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Note on the Crystal Structure of Vanadium Dichloride

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In a paper on transition metal halides¹ Klemm and Grimm were unable to determine the structure of VCl_2 and TiCl_2 . They stated, however, that VCl_2 was not isomorphous with TiI_2 , which was found to have the CdI_2 -type structure. Later Baenziger and Rundle have found a preparation of TiCl_2 to be isomorphous with CdI_2 .²

We have carried out an X-ray investigation of VCl_2 prepared by K. Riishede of this laboratory by heating vanadium powder in a stream of dry HCl at 950°C . The product was obtained in the form of apple-green, muscovite-like leaflets of a more or

less hexagonal appearance. The following data were obtained:

Unit cell dimensions: $a_0 = 3.60 \pm 0.01$ Å, $c_0 = 5.83 \pm 0.01$ Å. Observed density¹: 3.09 g/cm^3 , calculated density: 3.09 g/cm^3 . Diffraction symbol: $\bar{3}mP...$; test for pyroelectricity: negative. Probable space group: $P\bar{3}m$ (No. 164). Arrangement of atoms:

1 V at 0,0,0

2 Cl at $\pm (1/3, 2/3, u)$ with $u \sim 1/4$.

Shortest V-Cl distance: 2.55 ± 0.05 Å. Structure type: CdI_2 ($C6$).

Experimental: Laue photographs were taken along the c -axis. The lattice constants were calculated from Debye-Scherrer diagrams taken in a 19 cm camera using $\text{CrK}\alpha$ radiation ($\lambda = 2.2909$ Å). Intensities were recorded on an X-ray diffractometer with $\text{CuK}\alpha$ radiation. The value of the parameter u was found to deviate only insignificantly from the ideal value $1/4$ from a Fourier projection along the c -axis using the $00l$ reflections. The agreement between observed and calculated intensities of the $00l$ and $10l$ reflections is satisfactory but a different scaling factor had to be used because preferred orientation could not be totally depressed.

From the above it may be concluded either that TiCl_2 and VCl_2 both exist in two modifications or that the materials investigated by Klemm and Grimm have been partly decomposed before or during their X-ray exposure.

Added in proof: Very recently³ Ehrlich and Seifert have recorded the structure of VCl_2 in complete agreement with the results given above.

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