

By the "breathing mode" a sequence of large and small Te-squares is formed in such a way that a big Te-square is located between two Nb atoms of short bond distance and a smaller Te square is formed when the Nb-atoms are further apart. By the oscillatory motion of the libration mode Te-Te pair bonds occur between Te atoms of different antiprisms about $(0,0,z)$ and about $(1/2,1/2,z)$. The bond lengths vary between $2.90(1) \text{ \AA}$ and $2.95(1) \text{ \AA}$. In the Nb-chain along c the bond lengths vary between $3.08(1) \text{ \AA}$ for a Nb-Nb pair and 3.96 \AA between Nb_3 -groups.

By the refinement calculations in the space-group $P4$ the following R-values have been obtained: $R=0.062$ for the modulated structure (1024 unique reflections), $R=0.062$ for the average structure (290 unique main reflections) and $R=0.046$ for the complement structure (734 unique satellite reflections). The scale factor has been refined by the main reflections (average structure), whereas, the atomic shifts have been determined by the satellite reflections alone (complement structure). The evaluation of the Patterson-function as well as a Fourier-synthesis confirm the obtained results.

20.4-6 RE-EXAMINATION OF THE MODULATED STRUCTURE OF THE NaNbO_2 IN ANTIFERROELECTRIC PHASE.

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The structure of the antiferroelectric phase of NaNbO_2 has been refined (Kucharczyk et al., Ferroelectric (1978) 21, 445) for a mixed occupational and displacive modulation model. This was later supported by theoretical studies (Michel, Phys. Rev. B (1981) 24, 3998; Mc Connell & Heine, Phys. Rev. Lett. (1981) 46, 1091). However, due to a number of simplifications concerning the symmetry treatment, the refinement procedure and some arbitrariness in phase relationships of the modulating waves, the obtained structure is no longer the good base for more detailed studies. We decided, therefore, to reinvestigate this structure by applying the recently developed approach to modulated structure determination. The special least squares program for modulated structures refinement by use of $(3+1)$ -dimensional symmetry (de Wolff et al., Acta Cryst. (1981) A37, 625) has been written by one of us (W.A.P.). The refinement was carried out in two superspace groups (see Table) with a data set of 214 reflections (seven of them removed due to extinction reasons). At the beginning, in addition to positional and anisotropic thermal parameters, only the individual occupational waves were taken into account. Next, all the possible displacive waves were added. However, the components of the displacive waves along x and z were proved negligibly small and consequently set to zero. Furthermore, the rigid body like behaviour of NO_2 group was detected and for the final refinement all modulation parameters of the N and O atoms, were constrained. The final discrepancy indices obtained for different space groups for pure occupational and mixed modulation are as follows:

TABLE

Space groups	Type of modulation	R-indices		
		main reflections R_M	satellites R_S	common R
$P4^I$ mmm $1s1$	occupational	0.0611	0.1617	0.0894
$P4^I$ $2mm$ $ss1$		0.0619	0.1380	0.0833
$P4^I$ mmm $1s1$	mixed	0.0553	0.0908	0.0653
$P4^I$ $2mm$ $ss1$		0.0555	0.0822	0.0630

The improvement due to the superposed displacive wave (displacement of ions along y , only) is evident. The difference between the two space groups, solves the problem of phase shifts between the modulating waves. Contrary

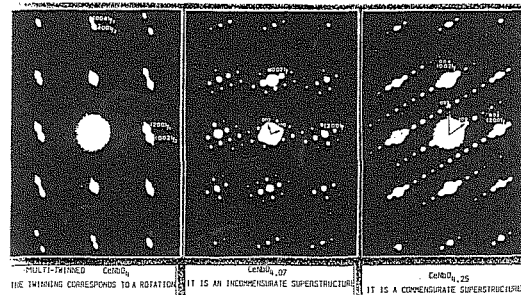
to $P4^I$ $2mm$, the $P4^I$ mmm group excludes all relative

phase shifts between the individual waves. The phase shifts, however, do exist as indicated by the significant lowering of R_S index (see Table). The occupational wave of NO_2 group is shifted in respect to Na^+ ion wave by about 22° . There are practically no phase shifts between the individual displacive and occupational waves. The amplitude of the displacive wave of Na^+ was found almost two times as big as that of NO_2 , with the occupational amplitudes being approximately the same.

20.4-7 ANION INSERTION IN THE COMMENSURATE-INCOMMENSURATE FERGUSONITE-LIKE PHASES CeNbO_{4+x} .

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The compound CeNbO_4 can be oxidized at relatively low temperatures ($\sim 600^\circ\text{C}$), the reaction products are discrete compounds CeNbO_{4+x} , $x = 0.07, 0.25, 0.33$. X-ray, electron diffraction and electron microscopy results on the two first compounds are reported:



Commensurate phase $\text{CeNbO}_{4.25}$

The supercell is 12 times that of the fergusonite. Its structure was determined by X-ray diffraction. The anion insertion mechanism corresponds to a rotation of one edge of the oxygen tetrahedra around some of the niobium atoms. The compression of the anion framework resembles that of Vernier structures. Oxygen clusters containing 3 extra anions are formed. The cation displacement are rather small, however, the anion clusters are located close to those zones of the crystal where the cation displacements are larger. The final values of the R fac-

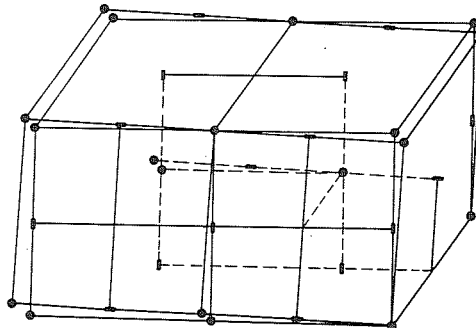
tors and the difference Fourier analysis show that the superstructure is disordered and that shifts of the anion clusters can occur along the c_f fergusonite direction.

Incommensurate phase $CeNbO_{4.07}$

The modulation vectors occur in the (010) plane of the fergusonite lattice. The modulation can be reduced to only one incommensurate component which is along the c_f axis. Its periodicity is the same for different preparations of this phase. Studies of the relationship between an approximate supercell (29 times the fergusonite cell) and that of the fergusonite structure shows that the modulation seems to correspond to an irregular distribution of the cation distorted zones. These zones are where the anion insertion occurs. From the comparison of the X-ray intensity distribution in reciprocal space and the fact that the two phases $CeNbO_{4.07}$ and $CeNbO_{4.25}$ could coexist in the same crystal, it can be deduced that the same anion insertion mechanism is valid for both phases. The cation distortion is closely related to the tetragonal twin formation and the distortion distribution in the crystal is parallel to the twin walls (this does not hold when Ce is substituted by (La, Th)).

The analysis and indexing of X-ray photographs for hydrogenated $Pd_{60}Cu_{40}$ single crystal made it possible to present the crystal reciprocal lattice as a superposition of two tetragonal lattices which have a coincident axial vector \bar{a}^* and are mirror symmetrical to each other (see the figure). The transformation from the cubic structure to the tetragonal one is accompanied by twinning with invariant plane (011). The ordered tetragonal structure has the type $CuAuI(4_1)$ the space group is $P4/mmm$.

This type of ordered structure corresponds to the equiatomic relation of the alloy components. Consequently, the ordering in PdCu alloy during hydrogenation is realized by $CuAuI$ -type and not by the BCC (B2) one. Probably, this is connected with the change in the electron concentration of alloys due to hydrogenation.



20.4-8 DISORDER-ORDER TRANSITION OF THE PALLADIUM-COPPER ALLOY BY HYDROGENATION. V.Sh.Shekhtman and V.F.Degtyareva. Institute of Solid State Physics, USSR Academy of Sciences, 142432 Chernogolovka, Moscow district, USSR

The investigation of hydrogen interstitial solid solutions in Pd-Cu alloys has culminated in the discovery of an unusual phenomenon: hydrogen stimulates the ordering of the alloy lattice. Under usual conditions the ordering in Pd-Cu alloys occurs near compositions $PdCu_3$ and $PdCu$; in alloys with a higher palladium content (> 50 at%) the ordering is not realized. Early experiments on polycrystalline samples had shown that in the alloy $Pd_{60}Cu_{40}$ the hydrogenation causes a tetragonal lattice distortion which is indicative of the ordering (Degtyareva et al., Phys.Stat.Sol., 66a, 77, 1981). This structure transformation has been studied in detail on a monocrystalline alloy $Pd_{60}Cu_{40}$ held in an atmosphere of hydrogen at $P_{H_2}=11$ kbar and $T=300^\circ C$ for 12 hours (the hydrogenation to the composition ~ 0.5).

The study has been carried out by oscillating $Pd_{60}Cu_{40}-H$ single crystal about the directions that correspond to [100], [001] and [110] of the initial cubic crystal. The oscillating-crystal X-ray photographs show the splitting of reflections which corresponds to the tetragonal lattice distortion.

The appearance of superstructural reflections have also been observed. By oscillating about $[110]_{cub}$ they formed new layer lines with the identity period $l \approx a_{cub} \cdot \sqrt{2}$.

20.4-9 STRUCTURE MODULATION OF K_xWO_3 AND RELATION TO PHYSICAL PROPERTIES. H. Brigitte Krause, Northern Ill. U., DeKalb, IL 60115, USA, A. J. Schultz and H. Horiuchi, Argonne Nat. Lab., Argonne, IL 60439, USA, and W. G. Moulton and R. C. Morris, Florida State U., Tallahassee, FL 30206, USA.

K_xWO_3 for $0.25 \leq x \leq 0.33$ crystallizes in the hexagonal tungsten bronze structure. However, electron diffraction patterns show composition- and temperature dependent incommensurate superlattice reflections along $[00l]$ and commensurate superlattice reflections within the a^*-b^* planes. The superlattices were attributed to ordering of the potassium vacancies within channels along the c -direction resulting in domains ranging between about 50Å and 250Å. The domain size is composition dependent with a discontinuity for $x=0.25$ where a phase transition occurs. This corresponds to a discontinuity for electric transport properties. The commensurate superlattices result from displacements of the ordered chains relative to one another. The superstructures within single crystals are not uniform, which is seen in high resolution electron microscope images.

Single crystal neutron data of $K_{0.25}WO_3$ have shown that potassium vacancy ordering alone cannot account for the observed intensities of the superlattice reflections. Models for displacement of the oxygen atoms around the vacancies--similar to a sinusoidal modulation of the oxygen positions--or a strictly sinusoidal modulation yield a reasonable agreement between the observed and calculated $00l$ -data.

This work was supported by the U.S. Department of Energy.