Note on a Phase Transition in VO_2

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It has been shown by Andersson [1,2] that the crystal structure of the room-temperature form of vanadium dioxide constitutes a deformation, akin to the MoO_2 structure [3], of the rutile-type structure, with the following relations [2] existing between the rutile-type subcell and the monoclinic unit cell of VO_2:

$$a = 2c_r, \quad b = a_r, \quad c = a_r - c_r$$

A sample of VO_2 was obtained by mixing appropriate amounts of V_2O_5 (L.K.B. Forskningslaboratorium, reagent grade) and V_2O_3 (obtained by hydrogen reduction of V_2O_5) and heating at 900°C for 20 days in an evacuated silica tube. The sample was quenched in water from the annealing temperature.

By heating the sample in a furnace [4] attached to a recording diffractometer, the powder diffractogram was registered at various temperatures. It was found to change, rapidly and reversibly, at $\sim$70°C, the most obvious feature being the disappearance (on raising the temperature) of all reflexions hkl with h odd. The effect was still more strikingly demonstrated by single-crystal photographs taken at about 180°C (Cu$K\alpha$ radiation). Using these X-ray data, the crystal structure of the high-temperature form was derived and found to be essentially of the rutile type. A small splitting, less than the $\alpha_1-\alpha_2$ separation, of the 101 and 210 powder reflexions (rutile indexing) indicates a slight residual deformation of the rutile-type cell.

The following structural data were obtained (180°C):

Space-group: $P4_2/mnm$ (No. 136)
Unit cell dimensions: $a = 4.530 \pm 0.009$ Å
$c = 2.869 \pm 0.006$ Å
Cell content: 2 VO_2
2 V in 2(a): 0,0,0; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$
4 O in 4(f): $x,x,0$ etc.
$x = 0.305 \pm 0.003$

The reliability factor R, for all observed reflexions, was found to be = 0.12.

The transition [5-12] is accompanied by changes in the expansion coefficient, the electrical resistivity and the magnetic susceptibility.

The lengthening, at the transformation temperature, of the short metal-metal distances [2] (2.65 Å) present in the low-temperature form, to 2.87 Å is in accordance with the unpariring of electron spins [12] (breaking of metal-metal bonds [3,13]) indicated by the magnetic data.

The oxygen-oxygen contact distances parallel to and at righ angles to the c axis are 2.87 Å and 2.50 Å, respectively. The latter one is notably shorter than the corresponding distance in low-VO_2[2] (2.62 Å) along a shared edge of the oxygen octahedra surrounding two metal atoms that form a doublet.

Inclined to the [001] direction the O—O distances are 2.73 Å, *i.e.* their changes at the phase transition are quite small (*cf.* Ref.[2]).

Thanks are due to the principal investigator of this programme, Dr. Arne Magnéli, for his never-failing interest in this study.

The investigation has been sponsored in part by the *Office, Chief of Research and Development, U.S. Department of Army*, through its European Research Office, and in part by the *Swedish Natural Science Research Council.*

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Received December 19, 1960.