PS08.00.39 $Na_4Co_3(PO_4)_2P_2O_7$, A NEW SODIUM COBALT PHOSPHATE CONTAINING A THREE-DIMENSIONAL SYSTEM OF LARGE INTERSECTING TUNNELS. C. Ruiz-Valero[1], E. Gutierrez-Puebla[1], A. Monge[1], U. Amador[2], C. Parada[2] and F. Sanz[2], [1]Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049, Madrid, Spain, [2]Facultad de Ciencias Químicas. UCM. 28040 Madrid, Spain

The phosphates of transition metals form a huge family of compounds. The association of metallic or semi-metallic rows or layers of MO_6 octahedra with insulating PO_4 rows or layers gives rise to original physical properties. Moreover, it is well known that many phosphates are good ionic conductors. Due to these reasons, a great effort, during the last years, has been devoted to the study of mixed transition-metal phosphates.

Single crystals of the new Co(II) phosphate $Na_4Co_3(PO_4)_2P_2O_7$ have been isolated and their structure has been determined by X-ray diffraction techniques. The structure of this compound is built up from corner- and edge-sharing between CoO_6 octahedra and PO_4 and P_2O_7 groups giving rise to a polyhedral connectivity which produces large tunnels running along the three main crystallographic directions The structure consists of infinite layers with composition $(Co_3P_2O_{13})_\infty$ parallel to the bc plane. Interlayer linkages are made via P-O-P bridges of the pyrophosphate groups in such a way that large tunnels extending along the [010] and [001] directions occur between two neighbouring sheets. Besides, there also exist channels along the [100] direction crossing the $(Co_3P_2O_{13})_\infty$ layers. A complex scheme of tunnel intersections gives rise to the formation of a three-dimensional channel network which hosts the sodium cations.

This compound crystallizes in the orthorhombic noncentrosymmetric space group $Pn2_1a$ with a=18.046(5)Å, b=6.533(2)Å, c=10.536(2)Å, V=1242.1(5)Å^3 and Z=4. The structure was refined from 1791 reflections with $I>2\sigma(I)$ were used for structure solution and refinemt (R=0.039).

PS08.00.40 LOW ORDER TRUNCATION ANALYSIS OF X-RAY INTENSITY DATA AS A NOVEL TOOL FOR ACCURATE SITE REFINEMENT. ORTHOPYROXENE AS A EXAMPLE. H. Schlenz, H. Kroll, T. Lueder, A. Fischer, A. Kirfel*, T. Vad*, Institut f. Mineralogie, Westf. Wilhelms-Universität, D48149 Münster, Germany, *Institut f. Mineralogie, Universität Würzburg, D-97074 Wurzburg, Germany

Extremely precise and accurate Fe^{2+},Mg distributions are required in order to derive meaningful cooling rates from the orthopyroxene geospeedometer. Comparison of Möβbauer and X-ray site refinement studies shows that X-ray diffraction usually gives a more ordered distribution than Möβbauer. This challenges the crystallographer to test X-ray site refinement procedures. Atomic site occupancies are expected to be influenced by a variety of factors: The part of reciprocal space from which observations are collected; the structure model, i.e. assumed valence states and type of extinction correction; criteria for excluding „unobserved" reflections and outliers from calculations; correlations between site occupancies and vibrational parameters; weighting of the observations. The discussion of X-ray data collection and refinement strategies, using new experimental data from various orthopyroxenes, discloses that the standard practice of single X-ray refinements is inadequate. A novel bivariate technique is suggested that is based on stepwise truncation of low order data (LOT analysis). Thereby, extinction and chemical bonding effects are reduced and correlations between site occupancies and thermal vibration parameters are circumvented, when a B(M2)/B(M1) ratio is chosen that provides invariance of site occupancies against the choice of subsets of data. This technique overcomes the main obstacles in deriving accurate site occupancies from X-ray intensities. As such, it is a generally applicable tool, not being restricted to orthopyroxene.

PS08.00.41 CRYSTALLOGRAPHIC STUDIES OF BROOKITE(TiO_2) WITH SYNCHROTRON RADIATION. Masahiko Tanaka, Photon Factory, National Laboratory for High Energy Physics, 1-1 Oho, Tsukuba, Ibaraki 305 Japan.

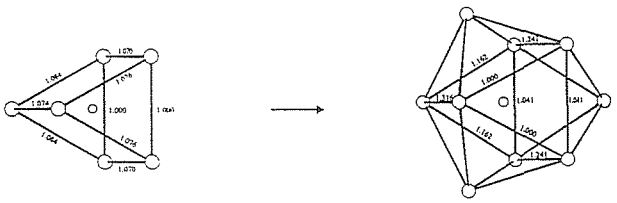
X-ray diffraction studies on single crystals of brookite(TiO_2) with synchrotron radiation have been performed. It is found that extra reflections are observed, which is forbidden by the extinction rule for the brookite space group. It is well known brookite crystal have two kinds of crystal habit, one is platy and the other is pyramidal. This is an interesting problem why two kinds of crystal habit are observed from the point of crystal morphology. Hartman[1] suggested that platy habit crystal made by epitaxial growth of SiO_2 on the {001} brookite as the result of PBC analyses. I think it may be possible to observe structural distortion caused by such epitaxial growth by using strong X-ray source, so I carry out single crystal X-ray diffraction studies of brookite with synchrotron radiation. A crystal with pyramidal habit from Magnet cove, Arkansas, USA used for diffraction studies. The diffraction experiments were done with vertical type 4-circle diffractometer at BL-10A, Photon Factory, National Laboratory for High Energy Physics, using radiation of the 0.7 Å wavelength. Intensity data of 1557 reflections were collected from the following range; $2\theta < 65$ degrees, $-17 < h < 17$, $0, 0 < k,l < 16$. As the results, some forbidden reflections for brookite space group Pbca, such as h00,k00,00l;h,k,l=2n+1, 0hk;h=2n+1, h0l;l=2n+1 or hk0;h=2n+1, are observed. The intensity of these reflections is lower than that of the fundamental reflection by three orders of magnitude. There is no reflection that suggests existence of super lattice by measurements of diffraction profile along h00. Diffraction studies using a platy habit single crystal are in progress. The reason these extra reflections appear and the relationship between the crystal habit and these extra reflections will be discussed.

[1] Hartman,P.(1965), C.N.R.S.,601-618

PS08.00.42 $NiAl_3$: A STRUCTURE TYPE OF ITS OWN? Per Viklund, Ulrich Häußermann, Sven Lidin, Inorganic Chemistry 2, University of Lund, S-221 00 Lund, Sweden

Generally, the intermetallic compound $NiAl_3$ is counted as a representative of the Fe_3C (cementite) structure type. We grouped the almost 200 different compounds with the cementite structure type according to geometrical and chemical parameters and found that $NiAl_3$ is not fitting the values typical of this structure type.

$NiAl_3$ was prepared by slowly annealing an Al-rich melt and dissolving excess Al in dilute hydrochloric acid. The crystal structure was redetermined from single-crystal data: Pnma, a=6.613(1), b=7.367(1), c=4.811(1), Z=4.

Compared to the parent structure Fe_3C, the coordination polyhedron for the minority component changes from a trigonal prism with nearly equal edges to a distorted prism with all quadrilateral faces capped.

We suggest that $NiAl_3$ is better described by a structure type of its own rather than by the cementite structure.