08-Inorganic and Mineralogical Crystallography

ATOM	POSITION	X	Y	Z	N	B[$\AA^2$]
La	6a	0	0	0.25	1.0	0.25(2)
Al	6b	0	0	0	1.0	0.43(5)
O	18e	0.474(1)	0	0.25	1.0	0.57(2)

Table 1 Structural parameters of $LaAlO_3$.

PS-08.04.19 A SINGLE-CRYSTAL X-RAY-DIFFRACTION STUDY OF THE ORTHORHOMBIC Al$_3$Mn PHASE. By N.C.Shi†, X.Z.Li‡, Z.S.Ma† and K.H.Kuo‡, † X-Ray Laboratory, China University of Geosciences, Beijing 100083, China. ‡ Beijing Laboratory of Electron Microscopy, Chinese Academy of Sciences, P.O.Box 2724, Beijing, China.

Al$_3$Mn (with a stoichiometrical composition Al$_{29}$Mn$_{10}$), M$_r$=1331.8, orthorhombic, Pn2$_1$a, a=14.837(4), b=12.457(2), c=12.505(2)$\AA$, V=2311.4(8)$\AA^3$, Z=4, D$_x$=3.56, Mo Kα=0.71069$\AA$, μ=5.62mm^{-1}, F(000)=2355.02, T=room temperature, R=0.068 for 1550 reflections. About 2/3 Mn atoms have icosahedral coordination. In a repeat unit b, there are 4 interlocked icosahedra (two Mn and two Al) consisting of 1 pentagonal prism and 4 antiprisms. The icosahedral subunits form a network on (010) constituting a layer structure, consisting of an almost "flat" layer F sandwiched between two puckered P and p layers in the sequence of PFpP'F'p'..., where P'F'p' is rotated from PFp by 180° around the layer normal. A similar layer structure has also been found in the π-AlMnM (M=Ni,Cu,Zn) phases. Both these two crystalline structures can be obtained from that of the Al-Mn decagonal quasicrystal with a periodicity of 12.4$\AA$ along the tenfold axis by substituting a rational ratio of two consecutive Fibonacci numbers F$_{n+1}$/F$_n$ for the irrational τ =(1+√5)/2 in two quasiperiodic directions on the plane normal to the tenfold axis.

PS-08.04.20 SYNTHESIS AND CRYSTAL STRUCTURE OF RNb$_3$(Se$_2$)$_6$, WITH R=In,Sb. By S.Q. Deng*,H.H. Zhuang, J.S. Huang and J.L. Huang, State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Academia Sinica, Fuzhou(350002), PRC.

In recent years, a number of intriguing physical phenomena related to the charge density wave (CDW) have been observed in some low dimensional materials. Because most of these materials were found to be of the early transition metal chalcogenides, we have studied the ternary system R-Nb-Se (R=In,Sb).

InNb$_3$(Se$_2$)$_6$ was synthesized by the reaction of Nb$_2$Se$_9$ and In with approximately stoichiometric proportions at 773-873K.

The preparation of SbNb$_3$(Se$_2$)$_6$ succeeded by an analogous procedure with the stoichiometric elements as the starting reactants at 973k.

The structures are determined by single crystal X-ray diffraction method. The results showed that InNb$_3$(Se$_2$)$_6$ (a=9.450(1), c=19.068(9)A, P4/mnc,z=4) and SbNb$_3$(Se$_2$)$_6$ (a=9.466(2), c=19.075(3)A, P4/mnc,z=4) are very similar in structural parameters. Both of the structures are composed of the one dimensional infinite chains [Nb$_3$(Se$_2$)$_6$]$_\infty$ along the c axis with the third component R (R=In,Sb) intercalated between them. In one [Nb$_3$(Se$_2$)$_6$]$_\infty$ chain, the distances between the niobium atoms are arranged in a periodic sequence of ···Nb-3.037-Nb-3.248-Nb -3.248A-Nb··· for InNb$_3$(Se$_2$)$_6$. According to the Nb-Nb distances

in the sequence, the Nb$_3$(Se$_2$)$_6$ unit can be formally viewed as the building block of a chain. In comparison with the Nb-Nb bond lengths in (MX$_4$)nY(Gressier, Meerschaut, Guemas,Rouxel & Monceau, J. Solid State Chem., 1984, 51, 141) and α-NbI$_4$ (Dahl & Wampler,Acta Cryst.,1962,15,903), the Nb-Nb distances in the above sequence should also involve chemical bonding. Therefore the Nb$_3$(Se$_2$)$_6$ units in one chain may be viewed as combined together by the bridging (Se$_2$)$^{2-}$ ligands as well as the Nb-Nb bonding. Considering the long distance (6.69A) between the center lines of different chains, the metal-metal interaction is very anisotropic and typical of the one dimensional character. The bond lengths of Nb-Se (2.558(1)~2.721 (2)A) and Se-Se (2.325(2)~2.356(2)A) are all in agreement with those in other known niobium selenides such as NbSe$_3$ (Hodeau,et al.,J. Phys. C.,11, 4117). The In atoms located in the one dimensional channels between different chains form the tetragonal pyramid coordination geometry with four equidistant Se atoms from four different chains. The height of the tetragonal pyramid, which shows the position of the intercalated atom in the channel, for InSe$_4$ is 0.364A, and which reveals the main difference between the structures of InNb$_3$(Se$_2$)$_6$ and SbNb$_3$(Se$_2$)$_6$ (0.589A for SbSe$_4$). The large distance of In···Se (3.233(1),3.263(3)A for Sb···Se) suggests that the In(Sb) atoms are inserted as in In$_{~3}$Mo$_{15}$Se$_{19}$ (Gruttner & Yvon, Acta Cryst.,1979,B35,285). Unusual high values of U$_{33}$/U$_{11}$ (2.42 and 4.51 for In and Sb, respectively) are indicative of the large thermal vibrations of the intercalated atoms along the c axis. Electrical resistivity measurements indicate that InNb$_3$(Se$_2$)$_6$: ρ_a=19.2(3), ρ_b=19.4(4), ρ_c=0.74(1)Ωcm (298K); SbNb$_3$(Se$_2$)$_6$: ρ_a=26.0(5), ρ_b=25.5(5), ρ_c=0.11(2)Ωcm (298K) and the dash rises of ρ_c at ~165 and 64K for InNb$_3$(Se$_2$)$_6$; ~185, 70 and 30K for SbNb$_3$(Se$_2$)$_6$ in the range of 289K-298K.

PS-08.04.21 A PATTERSON SYNTHESIS WITH PROFILES OF DIFFRACTION INTENSITIES. By Y.Ono* and M.Tokonami, Mineralogical Institute, Faculty of Science, University of Tokyo, Japan.

It has been shown previously (Kaplow, R., Rowe, T.A. & Averbach, B.L.(1968). Phys. Rev. 168, 1068-1079) that the 'Coupling coefficient' of atomic interaction to be defined in study of a radial distribution function of hexagonal selenium by the powder method. As for single crystals, with a conventional structure analysis by integrated diffraction intensities, we can only obtain average atomic interactions, such as thermal atomic vibration, of all unit cells in the crystal. In this work, to obtain the coefficients also in single crystals, a 'direct' Patterson synthesis which is unusually calculated with a data set of profiled intensities collected by step-scan is investigated. The sample was a monoclinic α-selenium crystal and the intensity data have been collected in the range of 2θ < 45° with wave length of 0.7Å. The scan width and step width of the peak profile data were +0.5° and 0.01° in ω and total data of hkl used were 778. In the Patterson map with profiled intensity data, the periodicity of unit cells have disappeared:Remarking the origin peak, usually 'equivalent' peaks' height and widths become the lower and the broader as far from the origin. This means that the stronger interactions of

the nearer neighbor atoms exist. The peaks far from the origin with a constant height show less atomic interaction between the atoms with longer interatomic distances than a certain distance. They are comparable with the averaged peak in the common Patterson map. These procedures are considered to be useful in assuming the coupling coefficients and calculations are in progress.

PS-08.04.22 STRUCTURES OF TWO TERNARY LAYERED TELLURIDES $FeNb_2(\mu_4-Te)_3(\mu_5-Te)$ AND $FeTa_2(\mu_4-Te)_3(\mu_5-Te)$ By S.X. Liu*, G.L. Cai, Z.M. Wang, J.L. Huang, Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, China; State Key Laboratory of Structural Chemistry, Fuzhou, Fujian 350002, China.

The two ternary tellurides $FeNb_2(\mu_4-Te)_3(\mu_5-Te)$ (I) and $FeTa_2(\mu_4-Te)_3(\mu_5-Te)$ (II) were obtained by direct combination of the elements. These two ternary chalcogenides crystallize in space group P mmn with a=12.412(2), b=3.8173(9), c=7.295(2) Å, V=345.6 Å^3, Z=2, Mr.=752.06, μ=216.87 cm^{-1}, F(000)=632, D$_x$=7.226 g.cm^{-3} for (I) and a=12.377(3), b=3.7687(6), c= 7.266(2) Å, V=338.9 Å^3, Z=2, Mr.=928.14, μ=507.66 cm^{-1}, F(000)= 760, D$_x$=9.094 g.cm^{-3} for (II). The crystal structures were solved by direct methods. Refinement was by full-matrix least-squares calculations with anisotropic thermal parameters. An occupancy factor of 0.5 for Fe atom on a mirror plane was proposed on the basis of peak heights in the difference Fourier map and thermal parameters for these two tellurides.
The two compounds are isostructural and have a layered structure. In crystal $FeNb_2(\mu_4-Te)_3(\mu_5-Te)$, every two niobium atoms form a pair Nb$_2$ with a Nb-Nb bond of 3.108(5) Å. Every iron atom is connected to two surrounding Nb$_2$ pairs, in which the Fe atom is 0.922 Å out of the square plane defined by the four Nb atoms. These FeNb$_4$ square pyramids are combined by sharing Nb-Nb edges to form an infinite metal cluster chain {Nb$_2$Fe}$_n$ along b axis, the distance between two Fe atoms from two neighbouring square pyramids is 3.968 Å; on the other hand, each niobium atom is bonded to six tellurium atoms with a distorted octahedral stereochemistry while each iron atom is bonded to four tellurium atoms with a distorted tetrahedral one. These Nb-centred octahedra and Fe-centred tetrahedra join via shared Te$_3$ triangular planes or Te-Te edges to form an infinite chain structure {Nb$_2$FeTe$_4$}$_n$ along b axis. In addition, every two adjacent Nb-centred octahedra from two adjacent chains are bridged in pairs by sharing a Te-Te edge; every two neighbouring Fe-centred tetrahedra from two neighbouring chains are connected by a common tellurium atom. Therefore these polyhedra are combined to form an infinite sandwich perpendicular essentially to the c axis. The neighbouring sandwiches

are held together by weak van der Waals interaction between Te atoms to form a layered structure in the crystal.
There are one μ_5-Te atom and three μ_4-Te atoms in a formula FeNb$_2$Te$_4$ or FeTa$_2$Te$_4$.

PS-08.04.23 STRUCTURE OF A NEW TERNARY LAYERED CHALCOGENIDE $Ni_2Ta(\mu_4-Te)_2(\mu_5-Te)$ By B. Zhang, Z.M. Wang, S.X. Liu, J.L. Huang*, Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, China; State Key Laboratory of Structural Chemistry, Fuzhou, Fujian 350002, China.

The new layered chalcogenide $Ni_2Ta(\mu_4-Te)_2(\mu_5-Te)$ has been prepared by high-temperature reaction of the elements. Ni$_2$TaTe$_3$ crystallizes with two formula units in a cell with dimensions a=7.473(2), b=3.708(1), c=10.074(2) Å, β=106.78(2)° in the monoclinic space group P 2$_1$/m. The structure was refined by full-matrix least-squares technique with anisotropic temperature factors for all atoms to R=0.053 and R$_w$=0.064.

The title compound displays a new layered structure type. Every layer contains square pyramidal Ta atoms and tetrahedral Ni atoms each coordinated by Te atoms. There are two unique chains that run parallel to the b axis in the crystal. One chain consists of Ta-centred square pyramids that share Te-Te basal edge; the distance between two Ta atoms from the adjacent Ta-centred polyhedra is 3.708(1) Å (the b repeat). The square pyramidal coordination around Ta atom is unusual in the known tellurides. On the other hand, the other chain is made up of numbers of building blocks each consists of two edge-sharing Ni-centred tetrahedra. The coordination about Ni atom is distinctly distorted such that the Ni-Te bond lengthes in tetrahedra are from 2.534 Å to 2.704 Å; the Te-Ni-Te angles from 92.4° to 122.46° . The distortion may be due to the Ni-Ni bonds described later. Every two neighbouring Ni-centred tetrahedra are related to each other by some complex operations including screw operation 2$_1$ [010], the closest distance between Ni atoms in adjacent tetrahedra is 2.526 Å. In each sandwich, each Ni atom is bonded to two neighbouring Ni atoms, forming two kinds of Ni$_n$ chains along the b axis with Ni-Ni bonds (2.526Å and 2.722Å respectively). The closest Ni-Ni distance in this compound is somewhat longer than the Ni-Ni distance of 2.492 Å in Ni metal. In each sandwich, every Ta atom between two adjacent Ni$_n$ chains is connected with five surrounding Ni atoms in the two Ni$_n$ chains, forming five Ta-Ni bonds of 2.661-2.848Å. Hence there is a two-dimensional metal cluster in the ternary