide research in high T_c superconductors has lead to the promise of a wide variety of industrial applications. To

implement these applications, the availability of low-cost, long-length, and high performance superconductor wire/tape and cable is critical. Preparation of these wires/tapes involve deposition of $Ba_2RCu_3O_{6+x}$ (R-213, R=lanthanides and Y) films on biaxially-textured buffer/substrates. Two promising processes for preparing buffer/substrates are the Ion Beam Assisted Deposition (IBAD) and the Rolling Assisted Biaxially Textured Substrates Buffer (RABiTS). For a given combination of buffer layers that has been found to promote epitaxial growth of $Ba_2RCu_3O_{6+x}$, there may be unavoidable reactions at the interface between layers. Understanding of interfacial reactions of R-213 phase with the buffer layers will provide information about how to avoid and/or control the formation of second phases. Crystallographic and phase equilibrium data will assist analysis of coated conductor interfaces. This paper describes the crystal chemistry and crystallography of the multi-component systems representing the interaction of $Ba_2RCu_3O_{6+x}$ with the al, $SrTiO_3$ buffer. X-ray and neutron Rietveld refinements were employed for structural studies. Examples of phases that will be discussed include $(Ba,Sr)_3RTi_2O_{8.5}$, $(Ba,Sr)R_2CuO_5$, $(Ba,Sr)Ti_2O_4$, and $(Ba,Sr)_2RCu_3O_{6+x}$, etc.

Keywords: superconductor-substrate interface, $Ba_2RCu_3O_{6+x}$-$SrTiO_3$, coated conductors

P.11.01.6

Acta Cryst. (2005). A**61**, C386

New Molecular Conductors based on [Ni(dmid)$_2$] with TMTTF, TTF and ET as Cations

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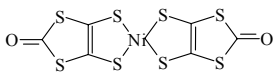
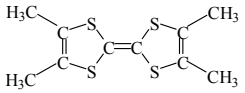
New molecular conductors based on rare π-electron acceptor [Ni(dmid)$_2$] with TMTTF, TTF and ET as cations were synthesized. Investigation of conducting properties revealed that they all are semiconductors. X-ray study of TMTTF[Ni(dmid)$_2$] was carried out.



[Ni(dmid) 2]



TMTTF

A lot of compounds have been obtained containing $[Ni(dmit)_2]^{n-}$ anion analogous to $[Ni(dmid)_2]^-$ anion, where O atom is substituted with S one. Among them are salts with organic π-donors ET, TTF, EDT etc. Some of those salts happened to be superconductors [1-2].

The new semiconducting TMTTF[Ni(dmid)$_2$] salt has a layered structure where cations and anions form mixed regular stacks.

[1] Cassoux P., Valade L., Kobayashi H., Kobayashi A., Clark R., Underhill A., *Coord. Chem. Rev*., 1991, **110**, 115. [2] Tajima H., Inokuchi M., Kobayashi A., Ohta T., Kato R., Kobayashi H., Kuroda H., *Chem.Lett*., 1993, 1235.

Keywords: organic semiconductors, structure-properties relationships, X-ray analysis

P.11.01.7

Acta Cryst. (2005). A**61**, C386

Novel Style of Structure Determination for π-d System by Synchrotron X-ray Diffraction

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Molecular conductor $(DBr\text{-}DCNQI)_2Cu$ undergoes a novel metal-insulator transition at 160K caused by π-d electron interaction, due to the simultaneous appearance of charge order in Cu ions [1] and the CDW in DCNQI molecules in the insulator phase. This phase transition is understood as a unique type of electronic instability caused by cooperation of the Peierls and Mott instabilities. However, the actual three-dimensional (3D) arrangement of these orderings has not been revealed.

In order to obtain the electron distribution in the unit cell by means of synchrotron x-ray measurements, the spatial relation between the charge ordering and the CDW was examined. The charge ordering in the Cu sites as Cu^+ Cu^+ Cu^{2+} along the stacking axis was observed by utilizing the anomalous scattering technique, consistent with previous studies. As for the CDW pattern on DCNQI columns, single crystal structure analysis was conducted.

As a result of these two x-ray experiments' combination, we successfully obtained the 3D pattern, which is different from the structure previously observed. We discuss the implementation to the mechanism.

[1] Hiraki K., Kobayashi Y., Nakamura T., Takahashi T., Aonuma S., Sawa H., Kato R., Kobayashi H., *J. Phys. Soc. Jpn.*, 1995, **62**, 1470.

Keywords: CDW, synchrotron X-ray radiation, structure analysis

P.11.01.8

Acta Cryst. (2005). A**61**, C386

Twin Formation in InP Nanowires Epitaxially Grown on Germanium and Silicon

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Semi conducting nanowires are promising for the integration of III-V based functionalities with Silicon technology. In this work the hetero-epitaxial growth of Indium Phosphide (InP) wires on Germanium and Silicon with a <1.1.1> orientation is discussed. Gold-mediated VLS growth of these wires was performed using either MOCVD or laser ablation. The epitaxial relation between wire and substrate was studied using SEM, cross-sectional TEM and X-Ray Diffraction.

On both Germanium and Silicon substrates, perfect epitaxy of InP was observed, despite the large lattice mismatch of 4% and 8%, respectively. The formation of a series of additional InP orientations was observed with X-Ray Diffraction pole figure measurements. All observed orientations could be ascribed to the presence of rotation twins in the <1.1.1> growth directions and at the substrate wire interface. The presence of some and absence of other orientations could be explained by the occurrence of multiple twinning at the initial stage of wire growth.

Keywords: twinning, iii-v semiconductors, nanowires

P.11.01.9

Acta Cryst. (2005). A**61**, C386-C387

Low Temperature Structural Investigations of the J_1-J_2 Model System $VOMoO_4$

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Frustrated magnets based on transition metal oxides have become subjects of many theoretical and experimental studies in the last ten years [1, 2]. One of the most widely studied model systems is the so-called J_1-J_2 model, i.e. the spin-1/2 Heisenberg antiferromagnet on a square lattice with competing nearest (J_1) and next-nearest (J_2) neighbor antiferromagnetic interactions. Thanks to their structure, Li_2VOSiO_4 and Li_2VOGeO_4 [3] are shown to be the first prototypes of this frustrated two-dimensional system [4, 5] and have enabled to check experimentally several theoretical predictions in the region of the phase diagram in which $J_1 \approx J_2$. This work has been extended these last two years to the closely related system $VOMoO_4$ [6]. $VOMoO_4$ crystallizes in the tetragonal space group $P4/n$ with 2 formula units per cell, the spin-1/2 V^{4+} ions forming a network of VO_5 square pyramids, sharing corners with MoO_4 tetrahedra. The main difference with respect to Li_2VOSiO_4 and Li_2VOGeO_4 (space group $P4/nmm$) is the absence of Li to separate the layers of XVO_5 (X = Si, Ge or Mo).

This contribution will give an overview of recent results obtained by low temperature x-ray and neutron diffraction on the $VOMoO_4$ phase. An anomalous evolution of the lattice parameters [7] which could be related to its magnetic properties was clearly revealed.