

CRYSTAL STRUCTURES OF $Y_5Ni_6B_6C_5$, $Y_5Ni_8B_8C_5$, AND $Y_5Ni_9B_9C_5$
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YNi_2B_2C and other rare earth (R) compounds of the type RNi_2B_2C are of large interest due to their superconducting and magnetic ordering properties. These compounds have tetragonal structure which is composed by stacking of RC and BNi_2B layers along c-axis. Reaction products from a melt sample series of $YNi_{2-x}Ni_{2+x}C$ ($x = 0.2, 0.35$ and 0.5) were investigated by X-ray single-crystal and TEM diffraction to verify that a change of the chemical composition and a variation of the layer arrangement had to lead to new structures. Apart from YNi_2B_2C and the known $YNiBC$ and $Y_3Ni_4B_4C_3$ three metastable compounds could be analysed: $Y_5Ni_6B_6C_5$ and $Y_5Ni_8B_8C_5$ - body-centred tetragonal structures with predicted layer sequences, $Y_5Ni_9B_9C_5$ - primitive tetragonal modulated structure.

Keywords: INTERMETALLICS, CRYSTAL STRUCTURE, X-RAY/ELECTRON DIFFRACTION

COMBINED X-RAY AND NEUTRON POWDER REFINEMENT OF THE MAGNETITE (Fe_3O_4) STRUCTURE BELOW THE VERWEY TRANSITION

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The crystal structure of Fe_3O_4 below the 122 K Verwey transition has been refined using high-resolution X-ray and neutron powder diffraction data ($R_{wp} = 6.81\%$, reduced- $\chi^2 = 5.92$, $a = 5.94437(1)$ Å, $b = 5.92471(2)$ Å, $c = 16.77512(4)$ Å, $\beta = 90.236(1)^\circ$, space group monoclinic $P2_1/c$ with orthorhombic $Pmca$ symmetry constraints applied). The refined model gives direct evidence for charge ordering over four independent octahedral Fe sites, two with a charge of +2.4 and the other two of +2.6. The charge order is driven primarily by a [001] electronic instability, which opens a gap at the transition through a charge density wave mechanism.

Keywords: MAGNETITE CHARGE ORDER Fe_3O_4

GRAPHITE FORMATION ON STEAM-REFORMING CATALYSTS

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Synthesis gas, a mixture of hydrogen, carbon-monoxide and carbon-dioxide, is an important intermediate product in chemical industry. It is produced by the steam-reforming process from a hydrocarbon feedstock and steam. The catalyst used in this reaction is based on supported Ni. At high temperatures and high carbon to oxygen ratio of the feedstock, the formation of graphitic carbon that destroys the catalyst, is a key problem. The study of the elementary chemical processes on single crystal Ni surfaces by scanning tunneling microscopy and density functional theory, combined with structure-activity studies on Ni catalysts, have lead to a detailed picture of the steam-reforming process. Two types of active sites are proposed: a very active one associated with defect sites at the Ni surface and a less active one associated with plane facets. Additives added to the Ni catalyst (e.g. K, Au, S) bind preferentially to the active step sites, which in this way also reduces the risk for graphite formation [1]. Here, the focus will be on the *in situ* characterization of Ni and Ni-Au catalysts by Monte Carlo simulations, X-ray Absorption Fine Structure measurements and simulations and X-ray diffraction [2,3]. Surface alloying of Au in the Ni surface was found by XAFS. Au atoms block defect sites at the Ni surface, increasing the tolerance towards carbon formation.

References

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Keywords: CATALYSIS, STEAM REFORMING, XAFS

CHARGE ORDERING IN MANGANITES: MECHANISMS FOR AN ELECTRONIC LOCALIZATION BEYOND THE ATOMIC LEVEL

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At low temperatures (LT), doped manganites are either ferromagnetic metals (F) or antiferromagnetic (AF) insulators. Nowadays, this experimental magnetism-transport correlation is understood combining theories based on the double exchange (DE) and super exchange (SE) interactions. They describe rather well the magnetic properties of the metallic and insulating phases respectively. The SE theory uses semi-empirical rules named the Goodenough-Kanamori-Anderson (GKA) rules. These rules, when applied to some supposed orbital ordering (OO) of the 3d metal orbitals, allow to predict the AF ordering in many transition metal oxides. Let us recall that the study of the AF phases of manganites by Goodenough has been one of the pioneering work that have helped in establishing these GKA rules, and have consequently justified OO in such compounds. But since doped manganites are mixed-valent systems, OO is concomitant to a Mn^{3+}/Mn^{4+} ionic-type charge ordering (CO) so that electron localisation, in the LT insulating phases of some manganites, is believed to be due to co-operative Jahn-Teller distortions and/or Coulomb repulsion forces. The precise determination, using single crystal neutron diffraction, of the octahedral distortions in the CO phase of $Pr_{0.6}Ca_{0.4}MnO_3$ evidences another possible interpretation for the CO mechanism. Our interpretation of the structural distortions emphasizes the appearance, just below TCO, of ordered Mn-O-Mn molecular objects with ferromagnetically coupled Mn moments. We show that the hypothesis of the existence of such Mn-pairs gives also a clue to interpret the anomaly in the magnetic susceptibility observed at the supposedly purely structural transition.

Keywords: MANGANITES CHARGE ORDERING SINGLE CRYSTAL NEUTRON DIFFRACTION