PS-10.01.14 SUPERCONDUCTIVITY AT 94 K IN A NEW Hg-BASED CUPRATE, $HgBa_2CuO_{4+\delta}$. By S.N.Putilin[1],*, E.V.Antipov[1], O.Chmaissem[2], and M.Marezio[3,4], [1]Chemical Department, Moscow State University, 119899, Moscow, Russia, [2]National Institute of Standards and Technology, Gaithersburg, Maryland, 20899, USA, [3]Laboratoire de Cristallographie CNRS-UJF, BP 166, 38042 Grenoble cedex 09, France, [4]AT&T Bell Laborator ies, Murray Hill, NJ 07974, USA.

A new high-T_c superconductor, $HgBa_2CuO_{4+\delta}$, 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 $HgBa_2CuO_{4+\delta}$ 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 $Ba_2CuO_{3+\delta}$ and HgO in sealed silica tubes heated up to about 800°C during 5 h and then cooled slow ly 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 = 28(1):47(2):25(1) with the standard diviations between parentheses. Beside 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 following lattice parameters: $a = 3.8797(5)$Å, $c = 9.509(2)$Å. This tetragonal compound is the first member of the homologous series $HgBa_2R_{n-1}Cu_nO_{2n+2+\delta}$ (n = 1). The another member of this family $HgBa_2RCu_2O_{6+\delta}$ (n = 2) was synthesized earlier (Putilin et al. Mat. Res. Bull., 1991, 26, 1299-1307). The value of the c-cell parameter for the different members of this homologous series can be calculated with a formula c ≈ 9.5+3.2(n-1) similar to that deduced for the $TlBa_2R_{n-1}Cu_nO_{2n+3}$ ones.

The structure of Hg-1201 was refined by Rietveld analysis of powder X-ray data. The structural arrangement of Hg-1201 is illustrated by the layer sequence $(CuO_2)(BaO)(HgO_\delta)(BaO)(CuO_2)$. It is quite similar to that of $TlBa_2CuO_{5-\delta}$, except for the oxygen stoichiometry of the HgO_δ and $TlO_{1-\delta}$ layers. For the former, δ is very small and this depletion is possible because the dumbbell coordination is appropriate for the Hg^{2+} cations. For the latter, the $TlO_{1-\delta}$ layer is only slightly oxygen depleted, which creates the appropriate coordination for the thallium cations, either a distorted octahedron or a five-coordinated polyhedron. This different behavior for attaining the optimal hole concentration is due to the different crystal chemistry of the Tl^{3+} and Hg^{2+} cations.

PS-10.01.15 MAGNETIC ORDER IN THE PHOSPHIDES $Ho_2Fe_{12}P_7$, $Nd_2Co_{12}P_7$ and $Ho_2Co_{12}P_7$. By M. Reehuis, B. Ouladdiaf, T. Vomhof and W. Jeitschko, Institut Laue-Langevin, Grenoble (France) and Anorganisch-Chemisches Institut, Universität Münster (Germany).

Magnetic susceptibility measurements with a Faraday balance show that the magnetic moments of the Co atoms of these hexagonal $Zr_2Fe_{12}P_7$-type phosphides order ferromagnetically at 140 K and 152 K for $Nd_2Co_{12}P_7$ and $Ho_2Co_{12}P_7$, respectively, while the Fe atoms of $Ho_2Fe_{12}P_7$ are essentially nonmagnetic (M. Reehuis and W. Jeitschko, J. Phys. Chem. Solids, 1989, 50, 563-569). Our magnetization measurements of single crystals with a SQUID magnetometer and our neutron powder diffraction data show that the

three Co sites with tetragonal phosporus environments carry magnetic moments of approximately 0.2 μ_B, while the Co site with square-pyramidal phosphorus coordination has a moment of 0.9 μ_B. The hexagonal c-axis is the easy axis of magnetization for both Co compounds. The magnetic moments of the Nd atoms in $Nd_2Co_{12}P_7$ order all antiparallel to the Co moments. In contrast, in $Ho_2Co_{12}P_7$ 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 μ_B and 7.74 μ_B for the Nd and Ho atoms, respectively. They are thus smaller than the theoretical values of 3.27 μ_B and 10.00 μ_B, indicating considerable deviations from the full order for this temperature.

In $Ho_2Fe_{12}P_7$ 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 μ_{exp} = 7.5 μ_B/Ho. This value is smaller than the theoretical one of μ_s = 10.00 μ_B most likely because of crystal field effects.

PS-10.01.16 CORRELATION BETWEEN TWEED, TWINNING, AND FLUX PENETRATION IN $YBa_2(Cu_{1-x}, Fe_x)_3O_{7-\delta}$. By W.W. Schmahl*, Y. Ren, E. Brecht and H. Fuess, Fachbereich Materialwissenschaft, Technische Hochschule Darmstadt, Germany.

The decrease of the orthorhombicity with increasing x in substituted $YBa_2(Cu_{1-x},M_x)_3O_{7-\delta}$, (M=Fe, Co, or Al), leads to a decrease in lamellar spacing between the {110} twin walls when x approaches 0.03. 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 (1̄10) twin orientations interpenetrate, resulting in a cross-hatched tweed 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 tweed regime, the pinning force density is independent of x while T_c 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 (1 1 0) / (1 1̄ 0) "twin walls" in the tweed microstructure for x > 0.03.

PS-10.01.17 ON THE STRUCTURE OF $NdSr_2Cu_2NbO_8$. By J.-E. Jørgensen and N.O. Hornshøj. Department of Chemistry, University of Aarhus, DK-8000 Århus C, Denmark.

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

$NdSr_2Cu_2NbO_8$ is a perovskite type compound isostructural with $LaBa_2Cu_2NbO_8$ which contains a CuO_2-La-CuO_2 sandwich as well as NbO_6 octahedra. The structure is therefore analogous to a $YBa_2Cu_3O_{7-\delta}$ structure in which the linear Cu-O chains have been replaced by NbO_6 octahedra. $NdSr_2Cu_2NbO_8$ was prepared by firing stochiometric mixtures of Nd_2O_3, $SrCO_3$, CuO and Nb_2O_5 in air at 1070°C for 16 hours. Attempts to introduce superconductivity in $NdSr_2Cu_2NbO_8$ by substitution of Ca for Nd was unsuccesful.

The structure of $NdSr_2Cu_2NbO_8$ was studied by time of flight neutron powder diffraction. Rietveld refinements were performed in space groups P4/mmm, P4/mbm and I4/mcm. The NbO_6 octahedra are corner shared 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. No super-lattice reflections were observed and the final refinement was therefore performed in space group P4/mmm with oxygen in the NbO layers statistically distributed over the 4n (x 1/2 0) positions. The rotation angle around the c-axis for the NbO_6 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/mbm symmetry. Bond lengths and bond valency sums for $NdSr_2Cu_2NbO_8$ will be compared with the corresponding quantities for high temperature superconducting cuprates.

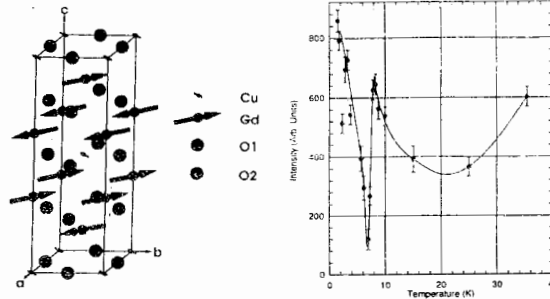Figure 1: Magnetic structure of Gd_2CuO_4.   Figure 2: Temperature variation of $\frac{1}{2}\frac{1}{2}1$ reflection.

believe that two dimensional ordering of the CuO_2 must still persist due to very strong exchange coupling but the three-dimensional ordering vanishes in a narrow temperature range just above the Gd ordering temperature. As the temperature is further lowered, the copper sublattice recovers its three dimensional ordering because the antiferromagnetically stacked ferromagnetic planes now have resultant zero field on copper. To our knowledge this type of frustration induced disappearence of magnetic ordering is quite unique and has not been observed in any other magnetic system.

PS–10.01.18 SUDDEN DISAPPEARANCE OF THREE–DIMENSIONAL MAGNETIC ORDERING IN Gd_2CuO_4

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We have studied the magnetic ordering of Gd_2CuO_4 by neutron diffraction on isotope (^{158}Gd) enriched single crystals. Below T = 6.4 K Gd magnetic moments order antiferromagnetically with the wave vector $\mathbf{k} = (0,0,0)$. Ferromagnetic Gd layers parallel to a-b plane are antiferromagnetically stacked along [001]. Cu^{2+} ions in Gd_2CuO_4 orders at T_N = 285 K to a La_2NiO_4 type antiferromagnetic structure with the propagation vector $\mathbf{k}$ = ($\frac{1}{2}$,$\frac{1}{2}$,0). Fig. 1 illustrates the magnetic structure of Gd_2CuO_4 at 1.5 K. We have investigated the temperature dependence of the intensity of a few magnetic reflections from room temperature down to 1.5 K. The intensity of $\frac{1}{2}$,$\frac{1}{2}$,1 magnetic reflection (Fig. 2) increases continuously with decreasing temperature up to 45 K below which it starts to decrease and shows a minimum 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 variation of the magnetic susceptiblity which also shows anomalies at 7 and 20 K. Search for magnetic reflection at Q = ($\frac{1}{2}$,$\frac{1}{2}$,0), ($\frac{1}{2}$,$\frac{1}{2}$,2) and ($\frac{1}{2}$,$\frac{1}{2}$,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. Low temperature anomalies in the temperature variation of the intensity of $\frac{1}{2}$,$\frac{1}{2}$,1 reflection obviously result from the interaction of the Cu and Gd sublattices which order with different and incomatible wave vectors. Above the ordering temperature of Gd sublattice the antiferromagnetic CuO_2 planes polarize antiferromagnetic gadolium 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. We

PS–10.01.19 STRUCTURAL FLUCTUATIONS IN METALLIC SODIUM. By H. Abe, K. Ohshima, S. Hoshino, T. Suzuki and K. Kakurai*, Institute of Applied Physics, University of Tsukuba, Japan, *Institute for Solid State Physics, The University of Tokyo, Japan.

Metallic sodium undergoes martensitic phase transformation from bcc to 9R structure at 37 K (Ms). We have performed neutron elastic and inelastic scattering experiments from metallic sodium to understand detailed structural informations over a temperature range of 10 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 5G of JRR-3M, JAERI. Phonon dispersion curves from 200 K to Ms were measured along high symmetry directions. There were no peculiar temperature changes for TA1[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 Ms 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 As (70-80 K), 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.