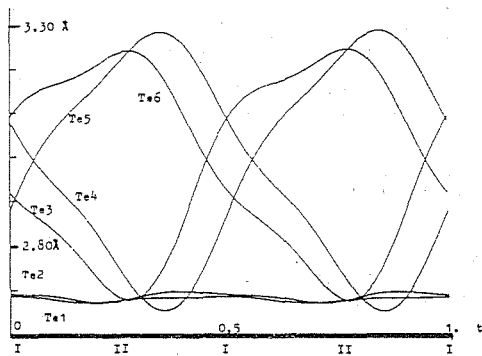


20.4-7 CRYSTAL STRUCTURE AND MORPHOLOGY OF THE INCOMMENSURATELY MODULATED COMPOUND AuTe_2 , CALAVERITE.

By W.J. Schutte, B. Dam, A. Janner, and J.L. de Boer, Department of Inorganic Chemistry, Paddepoel, Groningen and Research Institute for Materials, Faculty of Science, Nijmegen, The Netherlands.

The present investigation started from a suggestion by J.D.H. Donnay to reconsider an almost hundred year old problem of the non-applicability of the Law of Rational Indices to crystal growth forms of calaverite $\text{Au}_{1-p}\text{Ag}_p\text{Te}_2$ ($p < 0.15$) (Herbert Smith, Min. Mag. 13 1902, 125; Goldschmidt, Palache and Peacock, Neues Jahrb. Mineral. B.B.(A), 63 1931, 1). The reinterpretation of the 1931 data within a superspace approach (Dam et al., Phys. Rev. Lett. 55 1985, 2301) allows a consistent four integers indexing of all 92 different faces observed by Goldschmidt et al. and a precise determination of the modulation wave vector q . The basic structure, a deformed CdI_2 type, was determined by Tunell and Pauling (Acta Cryst. 5 1952, 375). In 1979 Sueno (Hawaii AIP Conf. Proc., 33, 333) recognized the incommensurately modulated character of the structure. That was confirmed in 1983 by electron diffraction (Tendeloo et al., J. Sol. St. Chem. 50 1983, 321). We determined the crystal structure of natural (Cripple Creek, Colorado) calaverite at 298 K and at 100 K. The superspace group is $\text{C2/m}(\alpha, 0, \gamma)(1, s)$ with $\alpha = -0.408$ and $\gamma = 0.448$ for the modulation wave vector q , in excellent agreement with the morphological results. All parameters (modulation waves up to third order) were refined with Yamamoto's (Acta Cryst. A38 1982, 87) program. Overall R_p for 1899 (2008) reflections of which about 2/3 are satellites is 4.6% (4.3%). The values at 100 K are in parentheses. Modulation parameters hardly vary with temperature. The largest modulation occurs for $y(\text{Te})$. The infinite Te-chains of the basic structure along b are now disrupted. Binding distances vary as well. The figure displays, as a function of t ($t = q \cdot r$ modulo 1, r is the average atom position) the six Au-Te distances from $\text{Au}(0,0,0)$ to $\text{Te1}(x = -0.31, y = 0, z = 0.29)$, $\text{Te2} = -\text{Te1}$, $\text{Te3} = (x + 1/2, -1/2, z)$, $\text{Te4} = (-x - 1/2, -1/2, -z)$, $\text{Te5} = -\text{Te3}$, and $\text{Te6} = -\text{Te4}$. The regions I ($t = 0, 0.5$) with two short metal-Te distances in linear coordination alternate with regions II ($t = 0.25, 0.75$) having four short distances in square coordination. This strongly resembles the situation in sylvanite where Ag^+ (d^{10} configuration) is linearly and Au^{3+} (d^8) is square coordinated. For calaverite we therefore observe a modulated valence state for Au around Au^{2+} with the extremes Au^+ and Au^{3+} located in regions I and II, respectively. This interpretation is reinforced when considering the occupation modulation of the Ag fraction at Au^+ positions in calaverite. The tellurium (its polarizability and electronic band structure) certainly plays a role as well as driving force for the modulation.



20.4-8 ELECTRON DIFFRACTION PATTERNS DISPLAYING 8, 10 AND 12 FOLD SYMMETRIES BUT NO BRAVAIS TRANSLATION SYMMETRY. By K.H. Kuo, Beijing Laboratory of Electron Microscopy, Academia Sinica, P.O. Box 2724, Beijing, P.R. China.

It has been shown earlier (H.Q. Ye, D.N. Wang and K.H. Kuo, Ultramicroscopy, 1985, 16, 273) that an electron diffraction pattern (EPD) displaying 10 fold symmetry may appear if the crystal size of a pentagonal Frank-Kasper phase consisting mainly of icosahedra or pentagonal antiprisms is diminished to the order of only a few nanometers. In such a case, the translation symmetry is very much suppressed while the orientation of icosahedra in various domains is still similar. This has now been explored in great details in V-Ni-Si alloys and its relation to the icosahedral quasicrystal is discussed. Moreover, EPDs displaying 8 and 12 fold symmetries have also been obtained in Cr-Ni-Si and V-Ni alloys, respectively, after rapid solidification. The crystalline phase in the former alloy has the β -Mn structure consisting mainly of octahedra and icosahedra while that in the latter alloy the phase consisting mainly of hexagonal antiprisms. Both alloys are of the microdomain structure and the translation order is also severely suppressed. On the other hand, the point group symmetry of the coordination polyhedra in these structures can still be manifested. For instance, similarly oriented hexagonal antiprisms, when projected in the direction parallel to these antiprisms, will show 12 fold symmetry. In other words, these non-crystallographic rotation symmetries in EPDs reflect the existence of oriented polyhedra with related rotation symmetries in microdomains of only a few nanometers in size. Such a conclusion has been proved by high resolution electron microscopic images.

20.4-9 ELECTRON DIFFRACTION STUDY OF ICOSAHEDRAL QUASICRYSTALS OF AN $\text{Al}_{74}\text{Mn}_{20}\text{Si}_6$ ALLOY. By M. TANAKA, M. TERAUCHI, K. HIRAGA* and M. HIRABAYASHI*, Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan. *The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan.

Convergent-beam electron diffraction (CBED) and small-area-parallel-beam electron diffraction have revealed the crystallographic nature of icosahedral quasicrystals in a melt quenched $\text{Al}_{74}\text{Mn}_{20}\text{Si}_6$ alloy. Electron micrographs show grains of μm scale dimensions. Misorientation between neighbouring grains is a few 10^{-3} rad. Each grain, however, consists of a number of subgrains less than 50 nm in diameter, making a misorientation of a few 10^{-4} rad. This quasicrystal possesses a much greater ordering in its atomic arrangement than an AlMn (M. Tanaka et al., Ultramicroscopy, 1985, 17, 279-285) and $\text{Al}_{71}\text{Mn}_{23}\text{Si}_6$ (L.A. Bendersky and M.J. Kaufman, Phil. Mag., 1986, B53, L75-L80). That is, the diffraction patterns of the present quasicrystal show the reflections of a lattice spacing 2.27 nm, which were not observed in those two quasicrystals and provide a larger number of weak spots between strong reflections. The reflection intensity shows a slower damping with scattering angle. The quasicrystal may have more than three different sized atomic sites and appears to be stabilized by an adequate addition of a different sized atom, Si. The intensities of the reflections appearing at high scattering angles hardly increase, even when the specimen is cooled down to the temperature of liq. N_2 , indicating a small change in Debye-Waller factor. The quasicrystal has two variants in its orientation, which are related with each other by 180° rotation about the five- or three-fold axis. Notwithstanding a much better ordering, there still exists a zig-zag deviation of the reflections from the radial line in a diffraction

pattern taken with the electron incidence parallel to the fivefold axis, as in the case of Al_7Mn . This deviation was interpreted in terms of inhomogeneously quenched phason strains (T.C. Lubensky et al., Phil. Rev. Letters, 1986, 57, 1440-1442). The detailed inspection revealed that two basic axes which make an angle of 36° or 324° exist in the patterns with a fivefold rotation symmetry. In one axis, the quasi period with $\tau = 1/2(1+\sqrt{5})$ is realized but in the other axis, a different period is formed. It was found that the deviated positions of all the reflections are generated by the addition of the vectors with quasi periods in the two directions. Convergent-beam electron diffraction patterns revealed the point group of the quasicrystal to be $m\bar{3}5$, even though a slight break down was observed in mirror symmetry, presumably due to an insufficient quality of the alloy. The weak reflections showing a fivefold symmetry, which we had observed and considered as an evidence of noncentrosymmetric nature (M. Tanaka et al., Proc. XIth Int. Cong. on Electron Microscopy, Kyoto, 1986, p.171-172), were identified as the tails of the first Laue-zone reflections 322101 and 333101 after Elser's indexing (V. Elser, Phys. Rev., 1985, B32, 4892-4898), these being expected from the centrosymmetric point group.

20.4-11 ICOSAHEDRAL SYMMETRY AND DIFFRACTION EXPERIMENT. By V.S. Shekhtman and E.V. Shulakov, Institute of Solid State, Academy of Sciences of USSR, Chernogolovka, USSR.

The observation of new principles of atomic packing in solids requires a more detailed consideration of the group theoretical relationship between the quasi-crystal model and crystal lattices. Only two syngonies, the cubic ($23, m\bar{3}, 432, 43m, m\bar{3}m$) and the icosahedral ($532, m\bar{5}m$) appear as maximal finite subgroups of $O(3)$. Two important subgroup chains are $23 \rightarrow 532 \rightarrow m\bar{5}m$ and $23 \rightarrow m\bar{3}m$. The pentagonal dodecahedron is a simple form for the group $m\bar{3}$, if the (10ψ) plane is taken as a starting face ($\psi = (1+\sqrt{5})/2$). Note, that in this procedure the application of the cube symmetry operations to the plane in the unique orientation leads to the figure, which is a simple form of the $m\bar{5}m$ supergroup. In view of this the aluminium-manganese, in which the effects of the "icosahedral catastrophe" were first observed should not have been a surprise. Actually, the alloys of aluminium with manganese, iron, silicon involve intermetallic compounds whose structures belong to the space groups $Im\bar{3}$, $Pm\bar{3}$. So, the possibility of a second order phase transition from the icosahedral group to its cubic subgroup should be taken into account. As far as the diffraction problems are concerned, we shall note that, though the publications in this field are numerous, all the experimental works employ only old methods of structural analysis, by "trial-and-error" methods. It is necessary to find a way to apply the structure factor and interference function in order to use the full set of diffraction maxima intensities in structure recovery. Preliminary experiments showed that the diffraction pattern depends on the icosahedral diffraction mask. We made transparencies, representing two algorithms for "strong" and "weak" Penrose tilings (Fig. 1a,b). The Fourier transforms, realized in an optical diffractometer, yielded different diffraction patterns (Fig. 2a,b).

These demonstrate not only the diffraction maxima, obtained from non-trivial patterns but, also, indicate the alteration of the diffraction pattern, depending on the tiling restructuring.

20.4-10 DEFECTS IN $Al-Mn-Si$ ICOSAHEDRAL QUASICRYSTALS STUDIED BY HIGH-RESOLUTION ELECTRON MICROSCOPY. BY K. Hiraga and M. Hirabayashi, The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan.

The new phase with the icosahedral symmetry, which has been discovered by Shekhtman et al. (Phys. Rev. Lett., 1984, 53, 1951) in rapidly solidified $Al-Mn$ alloys, is considered to be a "quasicrystal" with long-range quasiperiodic translational order and long-range orientational order. Appearance of defects such as phonon, phason and dislocation in the icosahedral quasicrystals have been theoretically discussed with mass-density description utilized for interpreting the icosahedral symmetry (Socolar J. E. S., Lubensky T. C. and Steinhardt P. J., Phys. Rev., 1986, 34, 334).

In this paper, we aim to examine directly structural properties of the defects in quasicrystals with high-resolution electron microscopy. The icosahedral quasicrystal examined was an $Al_{74}Mn_{20}Si_6$ alloy prepared by a melt-quenched method, which is known to form a high-quality quasicrystal. We found that linear phason strains tend to appear perpendicularly to the growth direction of the quasicrystal and to relax in the vicinity of a grown quasicrystal. Dislocations lying nearly perpendicularly to a specimen were observed in high-resolution micrographs taken with the incidence parallel to the five-fold symmetry axis. The Burgers vectors of the dislocations were determined by counting lattice fringes around the dislocation cores. The observed result of dislocations was consistent with a theoretical prediction by Levine et al. (Phys. Rev. Lett., 1985, 54, 1520).

