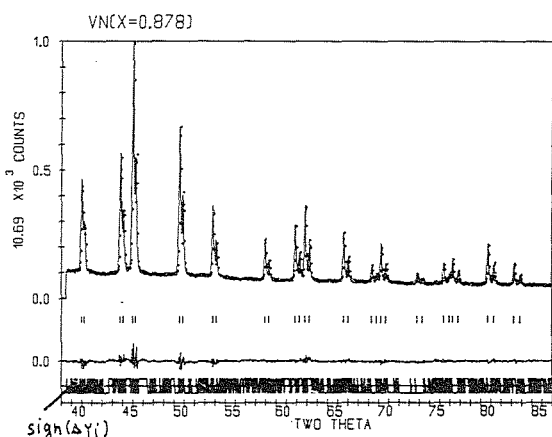


12.4-1 RIETVELD REFINEMENT OF TWO SUB-STOICHIOMETRIC VANADIUM NITRIDES. By L. Smrčok, Institute of Inorganic Chemistry CCHR, Slovak Academy of Sciences, 842 36 Bratislava, Czechoslovakia and P. Čapková, Department of Semiconductor Physics, Charles University, Ke Karlovu 5, 121 16 Prague, Czechoslovakia.

Physical properties of VN depend on the V/N ratio. The study of two such compounds ($x=.89$ and $.73$ determined by chemical analysis) was carried out with X-ray diffraction data collected using β -filtered MoK α radiation on a Philips powder diffractometer at $10^\circ/\text{step}$, $\Delta 2\theta=.05^\circ$. Calculations were performed with a modified version of DBW2.9 program (Wiles & Young, 1981) employing the ML profile function. Refined parameters included scale factor, isotropic harmonic temperature factors $B[A^2]$, population parameter of the non-metal site (n) three FWHM parameters, zero-point, specimen displacement and the lattice parameter. V and N atoms were placed in the 4a and 4b Wyckoff positions of the space group Fm3m, respectively. Background was interpolated between 12 mean intensities, each calculated from the three neighbouring observations, peak range: $\pm 12\text{FWHM}$. The results for $x=.89$ are: $a=4.13470(2)\text{\AA}$, $B(V)=.541(7)$, $B(N)=.208(39)$, $n=.878(16)$, $R_{wp}=.097$, $R_b=.014$, $S=1.23$, $d(\text{Durbin-Watson})=1.57$, B 's and n refined simultaneously in the final cycles. For $x=.73$: $a=4.06951(6)\text{\AA}$, $B(V)=.345(9)$, $B(N)=.476(30)$, $n=.760(9)$, $R_{wp}=.136$, $R_b=.016$, $S=1.55$, $d=.73$, but due to large correlations and poorer fit the values of B 's and n were not obtained from the same cycle. The TDS correction was not included in either case for its maximum contribution is $< 1.5\%$. It should be emphasized that only the total B parameters were determined in this work without any attempt to separate them into a static and a dynamic part. The results obtained can be explained by assuming a systematic static displacement of V-atoms adjacent to a N-vacancy along $[100]$ away from the vacancy. These static displacements lead to a shortening of the V-N bonds in VN $_{.89}$ and subsequent reduction of amplitudes of the thermal vibrations of N-atoms in this compound. On the other hand the high concentration of vacancies in VN $_{.73}$ leads to the compensation of static displacements of V-atoms and to relaxation of N-orbit resulting in increasing of the $B(N)$ value.



12.5-1 IS IT POSSIBLE TO DETERMINE A ZEOLITE STRUCTURE AB INITIO FROM SYNCHROTRON-QUALITY POWDER DIFFRACTION DATA? By Lynne B. McCusker, Clarendon Laboratory, Oxford University, U.K.

The solving of new zeolite framework structures without the benefit of single crystal diffraction data is a problem that has plagued zeolite crystallographers for years. A number of ingenious approaches have been developed, but ultimately all rely upon the experience and intuitive reasoning of the crystallographer.

Various characterization techniques can give clues about features of the structure. For example, sorption data can provide information about pore and cavity size, electron diffraction unit cell and symmetry information, ^{29}Si MASNMR the number of chemically distinct Si sites and their relative occupancies, and x-ray powder diffraction the unit cell dimensions and impurity or amorphous phase information. The usual approach is to 1) construct trial models which take into account all the available data, 2) optimize the framework geometry and assess its feasibility, 3) generate theoretical powder diffraction patterns for reasonable models, and 4) compare these patterns with the observed one. It is a long and tedious process with no guarantee of success. Is there an alternative?

The advent of synchrotron radiation as a viable source of high intensity x-rays has made very high resolution x-ray powder diffraction possible. The resolution is such that *ab initio* structure determination from powder data has become a real possibility even for relatively complex materials such as zeolites. This may be an alternative to, or provide an additional piece of information for, the present trial and error procedure.

Data from both the Daresbury and the Brookhaven synchrotron facilities have been collected to examine and evaluate this possibility. The data are now being processed through a series of computer programs. The critical steps are the extraction of reflection intensities from the diffraction pattern (a modified version of Pawley's ALLHKL program is being used), and the selection of input parameters for the structure determination package (G. Sheldrick's SHELXS-86 and M. Woolfson's MULTAN-84).

Results on the test example Silicalite I, which has a complex (but known) framework structure, and on a true unknown will be presented.