

The Crystal Structure of Vanadium Ditelluride, $V_{1+x}Te_2$

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Vanadium ditelluride, $V_{1.04}Te_2$, has a $Cd(OH)_2$ -type structure with unit cell dimensions $a_h = 3.638 \text{ \AA}$ and $c_h = 6.582 \text{ \AA}$ above the transition temperature T_t of 482 K. Below T_t the structure is monoclinic, space group $C2/m$, with cell dimensions $a_m = 18.984 \text{ \AA}$ ($\approx 3a_h\sqrt{3}$), $b_m = 3.5947 \text{ \AA}$ ($\approx a_h$), $c_m = 9.069 \text{ \AA}$ ($\approx \sqrt{(3a_h^2 + c_h^2)}$), $\beta = 134.62^\circ$. This low-temperature form is isostructural with $NbTe_2$ and $TaTe_2$ (which do not show a phase transition); the vanadium atoms form double zigzag chains with V-V distances of 3.316 \AA , which distort the Te lattice. Complex diffraction patterns were observed due to the simultaneous occurrence of the distortion of the $Cd(OH)_2$ -type structure of vanadium ditelluride in three equivalent directions. Similar patterns were found for the Nb and Ta ditellurides.

Introduction

Several authors have investigated the structure of vanadium ditelluride, $V_{1+x}Te_2$. Grønvold *et al.* (1), who studied several phases in the system V-Te, found the compound always to be metal-rich ($x > 0$); a sample with composition $VTe_{1.85}$ ($= V_{1.08}Te_2$) at room temperature was described as being orthorhombic with cell constants $a_o = 6.333 \text{ \AA}$ ($\approx a_h\sqrt{3}$), $b_o = 3 \times 3.618 \text{ \AA}$ ($\approx 3a_h$), and $c_o = 2 \times 6.427 \text{ \AA}$ ($\approx 2c_h$). The same cell was adopted by Ohtani *et al.* (2). Röst *et al.* (3) found the compound to be monoclinic with cell constants $a_m = 6.334 \text{ \AA}$, $b_m = 3.597 \text{ \AA}$, $c_m = 6.463 \text{ \AA}$, and $\beta = 90.43^\circ$.

Ohtani *et al.* (2) observed a phase transition to the $Cd(OH)_2$ -type structure (with cell constants a_h , c_h) at temperatures depending on composition: $V_{1.04}Te_2$ transforms at 474 K, $V_{1.11}Te_2$ at 390 K. They suggest that the room-temperature struc-

ture is a superstructure of a distorted $Cd(OH)_2$ -type structure.

Experimental

$V_{1+x}Te_2$ was prepared by heating a mixture of the elements in evacuated quartz ampoules at a temperature of about 1000 K for a week. The samples were slowly cooled. They consisted of powder and small hexagonal platelets with dimensions up to 1 mm. Powder diffraction showed that in addition to $V_{1+x}Te_2$ also elemental tellurium was present; obviously our samples correspond to the Te-rich limit of the homogeneity range of $V_{1+x}Te_2$. Attempts to grow single crystals by vapor transport (using Te or I) were not very successful; in some cases small crystals were formed.

X-Ray Diffraction

From high-temperature Weissenberg photographs we found that $V_{1+x}Te_2$ has a

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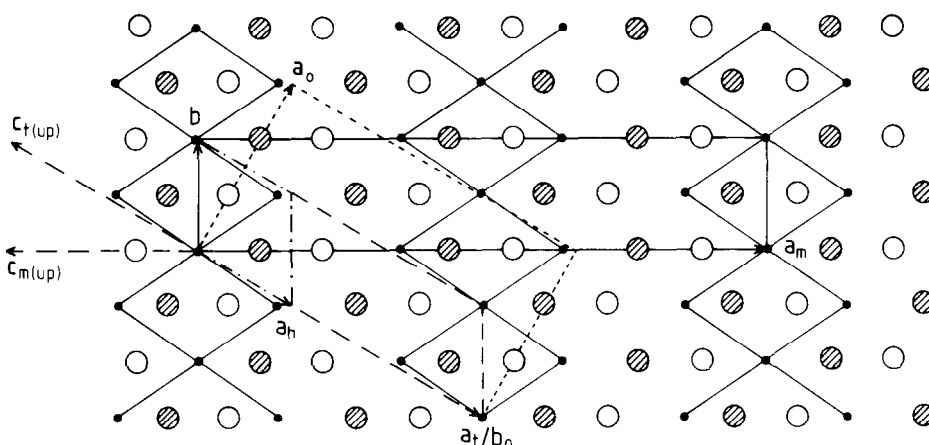


FIG. 1. Projection of a single VTe_2 layer on the pseudo-hexagonal plane. All unit cells mentioned in the text are shown. The (a_0, b_0) is the orthorhombic cell of Grønsvold (and the monoclinic cell of Röst). The (a_h, b_h) is the $Cd(OH)_2$ type cell. The (a, b, c) indicates the triclinic cell and (a_m, b_m, c_m) is the C-centered monoclinic unit cell. Closed circles are the V atoms, large open circles are Te atoms above, and the hatched circles are Te atoms below the plane of drawing.

simple $Cd(OH)_2$ -type structure above the transition temperature $T_t = 481.8$ K. A high-temperature powder photograph, taken with a Guinier-Simon camera (Enraf-Nonius) showed that the transition is reversible; the cell constants at 523 K of the $Cd(OH)_2$ -type cell are $a_h = 3.638(2)$ Å, $c_h = 6.582(3)$ Å, $c/a = 1.809$ (standard deviations in the last decimal place are given in parentheses). The room-temperature Weissenberg photographs of some crystals taken with an axis of 10.8 Å ($\approx 3a_h$) as rotation axis were complex. The $Cd(OH)_2$ subcell reflections were split up into two or three reflections whereas a number of (normal) extra reflections corresponding to a tripling of the a -axis (a_h) and the c -axis (c_h) of the original $Cd(OH)_2$ cell were present. Other crystals did not show a tripling of the rotation axis (≈ 3.6 Å $\approx a_h$), but still a tripling of a_h and c_h ; in this case the subcell reflections did not show a splitting.

These observations indicate that in the former crystals domains are present which make angles of 120° with each other, while in the latter case the crystals consist of domains making angles of 180° . Macroscopi-

cally triplets and twins are then observed, respectively. From electron-diffraction studies it was found that the domain size typically is 0.1–0.5 μm . The supercell we thus find is related to the $Cd(OH)_2$ -type cell as $(\sim 3a_h, \sim b_h, \sim 3c_h)$. If we allow also a tripling of the b_h axis, we find that only reflections with $h - k + l = 3n$ are observed, suggesting a rhombohedral symmetry. Such a cell was deduced from powder data of $TaTe_2$ and $NbTe_2$ by Brixner (4). However, the small difference in axial length between $3a_h$ and $3b_h$ indicate that we have to choose a different unit cell.

At first a triclinic unit cell with dimensions $a_t = 10.910$ Å ($\approx 3a_h$), $b_t = 3.5947$ Å ($\approx b_h$), $c_t = 9.7554$ Å ($\approx \sqrt{4a_h^2 + c_h^2}$), $\alpha = 68.38^\circ$, $\beta = 138.57^\circ$, and $\gamma = 119.60^\circ$ was adopted. This cell accounts for all observed reflections; the observed splitting of the subcell reflections is due to the difference in length of $a_t/3$ and b_t (difference about 1%).

The true symmetry of the structure is C-centered monoclinic, the triclinic cell mentioned above being the primitive unit cell. The C-centered cell has dimensions $a_m = 18.984(5)$ Å, $b_m = 3.5947(7)$ Å, $c_m = 9.069$

Å, $\beta = 134.62(3)^\circ$. The triclinic, monoclinic, and orthorhombic cells are given in Fig. 1, together with the $Cd(OH)_2$ subcell.

Comparison with the unit cells of $NbTe_2$ and $TaTe_2$ (5): $a = 19.39$ Å, $b = 3.662$ Å, $c = 9.375$ Å, $\beta = 134.58^\circ$ for $NbTe_2$ and $a = 19.31$ Å, $b = 3.651$ Å, $c = 9.377$ Å, $\beta = 134.22^\circ$ for $TaTe_2$, both being C-centered, indicate that low-temperature $V_{1+x}Te_2$ probably is isostructural with these compounds.

Structure Determination

For the intensity measurements a "twinned" crystal platelet, hexagonally shaped, with edges of about 0.3 mm and a thickness of 0.005 mm was used. Reflections (909) of both the normal and anti-variant of the twin (notation according to van Landuyt *et al.* (6)) were measured in the range $-28 \leq h \leq 5$, $0 \leq k \leq 5$, $0 \leq l \leq 13$ with a four-circle κ diffractometer CAD-4 (Enraf-Nonius) with monochromatic $MoK\alpha$ radiation using the θ - 2θ scan technique. Corrections were made for Lorentz and polarization effects and for absorption ($\mu = 234$ cm $^{-1}$) (7). Scattering factors were from Cromer and Mann (8). Reflections with $I > 3\sigma(I)$ were used in the refinement. All calculations were carried out on a CDC Cyber 170/760 using the X-RAY system (9). Reflections $3n, l, k$ (n, k, l integers) of the normal variant coincide with reflections $3\bar{n}, k, l + 2n$ of the anti-variant. From the ratio of the noncoinciding reflections we found within experimental error the two variants to be present in equal amounts. During refinement all coinciding reflections were omitted except those which are equivalent in monoclinic symmetry. The intensities of these reflections were halved to get the proper scale with respect to the intensities of the super-reflections. For the refinement we adopted space group $C2/m$ (Cm and $C2$ are also possible) being the same space group as found

for $NbTe_2$ and $TaTe_2$ (5). In this space group vanadium atoms are at special positions $2a: 0,0,0$ and $4i: \pm(x,0,z)$; tellurium atoms are also at $4i$. The final value of R_F obtained after anisotropic refinement was 0.061; final parameters are given in Table I. There was no indication for a space group of lower symmetry: no large values of the tensor element U_{22} of atoms at the mirror plane were observed. A difference Fourier synthesis did not give evidence for a (partial) occupation by vanadium of the octahedral sites in the van der Waals gap. This indicates that x in $V_{1+x}Te_2$ is close to 0.

Full details of the structure determination will be published in a forthcoming thesis from one of us (K. D. Bronsema).

From DSC measurements on a Perkin-Elmer DSC-2 with aluminum sample holder, calibrated with In and Sn, heating rate 5 K min $^{-1}$, we found that the phase transition is at $T_1 = 481.8(2)$ K with an enthalpy change of 514(20) cal · mole $^{-1}$. These values are close to those found by Ohthani *et al.* (2) for $V_{1.04}Te_2$. We may note that during the transition from $Cd(OH)_2$ type to the distorted structure the decrease in volume per formula unit is about 2.5%, the main change being in c (~1.5%) and b (~1.0%).

Discussion of the Structure

Compared to the $Cd(OH)_2$ -type structure

TABLE I
LIST OF ATOMIC PARAMETERS

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{13}
V(1)	0	0	0	.004(3)	.012(3)	.004(3)	.002(3)
V(2)	.1431(4)	$\frac{1}{2}$	-.0108(9)	.008(2)	.003(2)	.011(2)	.008(2)
Te(1)	.1447(2)	$\frac{1}{2}$.2764(4)	.0123(9)	.0033(7)	.0094(8)	.0074(8)
Te(2)	.2954(2)	0	.2141(4)	.011(1)	.0038(7)	.0124(9)	.0075(9)
Te(3)	.4915(2)	$\frac{1}{2}$.2897(3)	.012(1)	.0040(7)	.0076(9)	.0058(8)

Note. The temperature factor has the form of $\exp(-T)$ where $T = 2\pi^2 \sum_{i,j} U_{ij} h_i h_j a_i^* a_j^*$. a_i^* are reciprocal axial lengths and h_i are Miller indices. The e.s.d. of the last significant digit is given in parentheses.

of $V_{1+x}Te_2$ above T_1 , two-thirds of the vanadium atoms in a hexagonal plane are displaced by about 0.4 \AA to form double zigzag chains of symmetry mm , which are somewhat tilted out of the (001) plane. In response to the displacements of the V atoms the Te octahedra are distorted as a result of which a corrugation of the VTe_2 sandwiches is observed. The V atoms in the central row of a chain have relatively undistorted octahedral surroundings. In Fig. 1, in which the structure is projected on the pseudo-hexagonal plane, the two crystallographically independent types of V atoms forming the double zigzag chains are shown, whereas Fig. 2a, which is the projection of the structure on the (010) plane, illustrates the corrugation of the VTe_2 layers.

The V atoms in a central row have four neighbor metal atoms at distances of 3.316 \AA , which is 0.326 \AA shorter than in the undistorted $Cd(OH)_2$ lattice above T_1 ; this indicates a certain interaction between the

TABLE II
ATOMIC DISTANCES FOR VANADIUM DITELLURIDE
IN ÅNGSTRÖMS

V(1)-V(2)(4)	3.316(8)
V(2)-V(2)	4.32(1)
(M-X distances in the centric octahedron)	
V(1)-Te(1)(4)	2.718(2)
V(1)-Te(3)(2)	2.743(4)
(M-X distances in the acentric octahedron)	
V(2)-Te(1)(1)	2.58(1)
V(2)-Te(2)(2)	2.733(5)
V(2)-Te(2)(1)	2.79(1)
V(2)-Te(3)(2)	2.661(4)
(X-X distances parallel to layers)	
Te(1)-Te(2)	3.744(5)
Te(2)-Te(3)	3.737(5)
Te(1)-Te(3)	3.492(5)
(X-X distances between layers)	
Te(1)-Te(1)	3.590(3)
Te(1)-Te(2)	3.907(6)
Te(2)-Te(3)	3.778(3)
Te(3)-Te(3)	3.595(6)

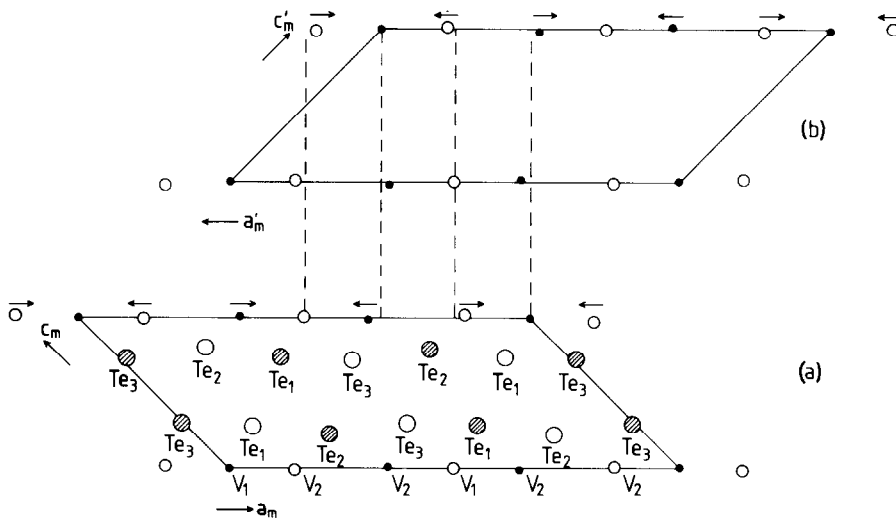


FIG. 2. Projection of the structure on the (010) plane: (a) of the normal variant; (b) of the anti-variant in which only the V atoms are indicated. Large open circles are Te at $y = \frac{1}{2}$, hatched circles are Te at $y = 0$. Small open circles are V at $y = \frac{1}{2}$ and closed circles are V at $y = 0$. The directions of displacements of the V(2) atoms from their positions in the $Cd(OH)_2$ -type structure are indicated by arrows.

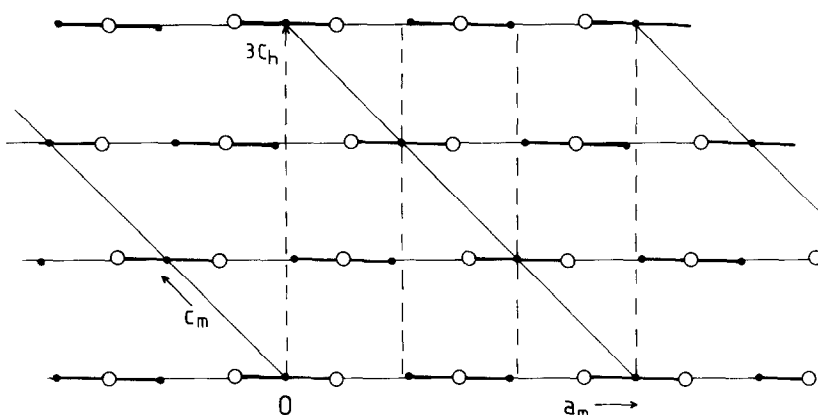


FIG. 3. Projection of several unit cells on the (010) plane. Only the V atoms are shown. The zigzag chains are indicated by the bold lines connecting the V atoms. The apparent tripling of c_h is due to the shift of $(\frac{1}{3})a_m$ of the double zigzag chain in adjacent VTe_2 sandwiches.

metal atoms, the nature of which will be the next object of study. The Te-Te distance between the layers are shortened or lengthened depending on the displacements of the V atoms. The shorter Te-Te distances are still much larger than those found in Te_2 pairs. All important atomic distances are summarized in Table II.

Except for these small distortions, the hexagonal close-packing of the Te lattice as found in the $Cd(OH)_2$ -type structure above T_1 remains intact below T_1 . In all VTe_2 sandwiches identical zigzag chains of V are formed, but in neighboring sandwiches the chains are shifted by a vector $-(2a_h + b_h)$ ($= a_m/3$). This shifting accounts for the observed apparent tripling of the c_h -axis (and its pseudo-rhombohedral symmetry in a tripled crystal) as is illustrated in Fig. 3.

Domain Structure in Vanadium Ditelluride

From the known structure it can be understood that $V_{1+x}Te_2$ crystals can be fragmented into domains, giving rise to the observed "twins" and "triplets."

During the phase transformation from the high-temperature $Cd(OH)_2$ -type structure to the monoclinic form a particular V(2) atom may be displaced in six possible direc-

tions, corresponding to three possible directions (six senses) of the a_m -axis. The directions of displacements of the V(2) atoms in the neighboring VTe_2 sandwich determines the direction of the c_m axis. This is schematically shown in Fig. 4. From this figure we can distinguish six possible domains: three of the normal variant and three of the anti-variant (Fig. 2b). These domains give rise to three different types of relative orientations, depending on whether the projected c_m -axes enclose angles of 60, 120, or 180°. For $NbTe_2$ the same effects have

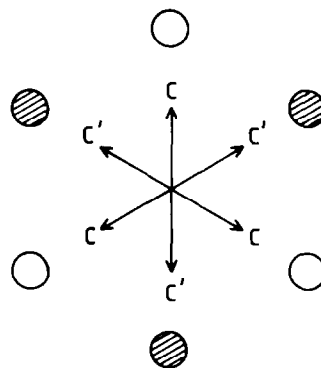
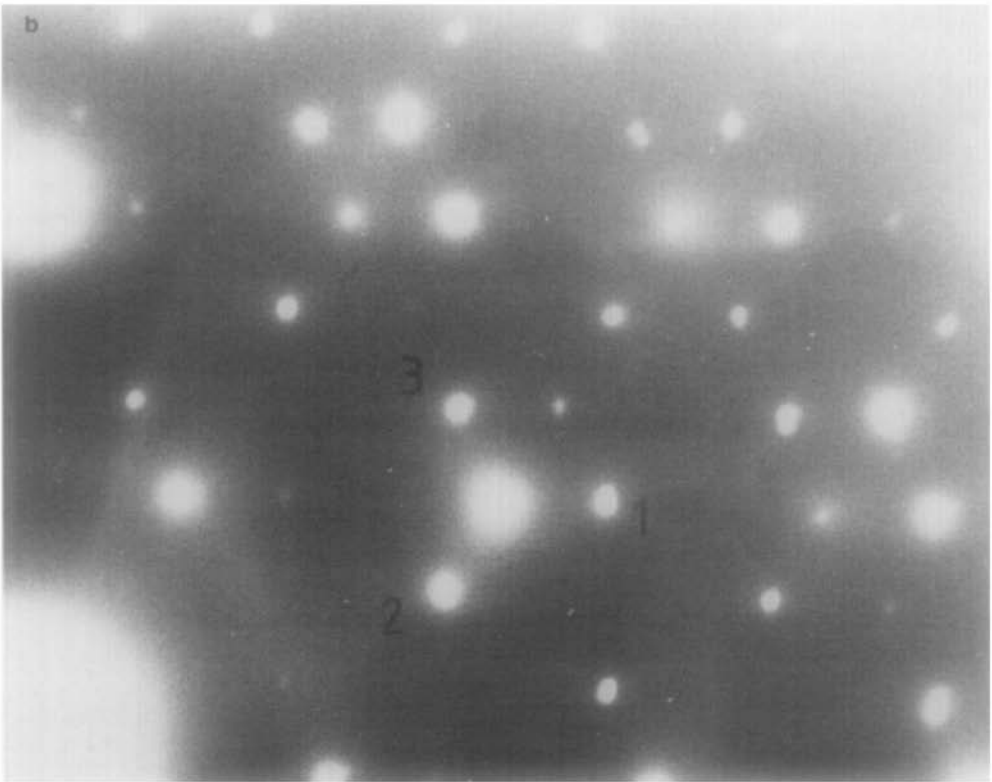


FIG. 4. Possible displacement directions of a V(2) atom in the octahedral surrounding. The possible directions of the c_m -axes of the normal variant (c) and the anti-variant (c') are indicated.



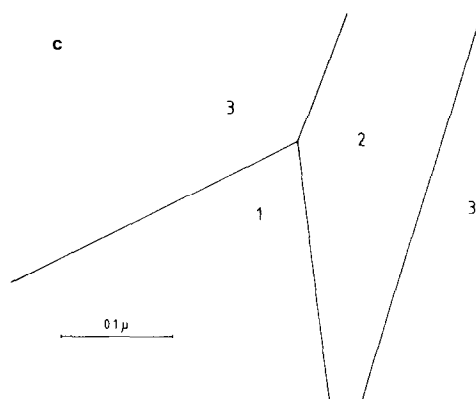


FIG. 5. (a) Electron micrograph of VTe_2 with (b) corresponding diffraction pattern (only $\frac{1}{4}$ of the pattern is shown; the central spot is shown left at the bottom of the photograph), and (c) schematic representation of the configuration shown in (a). For explanation see text.

been observed by van Landuyt *et al.* (6), who give an extensive analysis of these structural defects. A typical view of the domain structure is shown in Fig. 5. Figure 5a gives a bright field image of a VTe_2 crystal viewed along the c -axis; the domain boundaries are clearly visible. The diffraction pattern of this area is given in Fig. 5b (slightly tilted (hko) section). The superreflections originating from the different domains are numbered likewise in Figs. 5b and c as was verified with dark field images.

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