

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

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PS-10.01.14 SUPERCONDUCTIVITY AT 94 K IN A NEW Hg-BASED CUPRATE, $\text{HgBa}_2\text{CuO}_{4+\delta}$. By S.N. Putilin^{1,*}, E.V. Antipov¹, O. Chmaissem², and M. Marezio^{3,4}, ¹Chemical Department, Moscow State University, 119899, Moscow, Russia, ²National Institute of Standards and Technology, Gaithersburg, Maryland, 20899, USA, ³Laboratoire de Cristallographie CNRS-UJF, BP 166, 38042 Grenoble cedex 09, France, ⁴AT&T Bell Laboratories, Murray Hill, NJ 07974, USA.

A new high- T_c superconductor, $\text{HgBa}_2\text{CuO}_{4+\delta}$, 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 $\text{HgBa}_2\text{CuO}_{4+\delta}$ 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 $\text{Ba}_2\text{CuO}_3+\delta$ 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 = 28(1):47(2):25(1) with the standard deviations 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: $a = 3.8797(5)\text{\AA}$, $c = 9.509(2)\text{\AA}$. This tetragonal compound is the first member of the homologous series $\text{HgBa}_2\text{R}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ ($n = 1$). The another member of this family $\text{HgBa}_2\text{RCu}_2\text{O}_{6+\delta}$ ($n = 2$) 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 $c \approx 9.5 + 3.2(n-1)$ similar to that deduced for the $\text{TlBa}_2\text{R}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ 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 $(\text{CuO}_2)(\text{BaO})(\text{HgO}_\delta)(\text{BaO})(\text{CuO}_2)$. It is quite similar to that of $\text{TlBa}_2\text{CuO}_{5-\delta}$, except for the oxygen stoichiometry of the HgO_δ and $\text{TlO}_{1-\delta}$ 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 $\text{TlO}_{1-\delta}$ 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 $\text{Ho}_2\text{Fe}_{12}\text{P}_7$, $\text{Nd}_2\text{Co}_{12}\text{P}_7$ and $\text{Ho}_2\text{Co}_{12}\text{P}_7$. 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 $\text{Zr}_2\text{Fe}_{12}\text{P}_7$ -type phosphides order ferromagnetically at 140 K and 152 K for $\text{Nd}_2\text{Co}_{12}\text{P}_7$ and $\text{Ho}_2\text{Co}_{12}\text{P}_7$, respectively, while the Fe atoms of $\text{Ho}_2\text{Fe}_{12}\text{P}_7$ 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 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 $\text{Nd}_2\text{Co}_{12}\text{P}_7$ order all antiparallel to the Co moments. In contrast, in $\text{Ho}_2\text{Co}_{12}\text{P}_7$ 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 $1.8 \mu_B$ and $7.74 \mu_B$ for the Nd and Ho atoms, respectively. They are thus smaller than the theoretical values of $3.27 \mu_B$ and $10.00 \mu_B$, indicating considerable deviations from the full order for this temperature.

In $\text{Ho}_2\text{Fe}_{12}\text{P}_7$ 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 $\mu_{\text{exp}} = 7.5 \mu_B/\text{Ho}$. This value is smaller than the theoretical one of $\mu_s = 10.00 \mu_B$ most likely because of crystal field effects.

PS-10.01.16 CORRELATION BETWEEN TWEED, TWINNING, AND FLUX PENETRATION IN $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$. 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 $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$ ($\text{M} = \text{Fe}, \text{Co}, \text{or Al}$), 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 (30-50 Å). In the macroscopically tetragonal material, the (110) and (110) twin orientations interpenetrate, resulting in a cross-hatched tweed microstructure. From AC susceptibility measurements we found that, in the lamellar regime ($0 \leq x \leq 0.03$), the intergrain flux pinning force density is proportional to the spacing between twin walls, while T_c 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 1 0) "twin walls" in the tweed microstructure for $x > 0.03$.

PS-10.01.17 ON THE STRUCTURE OF $\text{NdSr}_2\text{Cu}_2\text{NbO}_8$. By J.-E. Jørgensen and N.O. Hornshøj, Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark.