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

PS-10.01.14 SUPERCONDUCTIVITY AT 94 K IN A NEW Hg-BASED CUPRATE, HgBa$_2$Cu$_3$O$_{y+6}$ by S.N. Putintseva, E.V. Anisimov, O.Chmaissenn, M. Maretzki, Chemical Department, Moscow State University, 119899, Moscow, Russia, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899, USA, Laboratoire de Cristallographie CNRS-IFJ, BP 166, 38042 Grenoble cedex 9, France, AT&T Bell Labs, Murray Hill, NJ 07974, USA.

A new Hg$_2$-Te$_2$ superconductor, HgBa$_2$Cu$_3$O$_{y+6}$, has been synthesized and characterized by X-ray powder diffraction, EDS analysis, scanning electron microscopy, a.c. magnetic susceptibility and electric resistivity. The latter measurements revealed a transition into a large diamagnetic state at 94 K and a drop of resistivity at the same temperature, indicating that HgBa$_2$Cu$_3$O$_{y+6}$ is the first Hg-based cuprate superconductor. The estimated susceptibility signal corresponds to more than 50% of ideal diamagnetism, indicating bulk superconductivity.

The samples were prepared by solid state reaction between stoichiometric mixtures of BaCuO$_2$ and HgO in sealed silica tubes heated up to about 800°C during 5 h and then cooled slowly in the furnace.

The composition of this phase was confirmed by EDS analysis. The average metal ratio found for 8 measurements was Hg:Ba:Cu = 38(1):47(2):25(1) with the standard deviations between parentheses. Besides Hg, Ba, Cu, and O, no other element was detected on the spectra.

The X-ray powder pattern was indexed in a space group P4/mmm with the lattice parameters: $a = 3.879(5)$Å, $c = 9.509(5)$Å. This tetragonal compound is the first member of the homologous series Hg$_2$Ba$_2$Cu$_3$O$_{y+6}$ ($y = 1$). The next member of this family HgBa$_2$Rco$_3$O$_{y+6}$ ($y = 2$) was synthesized earlier (Putintseva et al., Acta Crystallography A, 1991, 26, 1299-1301). The value of the $y$-cell parameter for the different members of this homologous series can be calculated with a formula $y = 9.5+3(n-1)$, similar to that for the TlBa$_2$Ca$_2$Cu$_3$O$_{y+3}$ ones.

The structure of Hg$_2$-1201 was refined by Rietveld analysis of powder X-ray data. The structural arrangement of Hg$_2$-1201 is illustrated by the layer sequence (CuO$_2$)(BaO)(HgO)(BaO)(CuO$_2$). It is quite similar to that of TlBa$_2$Ca$_2$Cu$_3$O$_{y+3}$, except for the oxygen stoichiometry of the HgO and TiO$_2$$_5$ layers. For the former, 5 is very small and this depletion is possible because the cumbell coordination is appropriate for the Hg$^{2+}$ cations. For the latter, the TiO$_2$$_5$ layer is only slightly oxygen depleted, which creates the appropriate coordination for the thallium cations, either a distorted octahedron or a five-coordinate polyhedron. This different behavior for attaining the optimal hole concentration is due to the different crystal chemistry of the Ti$^{4+}$ and Hg$^{2+}$ cations.

PS-10.01.15 MAGNETIC ORDER IN THE PHOSPHIDES Hg$_2$Fe$_2$P$_2$$^P_2$, Nd$_2$Co$_3$P$_2$$^P_2$ and Ho$_2$Co$_2$P$_2$$^P_2$. By M. Rechuis, B. Ohlaidid, T. Vonhoff and W. Jeitschko, Institut Lase-Langevin, Grenoble (France) and Anorganisch-Chemisches Institut, Universitat Münster (Germany).

Magnetic susceptibility measurements with a Faraday balance show that the magnetic moments of the CO atoms of these hexagonal Z$_h$Fe$_2$P$_2$-type phosphides order ferromagnetically at 140 K and 152 K for Nd$_2$Co$_3$P$_2$ and Ho$_2$Co$_2$P$_2$, respectively, whereas the Fe atoms of Hg$_2$Fe$_2$P$_2$ are essentially nonmagnetic (M. Reclus and W. Jeitschko, J. Phys. Chem. Solids, 1989, 50, 83-86). Our magnetization measurements of single crystals with a SQUID magnetometer and our neutron powder diffraction data show that the three Co sites with tetragonal phosphorus environments carry magnetic moments of approximately 0.2 $\mu_B$ while the Co site with square-pyramidal phosphorus coordination has a moment of 0.9 $\mu_B$. The hexagonal c-axis is the easy axis of magnetization for both Co compounds. The magnetic moments of the Nd atoms in Nd$_2$Co$_2$P$_2$ order all antiparallel to the Co moments. In contrast, in Ho$_2$Co$_2$P$_2$ the Ho moments are aligned parallel to the Co moments. The magnetic order of the lanthanoid moments sets in gradually below about 60 K and thus seems to be induced by the ferromagnetic cobalt sublattice. The magnetic moments obtained from the refinements of the 2 K neutron diffraction data are 1.8 $\mu_B$ and 7.7 $\mu_B$ for the Nd and Ho atoms, respectively. They are thus smaller than the theoretical values of 3.27 $\mu_B$ and 10.0 $\mu_B$, indicating considerable deviations from the full order for this temperature.

In Ho$_2$Fe$_2$P$_2$, the Ho moments order ferromagnetically at the Curie temperature $T_C = 3.3$ K. The refinement of the neutron diffraction data suggests, that only one half of the Ho moments is aligned nearly parallel to the c-axis with a magnetic moment $\mu_{ap} = 7.5$ $\mu_B$/Ho. This value is smaller than the theoretical one of $\mu_{ap} = 10.0$ $\mu_B$/Ho likely because of crystal field effects.

PS-10.01.16 CORRELATION BETWEEN TWEENING, TWINNING, AND FLUX PENETRATION IN YBa$_2$(Cu$_{1-x}$Fe$_x$)$_3$O$_{y+6}$. By W.W. Schmahl*, Y. Rco, E. Brecht and H. Fuchs, Fachbereich Materialwissenschaft, Technische Hochschule Darmstadt, Germany.

The decrease of the orthorhombicity with increasing x in substituted YBa$_2$(Cu$_{1-x}$Fe$_x$)$_3$O$_{y+6}$ (M=Er, Co, or Al), leads to a decrease in lamellar spacing between the [110] twin walls when x approaches 0.02. The phase change to macroscopically tetragonal symmetry (x > 0.03) occurs when the twin wall spacing gets approximately equal to or smaller than the thickness of the twin walls (30-50Å). In the macroscopically tetragonal material, the (110) and (100) twin orientations interpenetrate, resulting in a cross-hatched twin microstructure. From AC susceptibility measurements we found, that in the lamellar regime (0 ≤ x ≤ 0.03), the intergrain flux pinning force density is proportional to the spacing between twin walls, while Tc remains almost constant. In the twin regime, the pinning force density is independent of x while Tc decreases linearly with x. Hence the twin walls are not only ineffective for flux pinning but they rather act as channels for penetration of the intergrain magnetic flux into the grains. Flux line motion in any direction is facilitated by the cross-hatched network formed by the interpenetrating (110) and (110) "twin walls" in the twin microstructure for x > 0.03.

PS-10.01.17 ON THE STRUCTURE OF NdSr$_2$Cu$_2$NbO$_6$. By J.-E. Jørgensen and N.O. Hornshøj, Department of Chemistry, University of Aarhus, DK-8000 Århus C, Denmark.
NdSr₂Cu₄NO₃ is a pervoskite type compound isostructural with LaSr₂Cu₄NO₃ which contains a CuO₂-La₂CuO₃ sandwich as well as NO₃⁻ octahedra. The structure is therefore analogous to a YBa₂Cu₃O₇ structure in which the linear Cu-O chains have been replaced by NO₃⁻ octahedra. NdSr₂Cu₄NO₃ was prepared by firing stoichiometric mixtures of Nd₂O₃, SrCO₃, CuO, and NO₂ in air at 1370°C for 16 hours. Attempts to introduce superconductivity in NdSr₂Cu₄NO₃ by substitution of Ca for Nd was unsuccessful.

The structure of NdSr₂Cu₄NO₃ was studied by time of flight neutron powder diffraction. Rietveld refinements were performed in space groups P4/mmm, P4/mnm, and P4/m. The NO₃⁻ octahedra are spread in the a-b plane and initial refinements showed that the octahedra are displaced from ideal corner sharing in such a way that neighbouring octahedra are rotated in opposite directions around the c-axis. Slight reflections were observed and the final refinement was therefore performed in space group P4/mnm with oxygen in the NO₃⁻ layers statistically distributed over the 4n (x 1/2 0) positions. The rotation angle around the c-axis for the NO₃⁻ octahedra was found to be 14.4°.

Although no super-lattice peaks were found in the neutron data, electron diffraction indicates that the structure locally has P4/mnm symmetry. Bond lengths and bond valency sums for NdSr₂Cu₄NO₃ will be compared with the corresponding quantities for high temperature superconducting cerates.

**PS-10.01.18 EVIDENCE FOR A THREE-DIMENSIONAL MAGNETIC ORDERING IN Gd₄Co₄O₁₄**

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We have studied the magnetic ordering of Gd₄Co₄O₁₄ by neutron diffraction on isotopically enriched single crystals. Below T = 6.4 K Gd magnetic moments order antiferromagnetically with the wave vector k = (0,0,0). Ferromagnetic Gd layers parallel to a-b plane are antiferromagnetically stacked along [001]. Cu²⁺ ions in Gd₄Co₄O₁₄ order at T = 285 K to a LaCo₁₀ type antiferromagnetic structure with the propagation vector k = (4/3,4/3,0). Fig. 1 illustrates the magnetic structure of Gd₄Co₄O₁₄ at 1.5 K. We have investigated the temperature dependence of the intensity of a few magnetic reflections from room temperature down to 1 K. The intensity of 4/3,4/3 magnetic reflection (Fig. 2) increases continuously with decreasing temperature up to 45 K below which it starts to decrease and shows a maximum at about 20 K. There is a further sharp anomaly at about 7 K at which the intensity of the reflection becomes practically zero. These neutron results are in agreement with the temperature of magnetic susceptibility which also shows anomalies at 7 and 20 K. Search for magnetic reflection at Q = (4/5,4/5,0), (4/5,4/5,2) and (4/5,4/5,3) and other incommensurate positions at 7 K did not reveal any magnetic intensity. These results indicate that at this temperature three dimensional ordering of the Cu sublattice disappears. Long temperature anomalies at the temperature variation of the intensity of 4/3,4/3 reflection obviously result from the interaction of the Cu and Gd sublattices which order with different and incommensurate wave vectors. Above the ordering temperature of Gd sublattice the antiferromagnetic Cu²⁺ planes polarize antiferromagnetically gadolinium planes. But as the ordering temperature of Gd sublattice is approached, ferromagnetic exchange interaction becomes dominant in the Gd planes. At 7 K presumably due to this frustration effect the copper sublattice loses its three dimensional order.

**PS-10.01.19 STRUCTURAL FLUCTUATIONS IN METALLIC SODIUM.** By H. Abe, K. Unshima, K. Hoshide, T. Suzuki and K. Kurokawa, Institute of Applied Physics, University of Tsukuba, Japan.

Metallic sodium undergoes martensitic phase transformation from hcp to bcc structure at 37 K (Mm). We have performed neutron elastic and inelastic scattering experiments from metallic sodium to understand detailed structural informations over a temperature range of 15 to 300 K. The spherical single crystal was prepared in liquid paraffin above the melting point (97°C) and gradually cooled down to room temperature. The size of the specimen was 18 mm in diameter and the mosaic spread was 20°. The data were collected with the use of a triple-axis spectrometer at the beam line 50 of JRR-3M, JAERI. Phonon dispersion curves from 200 K to 4K were measured along high symmetry directions. There were no peculiar temperature changes for T(110) branch. The temperature dependence of integrated intensity and full width at half maximum (FWHM) was obtained from the (110)bcc Bragg reflection. They have increased drastically at 4K due to the structural change which took place, after an incubation time of the order of few hours. We also observed peculiar Huang scattering around the Bragg reflection. Above 4K both the integrated intensity and FWHM were decreased where Huang scattering disappeared. It is thought that these phenomena are important to understand the phase transformation in metallic sodium.