energy that separates the bonding & antibonding orbitals if one likens the formation of Hg dimer moiety to H_2 on the ground that Hg^+ has the configuration[Xe] $4f^{14} 5d^{10} 6s^1$. Details of the semiquantitative calculations will be presented.

PS-08.04.07 TERNARY NIOBIUM CHALCOGENIDE HALIDES: PREPARATION AND CHARACTERIZATION OF Nb_3SI_7 AND $(Nb_3SI_7)_2 \cdot NbI_5$. By J. Lin* and G. J. Miller, Department of Chemistry and Ames Laboratory–USDOE, Iowa State University, USA.

It has been shown that most of the Nb_3YX_7 (Y = Chalcogen, X = Halogen) compounds adopt the Nb_3X_8 layer structure (G. J. Miller, unpublished). The niobium atoms fill 3/8 of the octahedral holes of a close packed array of anions to form sandwich-type layers. A basic structural feature of this layer is that the niobium atoms form triangular clusters by sharing octahedral edges. All of these compounds crystallize in either hexagonal or trigonal symmetry depending upon the stacking sequences of the layers. In the Nb-S-I system, in addition to the hexagonal phase, an orthorhombic Nb_3SI_7, as well as a new compound, $(Nb_3SI_7) \cdot NbI_5$, were found.

All of the compounds were synthesized from elemental materials and characterized by single crystal X-ray diffraction. The crystals of $(Nb_3SI_7)_2 \cdot NbI_5$ were always found as twins, so the structure was refined with a twin program SFLS. The twin operation is (-1 0 0, 0 1 0, 1/6 0 1).

The anion array in the orthorhombic Nb_3SI_7 structure is cubic close packing. The niobium atoms occupy the octahedral holes in the sequence [AcBa*CbAc*BaCb*Ac]. A, B and C, a, b and c, as well as a*, b* and c* represent, respectively, the anion arrays, niobium arrays 5/8 filled and 1/8 filled sites of octahedral holes. The niobium triangular clusters in this structure are formed either within or between layers of metal atoms. The whole structure is also layered, but the sheets are buckled and run perpendicular to the $\vec{c}$ axis.
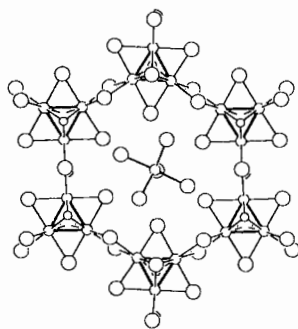

Fig. 1. Projection of the $(Nb_3SI_7)_2 \cdot (NbI_5)$ structure along $\vec{c}$.

In the monoclinic $(Nb_3SI_7)_2 \cdot NbI_5$ structure, the niobium atoms form the triangular cluster via sharing octahedral faces and each cluster connects with three other clusters by sharing edges to form a layer with large hexagonal holes, as shown in Fig. 1. The whole framework is constructed by stacking these layers one over another along $\vec{c}$ to achieve a channel-like structure. The isolated NbI_5 molecules with trigonal bipyramid geometry sit at the positions between the layers along the channels. We should point out that in the solid state, NbI_5 occurs with the niobium atoms in octahedral coordination and dimerized into Nb_2I_{10} cluster. The

trigonal bipyramidal coordination of niobium is known in the gas phase of $NbCl_5$ and in some niobium oxides. Extended Hückel band calculations show that this geometry increases the energy gap between the HOMO and LUMO, so as to reduce the electron transfer from the framework to NbI_5 molecules.

PS-08.04.08 STRUCTURAL CHANGES IN ISOSTOICHIOMETRIC SERIES OF ALKALI LANTHANUM NITRATES. By A.G.Vigdorchik*, Yu.A.Malinovsky, Institute of Crystallography Russian Acad. of Sci., Leninsky pr.59, Moscow, 117333, Russia.

Our investigation was peformed in the course of a systematic study of alkali rare - earth nitrates and is devoted to an analysis of the structural crystal - chemical characteristics of isostoichiometric series of alkali lanthanum nitrates $A_2[La(NO_3)_5(H_2O)_2] \cdot nH_2O$, where A = Cs, Rb, NH_4, K. Such a comparative analysis shows how far is the nature of the alkali metals influences the structure of these compounds. The Cs, Rb, and ammonium compounds have similar values of the unit cell parameters. We can note their similarity both in the structure of the rare - earth complexes and in the packing of these complexes in the structure. The only essential difference lies in the absence of water molecules outside the coordination sphere of the La atoms in the cesium compound. The channels in which the alkali ions lie have approximately equal dimensions. The cavities adequate for the Cs atoms are too ample for the smaller Rb^+ and NH_4^+ ions. This circumstance determines the possibility of water getting into the intraframework cavities of the rubidium and ammonium compounds. The ammonium on tends to form hydrogen bonds.They join the ammonium ions and the molecules of intermolecular water to form the chains along Y axis. That is why the ammonium ions are fixed in one position, while the Rb atoms occupy ststistically two independent positions. The organization of the structure of $K_2[La(NO_3)_5(H_2O)_2]$ is quite different as the ionic radii of cesium, ammonium and rubidium are too large in comparison with potassium.

PS-08.04.09 CRYSTAL STRUCTURE OF FERROELECTRIC $KGeOPO_4$ CRYSTALS. By N.I.Sorokina*,I.A.Verin, V.I.Simonov,Institute of Crystallography,Moscow, Russia; V.I.Voronkova,V.K.Yanovskii,Physics Department,Moscow State University,Russia.

Single crystals of $KGeOPO_4$(KGP) which belong to the family of ferroelectric and nonlinear optical compounds of the $KTiOPO_4$(KTP)type have been obtained. Their dielectric susceptibility has been measured and their crystal structure has been studied.The ferroelectric phase transition temperature for KGP is 785°C which is close to the temperature of incongruent melting of this compound at 805°C.Besides, relaxation phenomena due to a high ionic electroconductivity are observed.The KGP crystals at room temperature have the polar sp.gr.Pna2$_1$with the following unit cell parameters: a=12.6013(10), b=6.3051(5), c=10.0031(8) A. Our X-ray structural study (an "Enraf-Nonius"autodiffractometer,AgK$_\alpha$-radiation,

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$\sin\theta/\lambda < 1.0$ Å^{-1},6692 reflections with /F/>3σ/F/, R=2.53%) evidences that KGP and KTP are isostructural. The structures of these two crystals differ mainly in the following features: [GeO$_6$]-octahedra are essentially less distorted than [TiO$_6$] ones, besides, there was hardly any alternation of long and short chemical bonds in the chains of metal-oxygen octahedra. For instance, the corresponding bond lengths are as follows: Ge(1)-O(Ge2) 1.801, Ge(1)-O(Ge1) 1.791, Ge(2)-O(Ge2) 1.813, Ge(2)-O(Ge1) 1.823 Å. The results obtained for KGP are compared to the data available for similar KMeOPO$_4$ compounds, where Me = Sn and V, as well as for KTP crystals irradiated by fast neutrons.

PS-08.04.10 TEMPERATURE DEPENDENCE OF THERMAL VIBRATION AND POSITIONAL PARAMETERS OF ATOMS IN MAGNETITE. By H. Okudera*, K. Kihara and T. Matsumoto, Department of Earth Sciences, Faculty of Science, Kanazawa University, Japan.

Crystallographic parameters and their thermal changes in natural magnetite (Fe$_{3-\delta}$O$_4$) have been studied with single crystal X-ray diffraction method in the range from room temperature to 1069K. The cell dimension (a), oxygen coordinate (u-parameter), and atomic mean-square displacements (MSD's) are reversible as a function of temperature below 773K. The cell dimensions of four specimens are determined within the range from 8.3925(7) to 8.3962(3) (Å) at room temperature before heating and agree with the previous reports (e.g., Hamilton, W. C., Pys. Rev., 1958 110, 1050-1057; Fleet, M. E., Acta Cryst., 1981, B37, 917-920). The cell dimension a with increasing temperature is fitted with the quadratic form:

a (Å) = 8.3845 + 2.3947 × 10^{-6} T + 9.338 × 10^{-8} T^2

in the range from 299K to 773K. Discontinuity of the first derivative of expansion at 865K, reported by Gorton et al. (Trans. Metal. Soc. AIME, 1965, 233, 1519-1525), is not observed in the present magnetite.

The u-parameter remains nearly constant at $u = 0.25487(3)$, but begins to increase at 623K, suggesting random distribution of Fe^{3+} and Fe^{2+} over the tetrahedral and octahedral cation sites. This suggests that the structure would be ideally inverse type below 623K and Fe^{2+} and Fe^{3+} cations would be slightly disordered above the temperature. At the octahedral cation site, the MSD's of atom normal to [111] has smaller values than that along [111] at a low temperature. The former, however, has a larger rate of increase with increasing temperature, and becomes larger than the latter above 623K.

PS-08.04.11 A PRACTICAL V/P METHOD FOR ESTIMATING SMECTITE LAYERS PERCENTAGE IN MIXED — LAYER ILLITE/SMECTITE AND A STUDY OF FACTORS OF INFLUENCING THE V/P VALUES. By Xi—sheng Lin and Nai—Xuan Zheng, Scientific Research Institute of Petroleum Exploration and Development, Beijing, China.

Smectite layers percentage (%S) has been used to quantitatively describe mixed—layer illite/smectite(I/S). According to the method (R. C. Reynolds, 1970, 1980), the %S should be identified based upon the positions of 002 and 003

reflections of illite/smectite. However, these two peaks are often overlapped with 001 and 002 reflections of illite respectively. An equation $(\%)S = 66 \cdot \frac{V}{P} + 39$ (shown in Figure) has been derived here, according to the least squares principle, and by using information from E. Perry and J. Hower (1970) and our analyzed data. Obviously, it is easier to use the equation to determine the %S, and the error is 10%. The results suggest that both slit size of diffractometer and contents of I/S in samples affect the V/P values. Size of divergence slit should be fixed at 1° or $\frac{1}{2}$° and the equation be changed to $(66 \cdot \frac{V}{P} + 39) \cdot \sigma_i (i=1, 2, 3)$ because of the influence of the contents. σ_i are: $\sigma_1 = 1.888 - 0.1952\ln x$, for $(\%)S \geqslant 75$; $\sigma_2 = 1.633 - 0.14\ln x$, for $50 \leqslant (\%)S < 75$; $\sigma_3 = 1.129 - 0.0013x$, for $37 \leqslant (\%)S < 50$. Here, x are refered to the contents. The other factors such as crystallite thickness and lattice distortion, which influence the V/P values, are also discussed in brief.
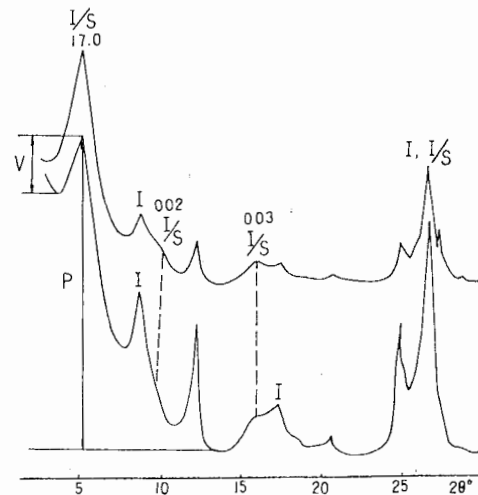
V/P of 17A peak of ethylene glycol treated
mixed—layer illite/smectite
I; illite   I/S; illite/smectite

PS-08.04.12 RECONSTRUCTIVE CRYSTAL-TO-CRYSTAL CONVERSION IN THE SOLID STATE. By U. Eigendorf, G.E. Herberich, T. Wagner, and U. Englert*, Institut für Anorganische Chemie, RWTH Aachen, Prof.-Pirlet-Straße 1, D-5100 Aachen, Germany.
Crystals of the etherate