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A Redetermination of the Parameter for Hauerite, MnS_2.

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(With 3 figures.)

In preparing their table of covalent radii, Pauling and Huggins[1]) found that the reported $Mn—S$ distance as obtained from hauerite, MnS_2, as well as the $Mn—Te$ distance from $MnTe_2$, gave an unexpectedly large covalent Mn radius of 1.55—1.59 Å. They also found that better agreement with observed interatomic distances was obtained if there was assigned a radius of 1.04 Å to S, corresponding to a $S—S$ distance of 2.08 Å, as compared with the observed values of 2.11 Å in hauerite, and 2.11—2.14 Å in pyrite.

On account of these discrepancies, it was thought desirable to repeat the structure determination of hauerite. The size of the unit of structure of hauerite has been measured a number of times. Pauling and Huggins[1]) give $a_0 = 6.097 \pm 0.005$ Å, as determined from oscillation photographs. I have used this value of a_0 in the present investigation.

The value of the parameter was determined by Ewald and Friedrich[2]) by the use of Laue photographic data. However, they mostly used comparisons of spots of widely different intensities, which does not allow the most accurate parameter determination. For example, they used the fact that the reflection (521) does not appear to show that the parameter must lie very close to 0.4, as the structure factor disappears at that parameter value. But as the intensity increases but slowly in this neighborhood, the non-appearance of such a reflection can probably be taken as only a rough indication of the parameter value. They took the value of the parameter as $u = 0.4000$, giving their limits of error as ± 0.0005. However, from the considerations given above, it is doubtful whether their value is accurate to better than ± 0.0015.

A Laue photograph was prepared from each of two crystals with the incident beam nearly normal to (111). The photographs so obtained gave a large number of well-shaped spots. Upon making a gnomonic projection, assigning indices, and calculating values of $n\lambda$ for the reflections, no spots with $n\lambda$ less than 0.24 Å, the short wave-length limit of the radiation used, were found. There is, therefore, no indication that the unit is larger than previously reported.

If hauerite has the pyrite structure, its space group is T_h^6. This requires first-order reflections with indices $(0kl)$ with k odd to be absent[3]). No such

1) Linus Pauling and M. L. Huggins, Z. Kristallogr. **87** (1934) 205.

2) P. P. Ewald and W. Friedrich, Ann. Physik **44** (1914) 1183.

3) Because of the symmetry of the group, planes involving cyclic interchange of the same indices are of the same form.

reflections were found on the photograph from the second crystal, substantiating this choice of space group. Several faint reflections of this type were found from the first crystal, indicating it to be slightly twinned.

In general, only intensities of reflections of nearly the same $n\lambda$ and the same interplanar distance were compared. In this way the calculations were much simplified, for the ratio of the intensities of two such reflections is just the square of the ratio of their structure factors.

The atomic positions in MnS_2, assuming the space group T_h^6, are:

Mn: $0,0,0;\ \frac{1}{2},\frac{1}{2},0;\ \frac{1}{2},0,\frac{1}{2};\ 0,\frac{1}{2},\frac{1}{2}$.

S: $u,u,u;\ \frac{1}{2}+u,\frac{1}{2}-u,\bar{u};\ \bar{u},\frac{1}{2}+u,\frac{1}{2}-u;\ \frac{1}{2}-u,\bar{u},\frac{1}{2}+u.$

$\bar{u},\bar{u},\bar{u};\ \frac{1}{2}-u,\frac{1}{2}+u,u;\ u,\frac{1}{2}-u,\frac{1}{2}+u;\ \frac{1}{2}+u,u,\frac{1}{2}-u.$

The structure factor for the reflection (hkl) with h, k, and l all odd is, then, for first order reflections,

$$F = 4f_{0_{Mn}} + 8f_{0_S} \cos 2\pi h u \sin 2\pi k u \sin 2\pi l u,$$

and for h, k even, l odd, or h, k odd, l even,

$$F = 8f_{0_S} \cos 2\pi h u \sin 2\pi k u \sin 2\pi l u.$$

The f_0 values used are those given by Pauling and Sherman[1]). It is to be noticed that in comparing the intensities of two reflections of the same interplanar distance, and where F for both reflections is given by the second equation above, the scattering factors do not enter into the expression for the relative intensities of the two reflections. The use of such comparisons makes possible a more accurate parameter determination, for uncertainties in f_0 values will then not affect the results.

The parameter was quickly narrowed down to the region near 0.4 by several comparisons. A fairly large number of comparisons were used in determining u more closely. Those used in the final determination are listed below: (These comparisons were taken from the first photograph.)

Index	$n\lambda$	$I_{obs.}$	Ratio[2])
832	0.372	0.30	1.6
823	0.362	0.18	
962	0.376	0.15	1.4
676	0.365	0.10	
481	0.308		1.3
732	0.341		1.0
651	0.354		

The approximate correction for difference in $n\lambda$ was made by plotting a curve $I_{obs.}$ vs. $n\lambda$ for the various reflections of the same form falling at different values of $n\lambda$. The squares of the structure factors are plotted

1) L. Pauling and J. Sherman, Z. Kristallogr. 81 (1932) 1.

2) Ratios corrected for difference in $n\lambda$.)

from $u = 0.398$ to $u = 0.404$ in Figures 1, 2 and 3. Each of the comparisons (832) > (823) and (962) > (676) rigorously limits u to values above 0.4000. Also, although (481) is at greater interplanar distance than (732), it is of greater intensity (when corrected for difference in $n\lambda$), and therefore its F^2 value must be greater than that of (732). As seen from Figure 3, this establishes a definite upper limit for u at 0.4026. This is checked by the second photo-

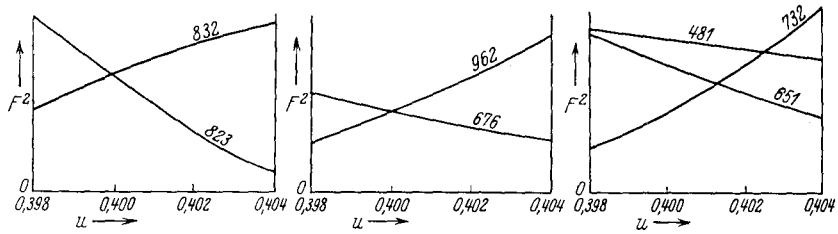

Fig. 1. Fig. 2. Fig. 3.

graph. In this one, (481) and (732) fall at the same $n\lambda$, and (481) is stronger than (732). From the comparison (832)/(823) $\cong$ 1.6, it is seen that u probably lies between 0.4008 and 0.4016, the estimated accuracy of these relative intensity values being about $\pm$ 30%. The comparison (962)/(676) $\cong$ 1.4 indicates a value of u between 0.4008 and 0.4020. The last comparison, (651) $\cong$ (732), gives a value of u from 0.4006 to 0.4016. This is probably the most useful comparison for the exact determination of the parameter. From a consideration of all these comparisons, the value of the parameter has been taken as

$$u = 0.4012 \pm 0.0004.$$

The limits given show the probable error.

Using this value for u, and the value for a_0 given before, the S—S distance is found to be 2.086 $\pm$ 0.008 Å, giving a bond radius for S of 1.043 $\pm$ 0.004 Å, in good agreement with the value taken by Pauling and Huggins. This small change in the parameter, however, leaves the Mn—S distance practically unchanged at about 2.59 Å, thus leaving Mn with the anomalous radius of about 1.55 Å.

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