

I thank Imperial Chemical Industries, Ltd., for a research fellowship.

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CRYSTALLOGRAPHY

Refinement of the Crystal Structure of Antlerite

THE crystal structure of antlerite, $\text{Cu}_2(\text{SO}_4)(\text{OH})_4$, was determined by Araki¹ while J. J. Finney was also working on the structure. This refinement represents the final results of the two independent determinations.

A specimen of antlerite from Chuquicamata, Chile, was used for the refinement. Data from nine reciprocal levels, zero, one and two for each of the a , b and c axes, were collected by means of multiple film pack Weissenberg photographs. Molybdenum $K\alpha$ -radiation was used throughout the investigation. Of a possible 991 unique reflexions, 723 were observed. Intensities were obtained by visual comparison with a known scale.

Antlerite is orthorhombic, space group $Pnma$. The cell dimensions, $a_0 = 8.226$, $b_0 = 6.046$, $c_0 = 11.978$ Å, determined from precession photographs agree with those determined by Araki. The cell formula is $\text{Cu}_{12}(\text{SO}_4)_4(\text{OH})_{16}$.

Refinement of the antlerite structure was effected by the method of least squares. Parameters obtained by the senior author's structure determination were used as input for the refinement and the final parameters are listed in Table 1.

Table 1. PARAMETERS OBTAINED BY LEAST SQUARES REFINEMENT

	Cu ₁	Cu ₂	S	O ₁	O ₂	O ₃	OH ₁	OH ₂	OH ₃
x	0.0052	0.2897	0.1304	0.262	0.195	0.033	0.285	0.701	0.046
y	0.2500	0.0032	0.2500	0.250	0.250	0.047	0.250	0.250	0.503
z	0.0015	0.1259	0.3641	0.283	0.476	0.348	0.026	0.779	0.102
B	0.65	0.65	0.49	0.80	1.00	1.17	0.58	1.39	0.90

Table 2. RESIDUALS OF THE ANTLERITE REFINEMENT

Level	Reflexions	R
$0kl$	65	0.092
$1kl$	75	0.107
$2kl$	55	0.099
$hk0$	54	0.120
hkl	54	0.086
$hk2$	38	0.107
$h0l$	194	0.089
$h1l$	50	0.124
$h2l$	138	0.087
Total observed	723	0.096
Unobserved	268	
Total	991	

For the refinement, the entire matrix was computed and inverted. Twenty-one positional parameters, nine temperature factors and nine scale factors were allowed to vary. Only isotropic thermal parameters were used. The residuals for each reciprocal level are given in Table 2. The correlation matrix was calculated for the last cycle, but no large interactions between parameters were observed.

There are two crystallographically distinct copper atoms in the structure each of which has a somewhat distorted octahedral co-ordination. Cu₁ has four hydroxyl groups (OH₃) nearly coplanar at distances of 1.97 Å and one hydroxyl (OH₁) and one oxygen atom (O₂) at 2.32 and 2.56 Å respectively. Cu₂ has three hydroxyl groups (OH₁, OH₂, OH₃) and one oxygen atom (O₃) also nearly coplanar at distances of 1.91, 1.91, 2.02 and 2.05 Å respectively and two oxygen atoms (O₁, O₂) at distances of 2.37 and 2.41 Å. Co-ordination about the sulphur atom is four-fold with the average bond-length being S—O = 1.46 Å. The average bond-angle O—S—O = 109.5°. Bond-lengths are considered accurate to ± 0.02 Å.

The structure consists of systems of connected Cu₁ and Cu₂ polyhedra extending parallel to b -axis. The Cu₁ and

Cu₂ polyhedra are linked to each other by one OH₃ group and also by OH₁ and O₂. However, one system is linked to another by only two weaker bonds, Cu₂—O₁ (2.41 Å), in the c -direction. This accounts for the perfect cleavage parallel to (001).

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Determination of Space-Groups using Anomalous Dispersion

IN the usual method of determining space-groups, the presence of face or body centring and of screw axes and glide planes is detected by examining the systematic absences of reflexions. However, it is not possible to establish by such a procedure the presence or absence of a centre of inversion, a rotation axis or a mirror plane. This is because the translation-free symmetry elements do not lead to any characteristic absences for the reflexions; also, the symmetry of the X-ray diffraction pattern of a crystal is not exactly the same as that of the point group of the crystal itself, but only the corresponding Laue group which has an additional centre of inversion added to it.

In order to test whether the crystal is centrosymmetric or not, statistical methods have been developed by Wilson *et al.*¹⁻⁴ and by Ramachandran and Srinivasan⁵. However, considerable doubts have been expressed about their practical applicability as distributions having properties in between the two limits have often been encountered, and the distributions are also affected by the presence of (a small number of) heavy atoms. It would therefore be worth while examining a more straightforward method of testing the presence or absence of centrosymmetry. This seems to be possible making use of anomalous dispersion.

When anomalous dispersion effects are taken into account, it is found that the symmetry of the X-ray diffraction pattern of a crystal is exactly the same as that of the point group symmetry of the crystal itself. Also, the translation-free symmetry elements, such as a centre of inversion, a rotation axis or a mirror plane, lead to the Bijvoet difference $\Delta I (= I_H - I_{\bar{H}})$, where I_H and $I_{\bar{H}}$ are the intensities of the direct and inverse reflexions including anomalous dispersion effects) being systematically zero along certain rows and planes in the reciprocal lattice. Thus, $\Delta I = 0$ for all reflexions for a centrosymmetric crystal. Similarly, $\Delta I = 0$ for all $0k0$ reflexions if a mirror plane is perpendicular to the b axis and for all $h0l$ reflexions if a 2-fold axis is parallel to the b axis. The systematic absences of the Bijvoet difference have been worked out for all the point groups, and it is found that an examination of these extinctions can reveal the presence or absence of the translation-free symmetry elements in a crystal.

Thus, the systematic extinctions of the Bijvoet difference can give uniquely the point group of a crystal. On the other hand, the usual systematic absences give the elements of the space-group which involve translational symmetry. Combining these two types of information, it is possible to write down a diffraction symbol for all the 230 space-groups, similar to that adopted by Buerger⁶, except that the new symbols will contain the point group of the crystal, the lattice type and the translational