

MS.58.4*Acta Cryst.* (2008). A64, C103**X-ray diffraction study on structures of vanadium dioxide films with metal-insulator transition**Kunio Okimura¹, Nurul Ezreena¹, Joe Sakai²¹Tokai University, Electronics, 1117 Kitakaname, Hiratsuka, Kanagawa, 259-1292, Japan, ²Laboratoire LEMA, UMR 6157 CNRS/CEA, Universite Francais Rabelais, Parc de Grandmont 37200 Tours, France, E-mail : okifn@keyaki.cc.u-tokai.ac.jp

Vanadium dioxide shows metal-insulator transition (MIT) at around 341 K with several orders of change in resistivity through structural transition from low temperature monoclinic phase to high temperature tetragonal phase. Thus, characteristics of MIT in vanadium dioxide strongly depend on crystalline structure. In this study, we investigated crystalline lattice parameters of vanadium dioxide films by X-ray diffraction analyses. The films were deposited on c-sapphire substrates by using ICP-assisted sputtering method. The vanadium dioxide film grows epitaxially on sapphire (001) surface with its a-c plane parallel to the substrate. Films fabricated by pulsed laser deposition (PLD) method were also served for lattice parameter analyses. We selected four diffractions in order to derive lattice parameters of monoclinic crystal, a, b, c and incline angle α . In sputter-deposited films prepared at 673 K, expansion of a with relative difference of around 0.5 % and shortening of c with relative difference of around -0.3 % compared to those in bulk crystal were observed. Angle α was smaller than bulk one keeping the c times $\sin \alpha$ close to bulk crystal. As for b axis perpendicular to the substrate, the length was coincident with bulk value within -0.1 %. On the other hand, in films prepared by PLD method at 773 K, lattice parameters were close to those of bulk crystal revealing high quality crystalline growth in PLD under adequate substrate temperature. We performed XRD measurements for in-situ heated vanadium dioxide films and found expansion of c axis and shortening of a axis than tetragonal bulk values. Matching of cell volume between two phases was examined. Minute correlation between crystalline structure and MIT characteristics will be presented in the convention.

Keywords: vanadates, metal-insulator transitions, lattice parameters

MS.58.5*Acta Cryst.* (2008). A64, C103**Modulated structure and ferromagnetic metallic state of SmNiC₂**Susumu Shimomura¹, Chieri Hayashi¹, Gou Asaka¹, Nobuyoshi Wakabayashi¹, Masaichiro Mizumaki², Hideya Onodera³
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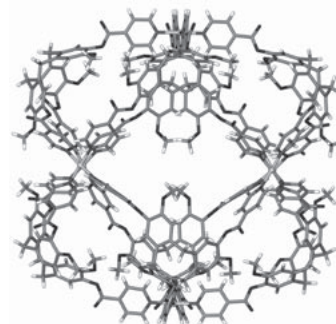
Ternary compounds $RNiC_2$ (R = rare-earth elements) have various magnetic transitions and exhibit anomalous temperature dependences of the electrical resistivity. In $SmNiC_2$, a first-order ferromagnetic transition takes place at $T_C = 17.5$ K. The electrical resistivity of this compound decreases with decreasing temperature down to 150 K below room temperature. It shows a sudden increase around 150 K. One of the possible origins of the anomalous temperature dependence is the formation of a charge-density-wave (CDW) state. In order to detect the transition to the CDW state as well as the critical phenomena associated with it, we have performed x-ray

diffraction and diffuse scattering measurements on $SmNiC_2$ using synchrotron radiation at the BL46XU of the SPring-8. We found that satellite peaks characterized by a wavevector $(0.5, \eta, 0)$ appear at 148 K, corresponding to the sharp inflection in the temperature dependence of the resistivity. Diffuse scattering peaks exist at the satellite positions even at room temperature. Their intensities increase with decreasing temperature toward 148 K. These results show that the CDW transition takes place and that the corresponding phonon softening occurs above the transition temperature. The satellite intensity increases with decreasing temperature, but the satellite peaks vanish below T_C . The resistivity measurement has revealed the discontinuous decrease in the resistivity at T_C on cooling. The CDW state is unstable against the ferromagnetic order. The synchrotron radiation experiments were performed with the approval of JASRI (Proposal Nos. 2005B0300 and 2006A1255).

Keywords: charge density waves, magnetic phase transitions, synchrotron X-ray diffraction

MS.59.1*Acta Cryst.* (2008). A64, C103**Star-burst metallo-supramolecular prisms and coordination polymers with pyramidal ligands**Michaele J Hardie¹, Christopher Carruthers¹, Julie Fisher¹, Lindsay P Harding², Timothy J Prior³, Pierre Rizkallah³, Tanya Ronson¹, Aleema Westcott¹¹University of Leeds, School of Chemistry, Woodhouse Lane, Leeds, West Yorkshire, LS2 9JT, UK, ²Department of Chemical and Biological Sciences, University of Huddersfield, Huddersfield, HD1 3DH, UK, ³STFC Daresbury Laboratory, Warrington, WA4 4AD, UK, E-mail : m.j.hardie@leeds.ac.uk

We have recently generated a series of pyramidal host-type ligands based on the cyclotrimeratrylene framework. These ligands are in shape and have rigid molecular cavities capable of binding other molecules. They can be incorporated into either discrete or polymeric metal-ligand systems, thus creating metallo-supramolecular assemblies or coordination polymers with specific molecular recognition sites. Thus far, we have characterised a number of transition metal species of these ligands, including discrete polynuclear complexes; chain, grid and 3-D coordination polymers; and metallo-supramolecular assemblies such as $[Ag_2L_2]^{2+}$ capsules and $[Ag_4L_4]^{4+}$ star-burst tetrahedra; giant $[Pd_6L_8]^{12+}$ stella octangula structures (pictured), and triply interlocked [2]catenane $\{[M_3(NO_3)_3L_2]\}_2$ where $M = Co, Zn$. We can use host-guest chemistry to manipulate the self-assembly outcome: the star-burst $[Ag_4L_4]^{4+}$ tetrahedron is isolated with acetonitrile guests, but with bulkier glutaronitrile guest molecules a 2-D coordination polymer with 4.82 topology is formed instead. These and other examples will be discussed.



Keywords: supramolecular assemblies, coordination chemistry, chemical crystallography