PS10.12.17 INTERSTITIAL TRANSITION METAL ORDERING IN WIDE RANGE NON-STOICHIOMETRIC $M_{2+x}Sn_2$ (M=Co,Ni) SOLID SOLUTIONS. R.L. Withers and A-K.Larsson, Research School of Chemistry, Australian National University, Canberra, ACT, 0200 Australia

An electron diffraction study of "disordered" γ-$Co_{2+x}Sn_2$ (0.76<x<1.26) and γ-$Ni_{2+x}Sn_2$ (0.70<x<1.19) has revealed the presence of a spectacular, sharp and highly structured diffuse intensity distribution to which the low temperature ordered γ' superstructures are clearly closely related. The underlying M_2Sn_2 average structure is of NiAs type (space group symmetry $P6_3/mmc$, a≈4.1 Å, c≈5.2 Å) with additional interstitial transition metal atoms occupying trigonal bipyramidal sites in the Sn sub-lattice. The ordering of these interstitial transition metal atoms and the associated structural relaxation gives rise to the observed diffuse distribution.

The basic shape of the diffuse distribution appears to be based upon intertwined, undulating, approximately cylindrical channels of diffuse intensity running along the c^* directions of reciprocal space. The intensity observed when rotating around c^*, however, depends strongly upon azimuthal angle. The general topology of the diffuse distribution does not change significantly with composition across the solid solution field, but the amplitude of the undulating channels does: this amplitude is shown to be directly proportional to composition. The strongest satellite reflections characteristic of the low temperature ordered γ'-phases fall directly onto the diffuse distribution of the γ-phase while the characteristic extinction conditions of the ordered γ'-phases are mirrored in the diffuse distribution of the γ-phase.

A modulation wave approach is used to deduce the implications of the observed diffuse distribution for local interstitial transition metal ordering. Minimization of macroscopic strain along close packed <110> directions is shown to be responsible for the characteristic absence of diffuse intensity in {h,-h,l}* reciprocal lattice planes.

PS10.12.18 POINT DEFECT CLUSTERS IN PbTe:In. A.K. Tkalich[a], K.D. Chtcherbatcheva[a] and V.P. Zlomanov[b], [a]Moscow Institute of Steel and Alloys, Moscow, Russia; [b]Moscow State University, Moscow, Russia

The asymptotic X-ray diffuse scattering (AXRDS) has been used to characterize the point defect structure in $Pb_{1-x}In_xTe$ (x=0.01) single crystals doped above the point of hole compensation x~0.004. From the AXRDS intensity profile (Fig.1) taken along the diffraction vector near to (400) reciprocal lattice point on a triple-crystal diffractometer, it is evident that there are microdefects (the submicron point defects clusters) of both vacancionic (at q<0) and interstitial (at q>0) type. Herewith, the concentration of the former is greater than that of the latter. The typical size of microdefects is approximately of ~0.01-0.1 μm. The interstitial microdefects are supposedly formed from the Te interstitials created during the post-crystallization cooling cycle due to the decomposition of solid solution enriched with Te, while the vacancionic microdefects should contain the In impurity atoms and vacancies of lead.

The role of the In impurity and native point defects in the effect of Fermi level pinning is discussed taking into account our recent photoemission data on In states in PbTe.
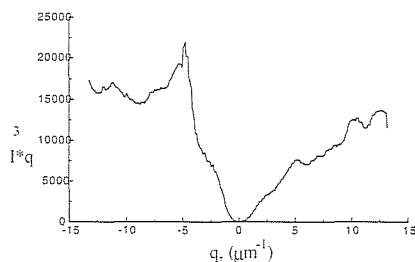

Fig.1 (400) AXRDS intensity profile in PbTe:In. I - intensity, q - deviation from the diffraction vector.

Materials XIII
Advanced Battery and Fuel Cell Materials

MS10.13.01 CRYSTAL CHEMISTRY OF LAYERED VANADIUM OXIDE CATHODE MATERIALS. Peter Y. Zavalij, M. Stanley Whittingham. State University of New York at Binghamton, Binghamton, NY 13902-6016, USA

Structural analysis of V_2O_5 layers as well as VO_3 and V_3O_8 polyanions has been done based on known structures with square pyramidal coordination of vanadium and stoichiometry V_2O_5, $M_xV_2O_5$, M_xVO_3, $M_xV_3O_8$, $M_xV_6O_{15}$, etc. including our new compounds ($LiV_2O_4·H_2O$, $TMAV_4O_{10}$, $TMAV_2O_5$ and $DTAV_3O_8$, where TMA = tetramethyl ammonium, DTA = dodecyl trimethyl ammonium) with novel topography of layers.

The unique layered structures of vanadium oxides and their derivatives are of particular interest because of their capacity to intercalate lithium and other cations between their layers that makes them promising candidates for cathode materials in secondary lithium batteries.

The most common V-polyhedron is a square pyramid VO_5 with double bonded oxygen in its vertex. Those polyhedra when sharing edges form double chain with stoichiometry VO_3 which exist by itself
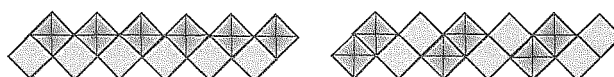
in $KVO_3·H_2O$ and $Co(VO_3)_2·4H_2O$. The topography of the double chains can be simply presented by symbolic formula using two symbols (U - up and D - down) which show the orientation of the square pyramid. The symmetry of the formula by using simple rules leads to 10 possible symmetry groups of the double chains. In most cases those double chains form layers by sharing single bonded oxygen atoms of basis. Using different ways of joining chains to the layers the possible symmetry, topography, and dimensions of V_2O_5 layers has been developed. Those conclusions are used to predict the structure of the layers in the novel compounds. The structure of V_2O_5 layers is also discussed from the point of view of their capacity to easily accept additional charges that yields rich intercalation opportunities in contrary to frameworks constructed with VO_4 tetrahedra.

MS10.13.02 STRUCTURAL ASPECTS OF TRANSITION METAL OXIDE CATHODE MATERIALS FOR LITHIUM BATTERIES. Christina Lampe-Önnerud, Massachusetts Institute of Technology, Cambridge MA 02139, S. Greenbaum, P.E. Stallworth, S. Kostov, and M. denBoer, The City University of New York, Hunter College, New York NY 10021, Denis Fauteux and Arthur Massucco, Arthur D. Little Inc., Battery Technology Center, Cambridge MA 02140

First-row transition metal oxides have over the years received much interest as cathode materials for lithium intercalation in rechargeable cells. Strong candidates for a future thin-film battery include $Li_xV_6O_{13}$, $LiCoO_2$, and spinel $Li_xMn_2O_4$ systems, exhibiting high capacity in an attractive voltage range for application devices. The crystallinity and atomic arrangement will be addressed in the light of X-ray and neutron diffraction in combination with spectroscopic evaluation by NEXAFS, EPR and NMR.

Neutron diffraction shows that as lithium is intercalated into V_6O_{13}, the (0,0,0) position starts to fill. However, upon further intercalation, powder diffraction identifies an increasing amorphous component. [51]V and ^{7}Li NMR line shape and spin-lattice relaxation time measurements for $Li_xV_6O_{13}$ (0<x<6) shows some changes in conduction pathways or mechanisms as a function of x, although the NMR results are dominated by the presence of paramagnetic V^{4+}. Our previous findings identifying four phases ($Li_xV_6O_{13}$; x=0.5, 1.5, 3, and 6) were confirmed by the spectroscopic measurements.

X-ray Rietveld refinements on $LiCoO_2$ and spinel $Li_xMn_2O_4$ show