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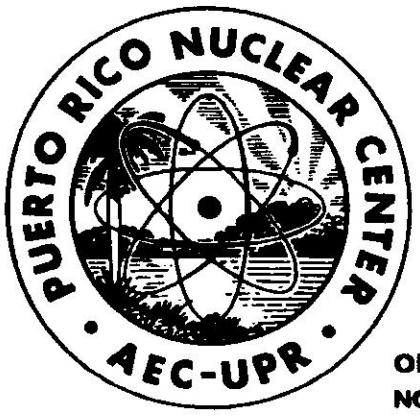
A LEAST-SQUARE REFINEMENT OF THE X-RAY DATA ON AZURITE, $Cu_3(OH)_2(CO_3)_2$



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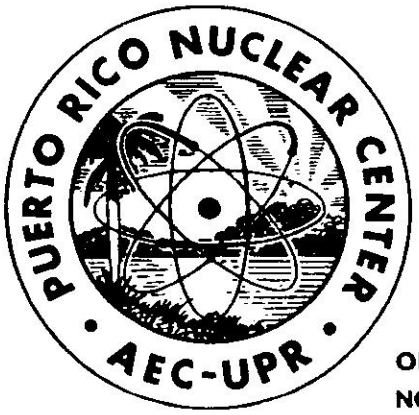

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A Least-Squares Refinement of the X-Ray Data on Azurite, $Cu_3(OH)_2(CO_3)_2$ *

by

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An isotropic least-squares refinement of reported x-ray data on azurite, $Cu_3(OH)_2(CO_3)_2$, 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 Å.

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* Work performed under the auspices of the U. S. Atomic Energy Commission.

INTRODUCTION

In conjunction with our neutron-diffraction determination of the crystal structure of azurite,[1] we have refined the x-ray data taken from the literature.[2] 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 Zemann,[2] has monoclinic symmetry, $P2_1/c$, with two molecules in a unit cell. The unit cell dimensions are:

$a = 5.00 \pm 0.02$, $b = 5.85 \pm 0.02$, $c = 10.35 \pm 0.02\text{Å}$,

$\beta = 92°20' \pm 20'$

The general position is four fold with equivalent sites at x,y,z; $\bar{x},\bar{y},\bar{z}$; $\bar{x},1/2+y,1/2-z$; $x,1/2-y,1/2+z$. 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 Zemann 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 $0k\ell$ $h0\ell$ and $hk0$ zones are 0.088, 0.072, and 0.066 respectively.

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 Program, GENLES.[3] A total of 149 independent nonzero, and 15 duplicate reflections from the three principal zones were used to obtain three scale, 8 isotropic-thermal, and 18 positional parameters. The quantity minimized was $\sum w \left| |F_o| - |F_c^*| \right|^2$, where F_c^* is equal to the calculated structure factor F_c, and the weights w are given by the expression $(1.0 + 0.01F_o)^{-1}$. Refinement was continued until $\Delta \xi_i / \sigma(\xi_i) < 1.04 \times 10^{-3}$ for all least-squares parameters ξ_i. At the end of refinement the reliability factor $R = \sum|\Delta F| / \sum|F_o|$, for the 0k$\ell$, h0$\ell$, and hk0 zones, and for all observed reflections, was 0.062, 0.077, 0.064, and 0.069 respectively. The weighted root-mean-square reliability factor $\left[\sum w |\Delta F|^2 / \sum w F_o^2 \right]^{1/2}$ was 0.093. Final positional and isotropic-thermal parameters with their standard deviations are listed in Table II.

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 precession-type extinction-correction program was not readily available. Therefore, the zero-level Weissenberg extinction correction which was available was adapted by using a wavelength of 1.6 Å. The quantity minimized was again $\sum w \left| |F_o| - |F_c^*| \right|^2$, with the only difference being that here

$$F_c^* = K F_c \cdot \left[1 + g \cdot \frac{F_c^2}{\sin 2\theta} \right]^{-1/4}$$

where g is proportional to the secondary extinction parameter.[4] At the end of refinement $\Delta\xi/\sigma(\xi) < 4.5 \times 10^{-2}$, 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 II.

DISCUSSION

Comparing the 18 positional parameters given by Gattow and Zemann, to those 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 0.062 Å. 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.

ACKNOWLEDGEMENTS

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2. G. Gattow and J. Zemann, Acta Cryst. 11, 866 (1958).
3. A. C. Larson, (private communication) Operators Manual for the Los Alamos Crystal Structure Least-Squares Program, GENLES.
4. A. C. Larson, Acta Cryst. 23, 664 (1967).

TABLE I. Positional parameters (x 10^3) in azurite determined from Patterson and Fourier work.

atom	x	y	z
Cu_I	0	0	0
Cu_{II}	252(2)[a]	495(2)	085(2)
O_H	092(4)	812(4)	444(4)
C	329(4)	298(4)	319(4)
O_I	098(4)	390(4)	338(4)
O_{II}	447(4)	224(4)	421(4)
O_{III}	431(4)	303(4)	212(4)

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

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

atom	x	y	z	B
Cu_I	0	0	0	0.46(7)
	0	0	0	0.56(7)
Cu_{II}	0.2520(4)[a]	0.4958(5)	0.0839(2)	0.27(6)
	0.2517(4)	0.4962(5)	0.0840(2)	0.40(6)
O_H	0.080 (3)	0.808 (3)	0.442 (1)	0.1 (2)
	0.080 (2)	0.809 (3)	0.443 (1)	0.2 (2)
C	0.339 (3)	0.297 (4)	0.320 (1)	0.1 (3)
	0.339 (3)	0.298 (3)	0.319 (1)	0.3 (2)
O_I	0.102 (3)	0.393 (3)	0.332 (1)	0.5 (2)
	0.103 (3)	0.396 (3)	0.332 (1)	0.6 (2)
O_{II}	0.447 (3)	0.222 (3)	0.417 (1)	0.3 (2)
	0.447 (2)	0.222 (3)	0.418 (1)	0.4 (2)
O_{III}	0.433 (3)	0.306 (3)	0.2078(9)	0.1 (2)
	0.436 (3)	0.305 (3)	0.2076(9)	0.3 (2)

[a] In each atom set of numbers, the upper and lower subsets were determined from isotropic least squares, without, and with extinction correction, respectively.

TABLE III. Some interatomic distances and bond angles in azurite.

$C\text{-}O_I$	1.32(2) Å	$O_I\text{-}C\text{-}O_{II}$	126° (1)
$C\text{-}O_{II}$	1.22(2)	$O_{II}\text{-}C\text{-}O_{III}$	127° (2)
$C\text{-}O_{III}$	1.27(2)	$O_{III}\text{-}C\text{-}O_I$	117° (2)
$O_I\text{-}O_{II}$	2.15(2)		
$O_{II}\text{-}O_{III}$	2.23(1)	$O_I\text{-}Cu_I'\text{-}O_H$	87.5° (5)
$O_{III}\text{-}O_I$	2.21(2)	$O_I\text{-}Cu_I'\text{-}O_H''$	92.5° (5)
$Cu_I\text{-}O_H'$	1.95(2)	$Cu_{II}\text{-}O_H'$	2.00(1) Å
$Cu_I\text{-}O_I'$	1.93(1)	$Cu_{II}\text{-}O_H'''$	2.02(1)
$Cu_I\text{-}O_{II}'''$	2.92(2)	$Cu_{II}\text{-}O_{III}$	1.91(2)
$Cu_I\text{-}O_{II}'$	3.29(2)	$Cu_{II}\text{-}O_{II}'$	2.01(1)
$Cu_I\text{-}O_{III}$	3.49(2)	$Cu_{II}\text{-}O_{II}'''$	2.38(1)
$Cu_I\text{-}O_{III}'$	4.21(2)	$Cu_{II}\text{-}O_{II}$	3.90(1)
$Cu_I\text{-}C'''$	2.83(2)	$Cu_{II}\text{-}C$	2.72(2)
$Cu_I\text{-}Cu_{II}$	3.27(1)	$Cu_{II}\text{-}C'$	2.85(2)
$O_I\text{-}O_H$	2.68(2)	$O_I\text{-}O_{III}'$	3.36(2)
$O_I\text{-}O_H''$	2.30(2)	$O_H\text{-}O_{III}'$	2.93(2)