

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

PS-10.03.11 CRYSTAL STRUCTURE AND CATION DISTRIBUTION OF A NEW PLANAR MAGNETIC ANISOTROPY M-HEXAFERRITE $BaFe_{12-2x}Ir_xCo_xO_{19}$ ($x=0.85$) IN RELATION WITH ITS MAGNETIC PROPERTIES. By H. Vincent, B. Sugg* and D. Boursier, ENS de Physique de Grenoble / LMGP, BP 46, 38402 St Martin d'Hères, France.

Barium M-hexaferrite has a very strong uniaxial anisotropy, and it is therefore an excellent starting material for permanent magnet. Substituting x (Co-Ti) for 2x Fe cations reduces its uniaxial anisotropy, which becomes planar for $x = 1.3$. Co-Ti substituted M-hexaferrites have been extensively investigated as promising materials for perpendicular magnetic recording. Unfortunately, the ordering temperature and the saturation magnetization are reduced in proportion to the substitution ratio.

According to our magnetic measurements and X-ray analysis of powder samples oriented under magnetic field, substituted Ir-Co barium M-hexaferrites which we have prepared, as powders and single crystals, have planar magnetic anisotropy as early as $x = 0.4$. The ordering temperature T_c and saturation magnetization M_s are consequently much higher than Ti-Co substituted ones with comparable anisotropy: 50% higher for M_s and about 100% for T_c .

The crystal structure of a single crystal with $x=0.85$ composition has been accurately determined, and cation distribution on the five Fe crystallographic sites refined. The Co cation positions were found by using bond length-bond strength relations. Magnetization measurements have been performed on single crystals of the same composition at room and helium temperatures, and magnetic anisotropy constants determined. Obtained values of K_1 and K_2 confirm the observed planar magnetic anisotropy and the observed saturation magnetization is in good agreement with the one calculated from the cation distribution determined by X-ray diffraction.

PS-10.03.12 CRYSTAL STRUCTURE AND PHYSICAL PROPERTIES of U_2Ru_3Si . By A. Vernière¹, P. Bordet², J.P. Brison¹, J. Chenavas*², P. Lejay¹, (1)C.R.T.B.T. - (2)Laboratoire de Cristallographie CNRS, BP 166-38042 GRENOBLE-Cédex 09 FRANCE.

Ternary silicides with a rare earth metal or uranium and a 3d,4d or 5d transition metal have been extensively studied because of the great variety of their physical properties. For example in the uranium system, URu_2Si_2 is an exciting compound which exhibits an antiferromagnetic order at 17 K coexisting with a superconducting state below 1.4 K. (T.T.M. Palstra, A.A. Menovsky, J. van den Berg, A.J. Dirkmaat, P.H. Kes, G.J. Nieuwenhuys and J.A. Mydosh, Phys. Rev. Lett., 1985, 55, 2727). We have undertaken a systematic study of this phase diagram which lead to the discovery of new ternary phases. We present here the crystal structure and some physical properties of the new URu_3Si_2 compound. A stoichiometric mixture was melted under a purified argon atmosphere in a water cooled copper crucible heated in a high frequency furnace. This technique was used in order to control the strong exothermic reaction, the reduction of the weight loss and the improvement of the homogeneity of the resulting sample. A single crystal of U_2Ru_3Si (5 mm long and 2mm diameter) has been grown using a "tri-arc furnace" Czochralski method for structure determination. The composition was determined by E.D.X. spectroscopy and a small piece of the crystal was used for single crystal X-ray diffraction analysis. In order to decrease absorption effects, graphite monochromatized $AgK\beta$ radiation was used. An empirical anisotropic absorption correction based on psi-scan measurements was applied. The corrected observations were averaged in the $R\bar{3}m$ point group, yielding 116 independent reflexions. After refinement the weighted and unweighted R-factors were 2.53% and 2.45%, respectively, with the following atomic positions: U in 6c (0,0,z; 0,0,z); Ru in 9c (5,0,0; 0,5,0; 5,5,0) and Si in 3b (0,0,5). In order to check the possibility of atomic substitution between Ru and Si, the occupancy factors of these two atoms were refined. The thermal parameters of Ru decreased by = 15% and the R-factors dropped to 2.14% and 2.19%, respectively. Then, the chemical formula of the sample analyzed becomes $U_2Ru_{2.83}Si_{1.17}$. The compound U_2Ru_3Si can be described as an ordered ternary $MgCu_2$ Laves phase with a Si / Ru order and is characterised by a c/a ratio (2.067) smaller than the theoretical one. This feature leads to very short uranium - uranium interatomic distances (3.22 Å). Some physical properties were measured on a single crystal for the U_2Ru_3Si compound. Magnetic measurements were carried out using a "Quantum Design"

Squid magnetometer with a superconducting coil in the 2 K - 300 K. temperature range. Electrical resistivities were measured between 4.2 K and 300 K by the a.c.-four probe method using silver lac.

The temperature dependence of the susceptibility of U_2Ru_3Si single crystal was measured with the magnetic field applied along the [001] direction of the triple hexagonal unit cell or perpendicular to it. No magnetic anisotropy was detected. U_2Ru_3Si exhibits an enhanced Pauli paramagnetic behavior.

The susceptibility $\chi = 1.76 \cdot 10^{-3}$ uem / mole at 100 K under 1 kOe, is nearly temperature independent from room temperature down to 50 K. Assuming that the Curie tail observed at low temperature is due to paramagnetic impurities, the data have been fitted from 2 K up to 100 K with a temperature independent contribution and a Curie-Weiss law $\chi = c_0 + C/T$. An effective moment of $9.2 \cdot 10^{-2} \mu_B$ can be deduced from this fit. This Curie enhancement of the susceptibility can be attributed to a crystallographic site exchange (stacking faults) on a very small scale between transition metal and p elements as it is possible in the Laves phases (G.B. Johnston and E.O. Hall J. Phys. Chem. Solids, 1968, 29, 201-207). These exchanges modify the environment of the uranium atoms, which can become magnetic. (F. Givord, P. Lejay, E. Ressouche, J. Schweizer and A. Stunault Physica, 1989, 805, 156-157). The Curie constant extracted from the fit leads to less than 1% of uranium ($3+$) ions in such configuration. To explain the magnetic behavior of U_2Ru_3Si at higher temperature, it has to be noted that the interatomic distances U-U is shorter than the Hill-limit of 3.5 Å (H.I.L. Hill, Plutonium and other actinides ed W.N. Miner AIME, New York, 1970). This suggests a direct overlap of the uranium 5f orbitals, leading to Pauli-type paramagnetic compounds, with no local moment on the uranium site. No superconducting transition was observed by a.c. susceptibility measurement down to 20 mK and 1.5 K, respectively. The resistivity of the single crystal decreases from 153 $\mu\Omega$ cm at room temperature to a saturated value of 7.6 $\mu\Omega$ cm at 4.2 K. These data can be fitted with a $T^{3.8}$ law from 4 K to 20 K which is characteristic of an almost normal metal behavior. The very short uranium - uranium interatomic distances seem to be the predominating factor for the physical properties of this new ternary compound.

PS-10.03.13 ON POLYMORPHISM OF POLY(ARYL ETHER KETONE): AN ELECTRON-DIFFRACTION STUDY. By A. Chenite and Y. Le Page, Institute for Environmental Chemistry, National Research Council of Canada, Ottawa, Ont. K1A 0R6, Canada

There is considerable interest in aromatic polymers for applications as high-temperature materials and in filtration membranes. Poly(aryl ether ketone), commonly called PEEK, has special applications as coating and insulation material for high wiring requiring good thermal stability and chemical resistance [Stening T. C., Smith C. P. and Kimber P. J. (1982). *Mod. Plastic Int.*, p. 54]. PEEK is semi-crystalline, with a degree of crystallinity over 50%, and several studies about its crystal structure have been reported, all with X-ray diffraction. Differential scanning calorimetry studies have shown the double-melting behaviour of this material [Lee Y. and Porter R. S. (1987). *Macromolecules* **20**, 1336], but X-ray results only disclose an orthorhombic structure with unit cell dimensions in the range: $a = 7.75 - 7.78 \text{ \AA}$, $b = 5.89 - 5.92 \text{ \AA}$ and $c = 9.88 - 10.06 \text{ \AA}$.

In the present study, PEEK was investigated by electron microscopy and diffraction. The advantage of electron microscopy is the ability to relate the structure to the morphology and chemistry of very small and very thin particules (dimensions about $1\mu \times 1\mu \times 0.02\mu$ and less). Images show two types of habits for crystals: needles and plates have been distinguished, in agreement with DSC results. In diffraction mode, the convergent beam electron-diffraction patterns recorded for each of the two populations, indicate the existence of two lattices: the above X-ray parameters correspond to needles, while the lattice of platelets is different. Details will be discussed and compared with previous reports.