energy that separates the bonding & antibonding orbitals if one likens the formation of H₂ dimers merely to H₂ on the ground that H₂ has the configuration [Xe] 4d¹ 5s¹ 6s¹. Details of the semiquantitative calculations will be presented.

It has been shown that most of the Nb₃XY₃ (Y = Chalcogen, X = Halogen) compounds adopt the Nbₓ₁₈ layer structure (G. J. Miller, unpublished). The niobium atoms fill 3/8 of the octahedral holes of a closed 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 N₅-S₅ system, in addition to the hexagonal phase, an orthorhombic Nb₅S₅₃ as well as a new compound, (Nb₃S₅)$_n$Nb₂, were found.

All of the compounds were synthesized from elemental materials and characterized by single crystal X-ray diffraction. The crystals of (Nb₃S₅)$_n$Nb₂ 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 Nb₅S₅₃ structure is cubic close packing. The niobium atoms occupy the octahedral holes in the sequence [A⁺B⁺C⁺][A⁺B⁺C⁺] · A⁺, B⁺ and C⁺ a, b and c, as well as a, b and c represen, 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 α or between layers of metal atoms. The whole structure is also layered, but the sheets are buckled and run perpendicular to the α axis.

In the monoclinic (Nb₅S₅)$_n$Nb₂ 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 α to achieve a channel-like structure. The isolated Nb₂ molecules with trigonal bipyramidal geometry sit at the positions between the layers along the channels. We should point out that in the solid state, Nb₂ occurs with the niobium atoms in octahedral coordination and dimerized into Nb₂[12] cluster. The trigonal bipyramidal coordination of niobium is known in the gas phase of NbCl₄ 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 Nb₂ molecules.

Our investigation was performed 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 isostructural with the alkali lanthanum nitrates A₃[La(NO₃)₃(OH)₂]·H₂O, where A = Cs, Rb, NH₄, K. Such a comparative analysis shows how far 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 NH₄⁺ ions. This circumstance determines the possibility of water getting into the intraframework cavities of the rubidium and ammonium compounds. The ammonium cations tend to form hydrogen bonds. They join the ammonium ions and the molecules of intermolecular water to form the chains along α axis. Then it is seen that ammonium ions are fixed in one position, while the Rb atoms occupy statistically two independent positions. The activation of the structure of K₃[La(NO₃)₃(OH)₂] is quite different as the ionic radii of cesium and ammonium and rubidium are too large in comparison with potassium.

In the monoclinic (Nb₅S₅)$_n$Nb₂ 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 α to achieve a channel-like structure. The isolated Nb₂ molecules with trigonal bipyramidal geometry sit at the positions between the layers along the channels. We should point out that in the solid state, Nb₂ occurs with the niobium atoms in octahedral coordination and dimerized into Nb₂[12] cluster. The trigonal bipyramidal coordination of niobium is known in the gas phase of NbCl₄ 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 Nb₂ molecules.
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\[ \text{sin} \theta / \lambda = 0.8^\circ, 1.0 \text{ A}^{-1}, 6692 \text{ reflections with } /P = 3\gamma, \gamma = 2/53 \% \] evidencess that KGP and KTP are isostructural. The structures of these two crystals differ mainly in the following features: (GeO\_4) - octahedra are essentially less distorted than \((\text{SiO}_4)\) - 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(2)(Ge2) 1.801, Ge(1)-O(3)(Ge1) 1.791, Ge(2)-O(4)(Ge2) 1.813, Ge(2)-O(3)(Ge1) 1.823 \text{ A}. The results obtained for KGP are compared to the data available for similar \(\text{KMePO}_4\) compounds, where \(\text{Me} = \text{Si and V}\) as well as for KTP crystals irradiated by fast neutrons.

PS-08.04.30 TEMPERATURE DEPENDENCE OF THERMAL VIBRATION AND POSITIONAL PARAMETERS OF ATOMS IN MAGNETITE. By H. Okada\(_1\), K. Kihara and T. Masumoto, Department of Earth Sciences, Faculty of Science, Kanazawa University, Japan.

Crystallographic parameters and their thermal changes in natural magnetite (Fe\(_{3}\)O\(_4\)) have been studied with single crystal X-ray diffraction method in the range from room temperature to 1036K. The cell dimension (a), oxygen coordinate (u-parameter), and atomic mean-square displacements (MSD\(_x\)) are reversible as a function of temperature below 773K. The cell dimensions of four specimens are determined within the range from 8.3926(7) to 8.3965(2) \text{ A} at room temperature before heating and agree with the previous reports (e.g., Hamilton, W. C., Phys. Rev., 1938 394, 1005-1037; Flexor, M. E., Acta Crystal., 1981, 457, 917-920). The cell dimension u with increasing temperature is fitted with the quadratic form:

\[ a (\text{A}) = 8.3845 + 2.947 \times 10^{-3} \times T + 9.338 \times 10^{-6} \times T^2 \]

in the range from 299K, to 773K. Discontinuity of the first derivative of expansion at 865K, reported by Crompton et al. (Trans. Metal. Soc. AIME, 1965, 233, 1519-1529), is not observed in the present magnetite.

The u-parameter remains nearly constant at \(u = 0.25\) to 0.30, but begins to increase at 623K, suggesting random distribution of Fe\(_3^+\) and Fe\(_2^+\) over the octahedral and octahedral cation sites. This suggests that the structure would be ideally inverse type below 623K and Fe\(_3^+\) and Fe\(_2^+\) cations would be slightly disordered above the temperature. At the octahedral cation site, the MSD\(_x\)'s of arsenic 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-08.04.34.3 PRINCIPAL V/P METHOD FOR ESTIMATING SMECTITE LAYERS PERCENTAGE IN MIXED — LAYER ILLITE/SMECTITE AND A STUDY OF FACTORS INFLUENCING THE V/P VALUES. By Xi — sheng Lin and Na — Xuan Zheng, Scientific Research Institute of Petroleum Exploration and Development, Beijing, China.

Smeclite layers percentage \((\% S)\) has been used to quantitatively describe mixed — layer illite/smeclite \((1/S)\). 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/smeclite. However, these two peaks are often overlapped with 001 and 002 reflections of illite respectively. An equation \((\% S = \frac{b}{P + 39}(\text{shown in Figure})\) has been derived here, according to the least squares principle, and by using information from E. Perry and J. Howar (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 \(\frac{1}{2}^\circ\) and the equation be changed to \((\% S = \frac{b}{P + 39})\) or \((\% S = \frac{b}{P + 39})\), because of the influence of the contents. \(\% S\) are typically 1.888 to 0.192% in x, for \((\% S < \% S = \frac{1}{2}^\circ = 1.633 - 0.141 x, for \% S < 0.018 x, for \% S < 0.018 x\).

\(x\) are referred to the contents. The other factors such as crystal lattice 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/smeclite

1. Illite
2. I/S. Illite/Smecite

PS-08.08.04.12 RECONSTRUCTIVE CRYSTAL-TO-CRYSTAL CONVERSION IN THE SOLID STATE. By U. Eignerd, G.E. Herberich, T. Wagner, and U. Englert* Institute for Anorganische Chemie, RWTH Aachen, Prof. -Priest-Straße 1, D-5100 Aachen, Germany. Crystals of the ethoxide