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An X-Ray and Neutron Diffraction Study of Metacinnabarite

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The crystal structure reported earlier in the literature [1,2] of HgS (metacinnabarite), which is isotypic with ZnS (blende), has been confirmed by means of X-ray single-crystal and neutron powder diffraction data.

A native crystal of metacinnabarite, kindly supplied by Professor Gavelin of the Mineralogical Institute, University of Stockholm, was investigated by means of Weissenberg photographs, registering the reflections of the zones 0-4 around the axis [110] Cu$K\alpha$ radiation was used. The Laue symmetry $m3m$ and the space group $F\bar{4}3m$ (No. 216 in the *International Tables* [3]) were confirmed from the intensities of the reflections and the systematic extinctions found in the photographs.

Two possibilities for the structure of metacinnabarite were compared by the least-squares treatment of the intensity data:

Space group $F\bar{4}3m$ (No. 216); (0,0,0;0,$\frac{1}{2}$,$\frac{1}{2}$; $\frac{1}{2}$,0,$\frac{1}{2}$;$\frac{1}{2}$,$\frac{1}{2}$,0) +
A) 4 Hg in 4(*a*) 0,0,0; 4S in 4(*c*) $\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$ and
B) 4 Hg in 4(*a*) 0,0,0; 4S in 4(*b*) $\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$.

The structural possibility *A* is the one derived by v. Olshausen [1] and by Goldschmidt [2] from X-ray powder data, *viz.* a zinc blende structure with an Hg-S distance of 2.54 Å. The possibility *B* should give the mercury atom a six-coordination similar to the one present in cinnabar [4] and a distance Hg-S of 2.93 Å. It might be noted, however, that a deformed octahedron around the mercury atom with a pair of short Hg-S bonds (*sp*) as in cinnabar is incompatible with the cubic symmetry, found from both the X-ray single-crystal photographs and from the neutron powder data, *v. infra*. The interatomic distances Hg-S actually found in cinnabar are 2.36, 3.10, and 3.30 Å. The following results were obtained from the least-squares calculations:

A) $R = 6.9$ %, $B_{Hg} = 3.92 \pm 0.07$ Å^2, $B_S = 2.03 \pm 0.34$ Å^2
B) $R = 20.6$ %, $B_{Hg} = 3.02 \pm 0.14$ Å^2, $B_S = 13.78 \pm 1.92$ Å^2

As seen from the temperature factors of the atoms and the discrepancy factors, the structure possibility *B* is definitely excluded by this study.

For case *A*, however, the outcome of the refinement is adequate. The shifts in the temperature factors at the final cycle of refinement were small and the weight analysis is satisfactory. The analysis of the weighting scheme and the list of observed and calculated structure factors will be reported elsewhere.[5]

The cell edge of a synthetic sample of metacinnabarite was found to be $a = 5.8717 \pm 0.0005$ Å from X-ray Guinier powder data. The list of $\sin^2 \Theta$ (obs.) and $\sin^2 \Theta$ (calc.) will be given elsewhere.[5]

The interatomic distance Hg-S is consequently 2.5424 ± 0.0002 Å.

The relative contributions of the sulphur atoms to the neutron intensities are larger than to the X-ray intensities, the scattering amplitudes [6] (in 10^{-12} cm) being as follows:

	Neutrons	X-rays ($\Theta = 0°$)
Hg	1.31	22.5
S	0.31	4.5

The amplitude values for neutrons are independent of the scattering angle while those for X-rays decrease with increasing Θ and relatively more so for sulphur than for mercury. Thus it looked to be of interest to study metacinnabarite by neutron powder diffraction methods.

The data were collected by the *Neutron Diffraction Group* at the *Swedish Research Council's Laboratory*, Studsvik. The reactor *R2* of the *Atomic Energy Company of Sweden* was run at an output of 30 MW during the exposure. The neutron wavelength was 1.07 Å. The intensities of the reflections observed in the neutron powder diffractogram were calculated for the alternatives *A* and *B*. A comparison between the observed intensities and the calculated ones is given in Fig. 1. The agreement here is also convincing for case *A*.

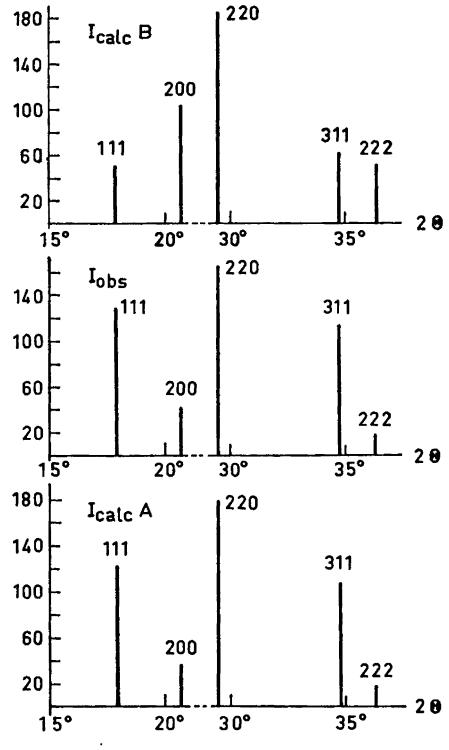

Fig. 1. Observed and calculated neutron intensities for the first five lines in a neutron powder diffractogram of metacinnabarite. $I_{calc,\,A}$ is calculated assuming a tetrahedral coordination of mercury and $I_{calc,\,B}$ an octahedral one.

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