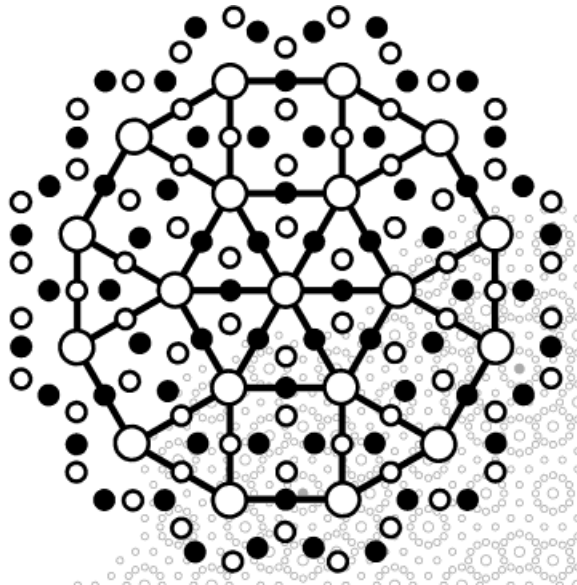

A hierarchical algorithm can be used to generate the dodecagonal pattern shown in the background. The similarity with a Ta_{151} cluster, which comprises 19 smaller, concentrically condensed antiprismatic Ta_{13} clusters, and with the electron diffractogram of $Ta_{1.6}Te$ is unmistakable.

More about this quasicrystalline chalcogenide is described by Harbrecht et al. on pages 1384 ff.

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A Dodecagonal Quasicrystalline Chalcogenide**

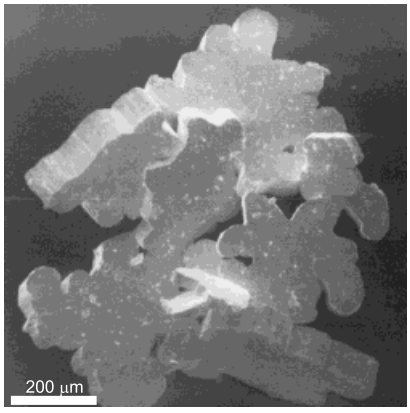
Matthias Conrad, Frank Krumeich, and Bernd Harbrecht*

Quasicrystals have their own particular type of order.[1] This leads to diffractograms with discrete intensity maxima, which indicates that there is long-range order. However, unlike in crystals this does not result from a periodic arrangement of the atoms in three dimensions; the particular type of order is expressed by a special symmetry in the diffractograms: characteristic for the quasicrystalline state are Fourier spectra with crystallographically forbidden five-, eight-, ten-, or twelvefold rotational symmetry.

The diffraction patterns from dodecagonal (dd) quasicrystals exhibit the symmetry of a regular dodecagon. This rare ordering was discovered by Ishimasa, Nissen, and Fukano in their investigations with electron diffraction and high-resolution transmission electron microscopy (HRTEM) of very small (≤ 100 nm) particles of a Cr–Ni alloy produced by chemical vapor deposition (CVD) in a flow of xenon.[2] Areas with dd symmetry have also been detected in extremely rapidly solidified Ni–V and Ni-V-Si melts as well as in thermally treated Bi–Mn double layer films, which had originally been amorphous.[3, 4]

The nickel-containing metastable dd phases appear to consist of columnar hexagonal-antiprismatic clusters,[2, 5] which occur as characteristic building blocks in some Frank–Kasper phases,[6] for example, the σ-phase. Frequently, microdomains of such crystalline phases are interspersed in the dd regions. The brightest spots in the HRTEM images are the vertices of a tiling comprising squares and triangles, whose edge length of about 0.45 nm corresponds to the shortest distance between the central atoms of neighboring hexagonal-antiprismatic columns. The tilings of squares and triangles in the dd phases are similar to those of the crystalline regions, however, they are irregular and aperiodic. Further experimental investigations of this ordering could not be conducted due to the insufficient stability and the limited access to these phases. This situation has changed with the discovery of a dd phase, which, according to all the results obtained so far, is stable and which we found in attempts to produce tantalum-rich tellurides.[7] Here we report on the synthesis, properties, and structural characterization of this first quasicrystalline chalcogenide.

dd-$Ta_{1.6}Te$ is accessible in preparative quantities as the final product of the stepwise reduction of $TaTe_2$ with tantalum at temperatures of 1270–1770 K and reaction times of between eight hours and several weeks. The compound is obtained as a black powder with lubricant-like mechanical properties. It decomposes in air to give an amorphous solid, which has not been further characterized. The synthesis was carried out in gas-tight sealed tantalum tubes to ensure the exclusion of further components during the formation of dd-$Ta_{1.6}Te$. The use of molybdenum as the crucible material allowed control and thus limitation of the composition of the phase. Energy dispersive X-ray spectroscopic (EDX) analyses (DSM-940, Zeiss, PV-9800, Edax) of various samples gave no indication of the inclusion of molybdenum or other possible impurities. The statistical evaluation of 20 EDX analyses (CM30ST, 300 kV, Philips, Tracor-Voyager-System) of a pure sample (by X-ray analysis) prepared in a molybdenum crucible (1.6 g, molar ratio $Ta:TaTe_2 = 2.5$), by using Ta_2Te_3[8] as the standard, gave a molar tantalum content of 63.2(4) %. Traces of iodine promote the formation of fine platelets, some of which contain pores, and which are extremely easily cleaved perpendicular to the main symmetry axis. The lamellar structure, atypical for metal-rich compounds, is clearly evident in Figure 1. Thermal treatment for several weeks at



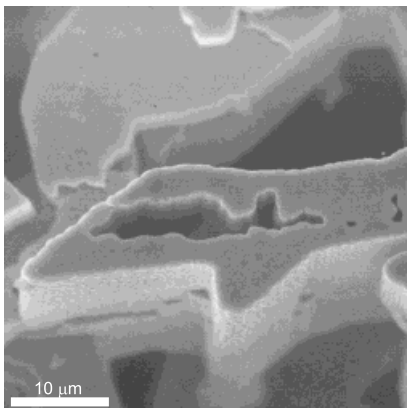


Figure 1. Scanning electron micrographs of dd-$Ta_{1.6}Te$ in two different magnifications.

1070 K did not produce any change in the diffractogram. However, above 1870 K, dd-$Ta_{1.6}Te$ transforms, with loss of the high rotational symmetry, into crystalline compounds that have almost the same chemical composition and structures in which

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the dodecagonal long-range order is relinquished to differing degrees in favor of translational periodicity.[9]

Characteristic for dd-$Ta_{1.6}Te$ are X-ray diffractograms (precession goniometer FR504, Enraf-Nonius) and electron diffractograms (CM30ST, 300 kV, Philips) with Laue symmetry 12*mm*. The intensity modulation of the electron diffractograms is dependent on the thickness of the sample. In the reflection-poor diffractogram (Figure 2a), which was taken of a thinner layer (ca. 10 nm), the intensity sequence is essentially in agreement with that of the precession photograph of the zeroth layer (Figure 3a). Although the reflections do not show a latticelike arrangement, they can still be indexed with integers, as for crystals, if instead of two, four base vectors are chosen $\vec{a}_i^*$ ($i = 1-4$). These four vectors point away from the center of a regular dodecagon towards four neighboring corners (Figures 3a and b). In precession photgraphs, which were taken perpendicularly to the dodecagonal layers, the reflections parallel to the twelvefold symmetry axis are equidistant, that is, the structure shows translational periodicity only in this direction. The location of all the measured reflections can therefore be given with suitable integral linear combinations of five base vectors; the fifth, independent vector $\vec{a}_5^*$ is perpendicular to the four coplanar vectors $\vec{a}_i^*$ ($i = 1-4$). In an equation analogous to the Bragg equation [Eq. (1)], they can be related to the experimentally

$$\frac{4\sin^2\theta}{\lambda^2} = (a_1^*)^2[\sum_{i=1}^{4} h_i^2 + h_1h_3 + h_2h_4 + \sqrt{3}(h_1h_2 + h_2h_3 + h_3h_4)] + (a_5^*h_5)^2 \quad (1)$$

found diffraction angles θ for the dodecagonal quasicrystal system.

λ is the wave length of the X-ray radiation, and h_1 to h_5 are five integers for addressing the points on the reciprocal quasilattice (corresponding to the three Miller indices h, k, and l for the three-dimensional reciprocal lattice). The evaluation of two chosen Guinier photographs (FR552, Enraf-Nonius, $\lambda(Cu_{K\alpha 1}) = 154.051$ pm) using the least-squares method gave the following values: $a_i^* = 2.1391(3)\ nm^{-1}$ ($i = 1-4$), $a_5^* = 0.481(2)\ nm^{-1}$, which gave $a_1 = \sqrt{2/3}/a_1^* = 0.38171(6)$ nm and $a_5 = 1/a_5^* = 2.079(9)$ nm.[10]

Since only two of the four base vectors $\vec{a}_1^*$ to $\vec{a}_4^*$ within the set of the real numbers are linearly independent, integral linear combinations of the four vectors do indeed give discrete points, however, in the dd plane they lie infinitely close together. Reflections can be perceived in the diffractograms only at particular positions. This subset shows some remarkable geometric characteristics. The possible locations of the reflections can be generated as follows (Figure 4): for the generator we chose two concentric dodecagons of different size; the larger of the two is expanded by the square irrational factor $\sqrt{\xi} = \sqrt{2+\sqrt{3}}$ and is also rotated by $\alpha = 15^\circ$ ($2\cos\alpha = \sqrt{\xi}$) relatively to the smaller one. In the next step we replace the center and the corners of the two dodecagons (large, open circles) by a copy of the original ordering, scaled down by a factor of $2-\sqrt{3} = 1/\xi$ (small, solid circles). If we repeat this step we obtain the pattern already described by Gähler in its third generation.[11] It corresponds to a section from an infinite pattern, which repeats itself in a similar manner on scale of lengths differing by the factor ξ. Thus, this pattern is invariant

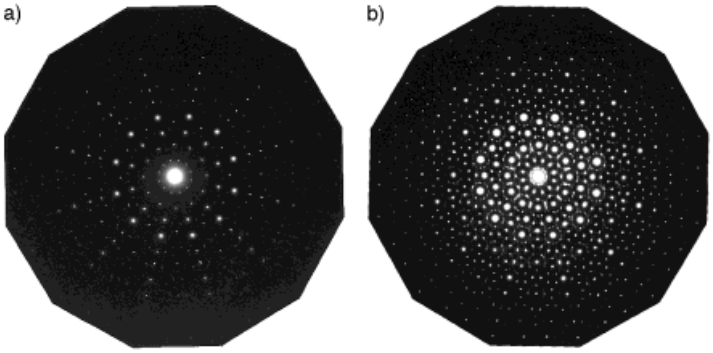

Figure 2. Reflection-poor (a) and reflection-rich (b) electron diffractograms of dd-$Ta_{1.6}Te$.

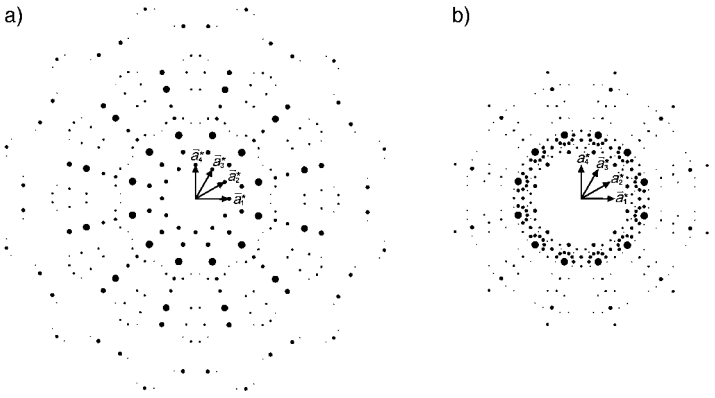

Figure 3. Schematic representation of the precession diffractograms of the zeroth (a) and fourth layer (b) perpendicular to the twelvefold axis. The size of the circles corresponds to the visually estimated intensity of the reflections.

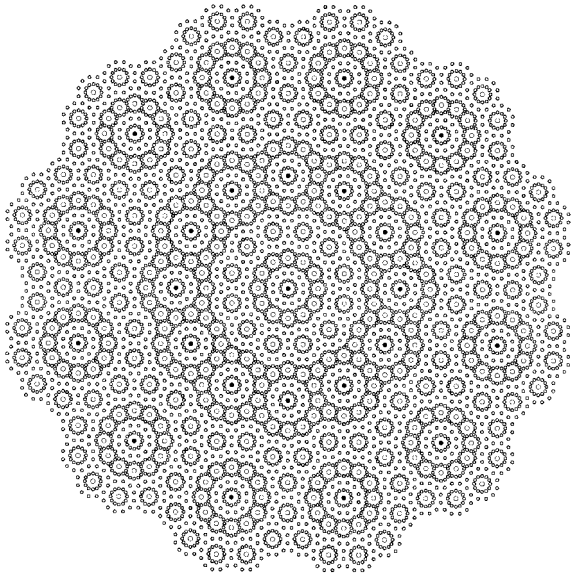

Figure 4. Result of an algorithm for the generation of a self-similar dodecagonal dot pattern.

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of scales with regard to the factor ξ, which represents the dodecagonal symmetry. In Figure 4 all the positions of the reflections can be seen that are visible in the diffractograms 2a and 2b as well as in that of 3a. Additional reflections appear in the precession photograph of the fourth layer ($h_1h_2h_3h_4$4, Figure 3b), the positions of which are only obtained in the pattern of the fourth generation. The finding that the reflections group together in this characteristic way in the X-ray diffractograms of higher dodecagonal layers is significant in that it clearly demonstrates the strange ordering upon which this tantalum-rich telluride is based.

Direct structural information on dd-$Ta_{1.6}Te$ can be obtained from HRTEM images recorded with the electron beam parallel to the main axis of symmetry. With favorable focal lengths (-80 nm) the motif of the diffractogram can be recognized locally (Figure 5); however, it is somewhat out-of-focus and organized differently. In the micrographs with

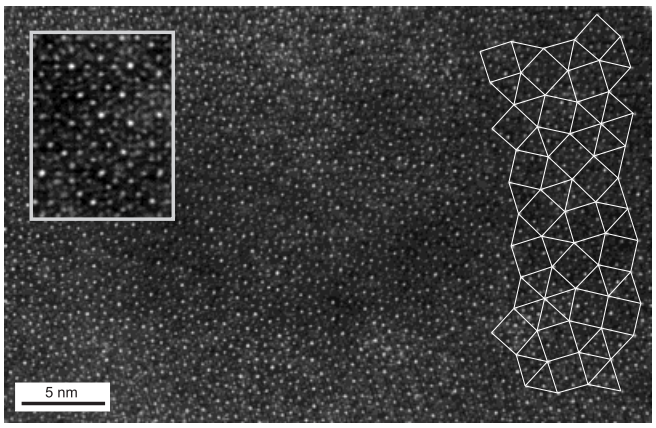

Figure 5. HRTEM image of dd-$Ta_{1.6}Te$. The inset (top left) shows an enlarged section.

almost atomic resolution, groups of 25 bright spots can be recognized that are arranged at the vertices of two concentrical dodecagons, which are rotated by 15° to each other and which exhibit an area ratio of ξ. Some of the outer dodecagons are connected, mostly by five, sometimes by four or six, common edges in such a way that the central contrasts of these groups define an aperiodic, probably random tiling of triangles and squares along a length scale of almost 2 nm. Since such dodecagons may also penetrate to such an extent that interior dodecagons are also edge-connected, the pattern is not unambiguously established. At the level of the aperiodic tiling, the dodecagonal telluride and the intermetallic dd phases are similar; however, there is a marked difference in the length scale upon which this pattern is based. Whilst the characteristic length in the nickel-containing dd phases corresponds to the size of the hexagonal-antiprismatic M_{13} clusters (M = metal atom) (ca. 450 pm), the corners of the pattern in dd-$Ta_{1.6}Te$ are almost 2 nm apart. In order to explain this result, we assume that dd-$Ta_{1.6}Te$ is also formed of hexagonal-antiprismatic M_{13} clusters. The distance between neighboring centers of these clusters can be estimated from the lattice constants of the σ-phase of $AuTa_2$[12] to be $a(AuTa_2)/\sqrt{\xi} = 521$ pm. Since the length scale for the square–triangle tiling of dd-$Ta_{1.6}Te$ is almost exactly extended by ξ compared to this value, it appears sensible to assume that correspondingly larger dodecagonal building blocks of 19 concentrically condensed Ta_{13} clusters pave the plane. The sandwiching of these aperiodically ordered dodecagonal clusters by tellurium atoms leads to lamellar structural units consisting of five atomic layers (thickness: ca. 1 nm). These arrange themselves along the stacking direction through weak chalcogen–chalcogen interactions, in a similar manner to the metal-rich layered structures of Ta_2Te_3[8] or Ta_2Se.[13] This structural model is in agreement with the information obtained from diffraction experiments and HRTEM images, explains the unusual morphological and mechanical properties of this quasicrystalline phase, and also gives a geometric and structural chemical interpretation of the scaling factor ξ.

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[10] It must be noted that the contribution of the first four vectors $\vec{a}_i^*$ remains undetermined with respect to the factor $\sqrt{2+\sqrt{3}}$. The indexing of the reflections chosen here takes account of the fact that in precession diffractograms parallel to $\vec{a}_5^*$, there are additional weak reflections with $h_5 = 2n+1$. The value of the lattice parameter for the substructure along the main axis of symmetry is 1.04 nm.
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