

PRNC ~ 145 PUERTO RICO NUCLEAR CENTER 'A LEAST-SQUARE REFINEMENT OF THE X-RAY DATA ON AZURITE, $\text{Cu}(\text{OH})_2(\text{CO}_3)$, OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT NO. AT (40-11-1833) FOR U.S. ATOMIC ENERGY COMMISSION ---Page Break---

PRNC ~ 145 PUERTO RICO NUCLEAR CENTER 'A LEAST-SQUARE REFINEMENT OF THE X-RAY DATA ON AZURITE, $\text{Cu}(\text{OH})_2(\text{CO}_3)$, OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT NO. AT (40-11-1839) FOR U.S. ATOMIC ENERGY COMMISSION ---Page Break---

A Least-squares Refinement of the X-Ray Data on Azurite, $\text{Cu}_2(\text{OH})_2(\text{CO}_3)_2$, by ROBERT KLEINBERG Puerto Rico Nuclear Center, and Physics Department University of Puerto Rico at Mayaguez, Mayaguez, Puerto Rico 00708 A least-squares refinement of reported X-ray data on azurite, $\text{Cu}_2(\text{OH})_2(\text{CO}_3)_2$, gives a set of positional parameters which is statistically equivalent to the set originally determined from two-dimensional Patterson and Fourier work. The largest difference between any two corresponding positional parameters is equivalent to a distance of 0.062 \AA . * Work performed under the auspices of the U.S. Atomic Energy Commission. ---Page Break---

In conjunction with our neutron-diffraction determination of the crystal structure of azurite, we have refined the X-ray data taken from the literature. This was done because there were some rather large differences between some of the positional parameters obtained from the neutron and X-ray determinations, and because the original analysis was performed by means of two-dimensional Patterson and Fourier work. The heavy-atom structure of azurite deduced by Gattow and Zenann has monoclinic symmetry, $P2/c$, with two molecules in a unit cell. The unit cell dimensions are $a = 5.00 \pm 0.02$, $b = 5.85 \pm 0.02$, $c = 10.35 \pm 0.02 \text{ \AA}$, $\beta = 92^\circ 20' \pm 20'$. The general position is fourfold with equivalent sites at (x, y, z) , $(x+1/2, -y+1/2, z)$, $(1-x, y, z)$, $(1-x+1/2, -y+1/2, z)$. One set of copper atoms is located in a general position set, while the other is located in the special position set $(0, 0, 0)$, $(0, 1/2, 1/2)$. All other atoms are located in general.

positions. The parameters given by Gattow and Zenann were determined from two-dimensional Patterson and Fourier work and are reproduced here in Table I. Using isotropic zonal temperature factors, the reliability factors over observed reflections for the Okf hOL and hkO zones are 0.088, 0.072, and 0.066 respectively. ---Page Break---

REFINEMENT OF THE STRUCTURE The data were refined by full-matrix isotropic least squares based on F, using the Los Alamos Crystal Structure Least-Squares Total of 149 independent nonzero, and 15 duplicate reflections from the three Principal zones were used to obtain three scale, isotropic-thermal, and 18 positional parameters. The quantity minimized was $\text{Swing} \sim |r_{\text{int}}|$, where FE is equal to the calculated structure factor F_{c} , and the weights are given by the expression $(1.0 + 0.018)^{-1}$. Refinement was continued until $4 \sigma(E) < 1.06 \times 10^6$ for all Least squares parameters f_j . At the end of refinement the reliability factor $R = \Sigma |r_i| / \Sigma r_i$, for the hOI, nOI, and kO zones, and for all observed reflections, was 0.062, 0.077, 0.064, and 0.069 respectively. The weight of the nyo! wares. tint postin ant tone. Since the thermal parameters were quite low, and since the structure factors appeared to be affected by extinction, a second least-squares analysis, with an extinction correction, was performed. Unfortunately, a precision type extinction-correction program was not readily available. Therefore, the tensor-level Weissenberg extinction correction which was available was adapted by using a wavelength of 1.6%. The quantity minimized was $\text{Liv lig} - \text{ifi}$, with the only difference being that here $n_e \text{ Me rte. [teats] a}$, ---Page Break---

where is proportional to the secondary extinction parameter.* At the end of refinement $\text{AE}/\sigma(\xi) < 4.5 \times 10^6$, and the reliability factors in the order given above are 0.074, 0.061, 0.052, 0.064, and 0.085. Final positional and isotropic-thermal parameters are given in Table 11, ---Page Break---

Discussion Comparing the 18 positional parameters given by Gatto and

Zemann, to the: Determined by the least-squares refinement we find that all differences are less

than or equal to three times the estimated standard deviations given in the former work, and less than six times the standard deviations given in the present work. The largest parameter shift corresponds to a distance of 0.0624. Thus the two sets of parameters are statistically equivalent. Some interatomic distances and bond angles in azurite, calculated from the refined set of data, are given in Table III.

---Page Break---

ACKNOWLEDGEMENTS

This work was performed while the author was a Visiting Research Associate at the Los Alamos Scientific Laboratory of the University of California. The author wishes to express his thanks to the Laboratory for making available its facilities and computers, and his appreciation to Drs. A.C. Larson and Don T. Cromer of LASL, for the use of their programs and for their many helpful suggestions.

---Page Break---

REFERENCES

1. R. Kleinberg, to be published
2. G. Gattow and J. Zemmann, *Acta Cryst.* 11, 866 (1958).
3. A. G. Larson, (private communication) Operators Manual for the Los Alamos Crystal Structure Least-Squares Program, CENLES.
4. A.C. Larson, *Acta Cryst.* 23, 664 (1967).

---Page Break---

TABLE I. Positional parameters (x 10%) in azurite determined from Patterson and Fourier work.

atom	x	y	u	uy	°	°	°	oy
252(2)*	4950	085(2)	4, 0924)	842	4464)	ø	329(4)	298ø6)
n19ø4	%	ø9a(uy	380(4)	338ø4)	on	wa7øay	224ø4	aan)
Oy	ann	303(4)	2124)					

Throughout this paper the standard deviation of a function is given in the parentheses following the function, and its value corresponds to the least significant digits in the function value.

---Page Break---

TABLE II. Positional and thermal parameters of azurite determined from isotropic least-squares refinement of x-ray data.

atom	x	y	z	2	2	eee
cuy	°	°	°	0.4607)	°	°
copy	9.282004)"	0.4958(5)	-0.0839(2)	0.276)	0.251706)	0.1436205)
0.408)	%	9.080 (3)	0.808 (3)	42	«ay	0.1 (2)
					8.080 (2)	0.809 G3)

saa 0:2 (2) © 0.339 (3) 9.287

(@) 0.320 a) 0.1 Gy 0.3393) 0.2983) 318 0:3 @ 7 2.102 (30.3933) 0.332 ay 0.5 2) 0.1033) 0.1396.
G) 0.332) 0.6 2) on 9.467 (3) 0.222 (3) oa? ay 0.3 @) 0.447 (2) 0.222 GG) onate (Ly 04 @) Ont
0.439 (2) 0.308 (3) 0.207809) 0.1 @ 0.436 Gy 0.308. (3) 0.07et3) 0.3 @) oe eS "In each atom set
of unbere, the upper and lower subsets were determined from isotropic 1st squares, without, and
with extinction correction, respectively, ---Page Break--- TABLE 21, Some interatomic distances
and bond angles in azurite. ee 5 1.3e(e) neq) eae) LT (2) Lette) ur (2) 2.19(e) 2.23(2) 87.55)
eveu(e) 9.9 (5) 1.95(2) £00(2) 2.9302) #,02(2) 2.92(4) 2.9u(e) 2.01(a) +362) 5.90(2) -7(2) £.85(2)
oy 01, = 35(2) Oy *.93e) ---Page Break---