

LOW TEMPERATURE: A 'NON-INNOCENT' MUST FOR ACCURATE ELECTRON DENSITY STUDIES

P. Macchi A. Sironi

Department of Structural Chemistry, University of Milan, via Venezian 21 20133 Milano

When applying temperature gradients to molecular crystals, significant changes can occur to molecular geometry, intermolecular packing and electronic structure. This may affect the interpretation of the experimental accurate electron density, which becomes less comparable with the gas phase theoretical one. Soft organometallic bonds are easily perturbed, thus offering a vast variety of examples, which will be briefly discussed. Special focus will be on $[\text{FeCo}(\text{CO})_8][\text{N}(\text{Ph}_3\text{P})_2]$, where changes in the molecular geometry occur on cooling the crystal, however without affecting qualitatively the chemical bonding frame. In this context, an extension of the structure correlation principle to the electron density distribution is proposed and interpreted according to the theory of atoms in molecules.

Keywords: ELECTRON DENSITY LOW TEMPERATURE CRYSTALLOGRAPHY TOPOLOGICAL ANALYSIS

NEUTRON DIFFRACTION STUDIES OF OXYGEN ION CONDUCTORS

S. Hull

The ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, United Kingdom

Compounds, which possess high oxygen ion conductivities, have been widely studied owing to their potential applications in fuel cells. The two largest classes of compound are those adopting the cubic fluorite and cubic perovskite structures, or derivatives thereof. Stoichiometric compounds, of which UO_2 and BaCeO_3 are examples of each case, generally only exhibit significant oxygen ion disorder at very high temperatures (>1000 K). Attempts to promote the onset of significant oxygen ion motion at temperatures closer to ambient have concentrated on the use of cation doping, often with the use of lower valence species which generate vacancies on the anion sublattice in order to maintain overall charge neutrality. In general, the ionic conductivity initially increases rapidly with dopant concentration, before falling, as the vacancies tend to aggregate. However, the factors which influence the maximum values of ionic conductivity and the structural features associated with the optimum vacancy concentration are not fully understood. To probe these issues we have conducted single crystal neutron diffraction studies of cubic fluorite structured ZrO_2 doped with Y_2O_3 , using analysis of the quasielastic coherent diffuse scattering to determine the structure and dynamics of the defect clusters present and their dependence on dopant concentration and temperature. In addition, powder neutron diffraction investigations of the perovskite-related (brownmillerite structured) $\text{Ba}_2\text{In}_2\text{O}_5$ have been performed, indicating a phase transition to a dynamically disordered cubic perovskite structure at a temperature of around 1180 K.

Keywords: ZIRCONIA PEROVSKITES DEFECTS

DEVELOPMENT OF LTV CAMERA AT SPring-8 AND VALENCE ORDERING STRUCTURES OF MMX CHAIN COMPOUNDS

K. Toriumi¹ M. Mitsumi¹ Y. Ozawa¹ K. Kusaka¹ H. Kitagawa² T. Mitani³

¹Graduate School of Science, Himeji Institute of Technology ²Department of Chemistry, University of Tsukuba ³Japan Advanced Institute of Science & Technology

For phase transition studies at low temperature, micro-crystal structure analyses, and photo-excited crystallography, a new low-temperature vacuum X-ray camera (LTV camera) has been developed and installed at SPring-8. The camera consists of two vacuum chambers, a crystal on a cold head of He cryostats and an imaging plate detector (IP) being in the main chamber and IP read-out and erasing units in the sub-one. By eliminating X-ray scattering from air and window, we successfully obtained high quality data below 80 K.

We report an application to the study of valence ordering structures and magnetic properties of new metallic MMX chain compounds, $\text{Pt}_2(\text{RCS}_2)_2 \sim \text{I}$ ($\text{R}=\text{Et}(1)$, $\text{n-Bu}(2)$). Magnetic properties of 2 exhibits an abrupt drop of the magnetic susceptibility which corresponds to a change from 1-D antiferromagnetic spin to a spin-singlet state, in contrast to the spin degree of freedom of 1 surviving down to 2 K. It has been revealed by X-ray structure analyses that the valence-ordering structures of 1 and 2 are close to $-\text{Pt}^{2.5}-\text{Pt}^{2.5}-\text{I}-\text{Pt}^{2.5}-\text{Pt}^{2.5}-\text{I}$ in room temperature phase but change to $\text{Pt}^{2+}-\text{Pt}^{3+}-\text{I}-\text{Pt}^{2+}-\text{I}$ with lattice distortion in low-temperature phase. The lattice distortion in LT phase causes alternation of the exchange interaction between spins on each dimer units. The alternation increase with increase of the lattice distortion, resulting in the spin-singlet state of 2, though the spin degree of freedom in 1, in which the lattice distortion is small, is persisted at low temperature.

Keywords: NEW X-RAY CAMERA, LOW TEMPERATURE CRYSTALLOGRAPHY, VALENCE ORDERING ANALYSIS

POLYMER ELECTROLYTES-FROM CRYSTAL STRUCTURE TO CONDUCTIVITY

Y. G. Andreev I. Martin-Litas Z. Gadjourova P. G. Bruce

¹School of Chemistry, University of St. Andrews, St Andrews, Fife KY16 9ST, Scotland

Over the last decade the St. Andrews group established crystal structures of a number of polymer electrolytes, which consist of salts dissolved in high molecular weight poly(ethylene oxide) (PEO). We have carried out systematic studies of 1:1, 3:1 and 4:1 (number of ether oxygen atoms per cation) crystalline peo:salt complexes. The most recent and complex structures were solved using a new powerful structure determination technique based on simulated annealing. This method was developed by us for ab initio solution of crystal structures containing highly flexible molecules, e.g. PEO, from powder diffraction data. The method has been successfully applied to the structure solution of a 6:1 complex with lithium hexafluoroarsenate which still remains the most complex molecular structure determined to date from powder diffraction. The unusual structural features of this and similar complexes, with lithium hexafluorophosphate and lithium hexafluoroantimonate, in which the cations are located in cylindrical tunnels formed by PEO and are not coordinated by anions, have prompted conductivity studies. Surprisingly the crystalline 6:1 complexes conduct and conduct better than the amorphous phases of the same composition. Subsequent studies show that the conductivity in crystalline polymer electrolytes can be further enhanced by using anionic dopants.

Keywords: POLYMER ELECTROLYTES POWDER DIFFRACTION STRUCTURE DETERMINATION