The complete structure determination will be published later.

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Unit Cell and Space Group of VS_4

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In an X-ray and magnetic study of the system V/S by Klemm and Hoschek [1] a polysulphide of vanadium was discovered. By means of vapour pressure measurements the composition of this compound was decisively determined as VS_4 by Biltz and Køcher [2]. A polysulphide of vanadium is also found in nature as patronite first described by Hewett [3]. On the basis of analytical data given by Hillebrand [4], Biltz and Køcher [2] concluded that patronite is VS_4. A sample of this mineral was kindly placed at our disposal by the Curator of Harvard Museum, Dr. C. Frondel. Powder photographs showed that the major phase present was the same as synthetic VS_4. — No crystallographic data on VS_4 seems to have been reported.

In a recent investigation of the vanadium sulphides [5], single crystals of VS_4 were obtained by heating a mixture of $VS_{1.5}$ and sulphur, corresponding to the formula VS_4, in an evacuated and sealed silica tube for four months at 400°C and slowly cooled to 100°C over another four months. The reaction was not complete, however, as some sulphur was still present in the tube. The crystals had grown as clustres of long, black needles with metallic lustre. Most of them were unsuitable for X-ray work, but after some search a crystal with very good properties was found. Its dimensions were: $0.33 \times 0.06 \times 0.07$ mm^3.

Oscillation and Weissenberg photographs taken with CuK-radiation ($\lambda_{\alpha_1} = 1.5405$ Å) around the needle axis (the c-axis) showed the crystal to be monoclinic. This was confirmed by precession photographs taken with MoK-radiation of the $h0l$-plane. From Guinier powder photographs the cell dimensions were found to be:

$a = 12.67$ Å $b = 10.41$ Å $c = 12.11$ Å
$\beta = 148.37°$

Missing reflexions were: hkl when $h+k = 2n+1$, $h0l$ when $l = 2n+1$ and $(h = 2n+1)$ and $0k0$ when $(k = 2n+1)$. This is characteristic of the space groups No. 9, Cc and No. 15, $C2/c$. The density was determined by flotation to be 2.80 g/cm^3, which indicates the presence of eight VS_4 groups in the unit cell ($d_{calc} = 2.835$ g/cm^3).

As the basis for a structure determination, the intensities of the $hk0$- and $h0l$-reflexions were estimated visually. The intensities were corrected for Lorentz and polarisation effects, but not for absorption and extinction.

This intensity material was used to decide between the two characteristic space groups by means of the Wilson ratio for detection of centers of symmetry, $\varrho = \langle|F_0|\rangle^2/\langle|F_0|^2\rangle^6$. For the 48 $hk0$- and 38 $h0l$- reflexions ϱ was calculated as 0.77 and 0.71, respectively. The predicted value for ϱ is 0.635 for centrosymmetric crystals and 0.785 for noncentrosymmetric crystals. Thus the Wilson ratio indicates that the crystal is noncentrosymmetric and the space group accordingly No. 9, Cc.

Some crystals were kindly tested for piezoelectricity by Dr. W. G. Perdok of the University of Groningen, but with negative results. This might perhaps be due to the smallness of the crystals (< 0.06 mm) in the direction of the polar axis.

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