10-Physical and Chemical Properties of Materials in Relation to Structure (Superconductors, Fullerenes, etc)

PS-10.01.10 X-RAY DIFFRACTION STUDY OF Nd₄CuO₄ By I.P. Makarev∗, V.N. Molchanov, R.A. Tarayan and V.I. Simonov, Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia; M. Bleiberg and M. Merisalo, Department of Physics, University of Helsinki, Helsinki, Finland.

Single-crystal X-ray diffraction studies have been carried out on Nd₄CuO₄, a parent structure for electron-doped superconductors, at 296K and 20K. The data have been collected on a spherical specimen (0.01400(5) cm in dia.), previously tested for absence of violations of the space group I4/mmm, and for absence of twinning.

In the specimen under study, the refined site occupancies indicate deficiency in neodymium (qₙₐ₈=0.945(1)) and oxygen content (qₒ₈=0.922(1)). The results of our investigation show the significant deviation of the displacement parameters of Nd from the harmonic law. From the obtained structure parameters, the deformation electron density distribution has been determined. This distribution shows the peak of 4l electrons and an asphericity of the inner shells of electrons for the Nd atom. The residual density peaks of 3d electrons of the Cu atom are also observed. Recent results from this study will be presented and discussed.

PS-10.01.11 ON THE STRUCTURE OF SUPERCONDUCTING ORTHO-II PHASE OF YBa₂Cu₃O₇−Δ By Thomas Zeiske, Dietmar Holthuizen and Rainer Sonntag, Hahn-Meitner-Institut Berlin and Institut für Kristallographie der Universität Tübingen, D-1000 Berlin 39, Glienicker Str. 100, Germany.

Our studies of oxygen ordering in superconducting YBa₂Cu₃O₇−Δ (Tc=53K) by single crystal X-ray diffraction lead to a quantitative structure for the ortho-II phase in the Y-Ba-Cu-O system.

From the intensities of superstructure reflections, we derived a structural model that confirms the ortho-II type of oxygen ordering by alternation of Cu-O-Cu and Cu-Cu chains in the basal plane. Furthermore, and probably most important, we could show that the asymmetric oxygen coordination of Ba cations caused by this oxygen ordering leads to displacements of Ba. The Ba cations shift by about 0.03 Å in the [100] direction towards the Cu-O-Cu chains (Zeiske et al., 1992. Physica C, 194, 1). These displacements are confirmed by anomalous scattering near the K absorption edge of Ba observed by synchrotron X-ray diffraction. Changes in structure factors of h02 0 (0 h 0) ortho-II superstructure reflections are due to Ba displacements. Possible contributions from displacements of other atoms were found to be 5(13)% of basal contribution (Zeiske et al., 1993, Physica C, in press). A rigid ion model shows that the Ba displacements stabilize the ortho-II structure by reducing its lattice energy. The Ba shift calculated by the model for δ = 0.035Å is in close quantitative agreement with the experimental observations.

PS-10.01.12 NEW SUPERSTRUCTURE IN YBa₂Cu₃O₇−Δ DETERMINED BY X-RAY DIFFRACTION. By R. Sonntag∗, D. Holthuizen and Th. Zeiske, Institute of Crystallography, University of Tübingen and Hahn-Meitner-Institut, Berlin, Germany.

The superconducting transition temperature, Tc, of the high temperature superconductor YBa₂Cu₃O₇−Δ is known to depend not only on the oxygen stoichiometry, but also on the specific ordering of the oxygen atoms in the basal Cu-O planes. Such details are established by precise structure determinations, which can only be performed by neutron or X-ray diffraction.


X-ray measurements on a YBa₂Cu₃O₇−Δ crystal have shown a new superstructure with wave vector (0.55, 0, 0). We found 8 symmetry independent superstructure reflections in the 00l layer. Q-scans over the superstructure reflections in the directions of the reciprocal axes did not show broadening with respect to Bragg reflections. A detailed structure determination is in progress and will be presented at the conference.

PS-10.01.13 (CRYSTALLINE AND MAGNETIC ORDERING IN THE MONOCLINIC PHASE OF THE LAYERED PEROVSKITE PAMC). By P. Harris∗, J. Lebech, Department of Solid State Physics, Risø National Laboratory, Denmark, F.K. Larsen, Department of Chemistry, University of Aarhus, Denmark, and N. Achim, Department of Physics, Københavns Universitet, Copenhagen, Denmark.

The layered perovskite (CH₃)₂(CH₃CO)₂Br (PAMC) is an example of an antiferromagnet that shows weak ferromagnetism. The small ferromagnetic moment is believed to originate from antiferromagnetic exchange interactions of the form D (1 0 2) (N. Achim, T. Matsuyama and T. Yoshimura, Phase Transitions 1989, 28, 71), an interaction which is possible because the low crystal symmetry allows the magnetic moments in the pure antiferromagnets to tilt without change of symmetry. In addition PAMC exhibits a large sequence of structural phases. It consists of (CH₃COO)₂ layers sandwiched between propylammonium chains. The anisotropy group-hypersurfaces may lead to the C₂ axis in the octahedra in four different positions (P. Mørløf, H. Kind and W. Høiør. Phys. Rev. B, 1988, 38, 5012). At high temperatures all four positions are equally probable (tetragonal symmetry), but upon cooling there is a gradual freezing of the bond and the structure becomes orthorhombic and finally monoclinic.

In order to understand the interactions between the crystal structure and the magnetic structure we have performed an elastic neutron scattering experiment and a neutron X-ray experiment on the low temperature monoclinic C₂ plane of PAMC. The neutron experiment was done on the double-axis spectrometer TAS at Risø, Roskilde, Denmark, using neutrons of wavelength 2.0 Å. The X-ray experiment at 8 K was done at Department of Chemistry, University of Aarhus, Denmark, using MoKα radiation.

We have determined the crystal structure of the low temperature C₂ plane and found superstructure reflections of the form C₂n+1≌ with a modulation vector of [100]. The modulation wave is a twinning vector of [100]. In addition, the temperature dependence has been determined of the monoclinic distortion and of the intensity of the scattered reflections. The new conclusion is that there seem to be strong interactions between the magnetic structure, the monoclinic distortion and the modulation wave.