THE UNIT CELL AND SPACE GROUP OF LINDGRENITE

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ABSTRACT

The unit cell constants and the space group of lindgrenite, $2CuMoO_4 \cdot Cu(OH)_2$, have been determined by the Buerger precession method with the following results: $a=5.613$ Å, $b=14.03$ Å, $c=5.405$ Å, $\beta=98°23'$; $a:b:c=0.4001:1:0.3852$; $Z=2$; calculated density $=4.295$ g./cc.; space group $P2_1/n$.

INTRODUCTION

Lindgrenite, $2CuMoO_4 \cdot Cu(OH)_2$, was described by Professor Charles Palache in 1935 as monoclinic, $a:b:c=0.5941:1:0.5124$, $\beta=92°12'$, specific gravity $=4.26$ (1). On the basis of b and c axis zero level Weissenberg photographs and three rotation photographs the dimensions of the unit cell were determined as $a=8.45$ Å, $b=14.03$ Å, $c=7.04$ Å, $\beta=92\frac{1}{2}°$ and it was concluded that the most suitable structural axes were identical with the morphological axes.

The present investigation was undertaken to verify the unit cell constants and to determine the space group as a preliminary step in a complete structure study. The unit cell and space group results are being reported at this time partly because the improved and more extensive data furnished by the precession method has led to a change in the axes most suitable for describing the structural unit and partly because of a change in laboratories and attendant delay in intensity measurements and computations.

Crystals of lindgrenite were kindly supplied by Dr. Clifford Frondel from the same specimen which served for the original morphological study.

X-RAY DATA AND RESULTS

X-ray photographs of the zero and first two or three reciprocal lattice levels normal to the morphologically assigned a and b axes were taken with Professor M. J. Buerger's precession instrument (2). Both copper (nickel foil filter) and molybdenum (zirconium oxide filter) radiations were employed. Cone axis photographs were used as a check on the identity of the several levels photographed. The best of the zero level a and b axis photographs were measured with the instrument devised by Professor Buerger (3) for this purpose.

Typical precession photographs are reproduced in Figs. 1, 2, 3, 4. The central area of the plane nets characteristic of the zero, first and second

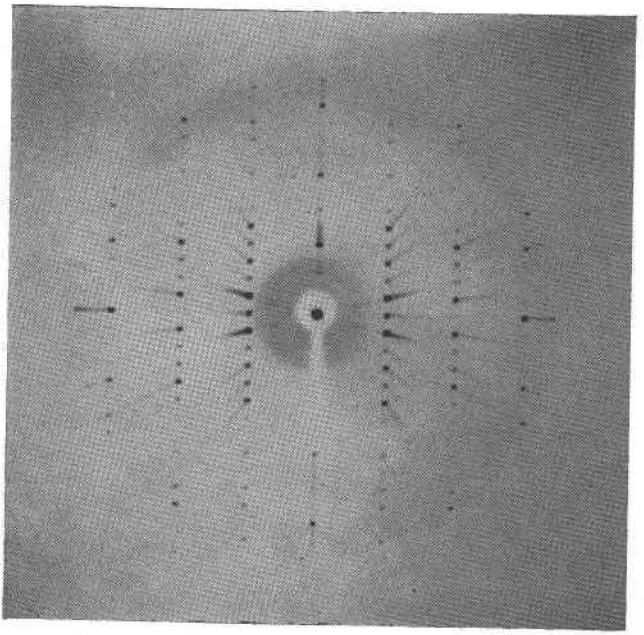

FIG. 1. Lindgrenite, *a* axis, zero level (Mo) (c^* horizontal)

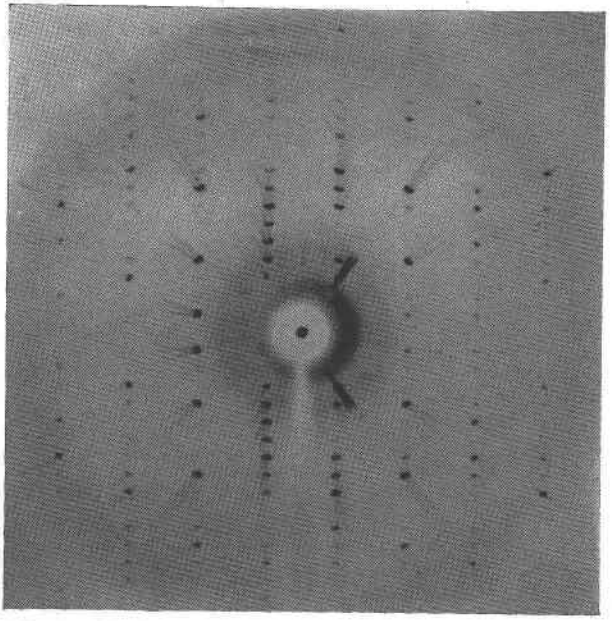

FIG. 2. Lindgrenite, *a* axis, first level (Mo) (c^* horizontal)

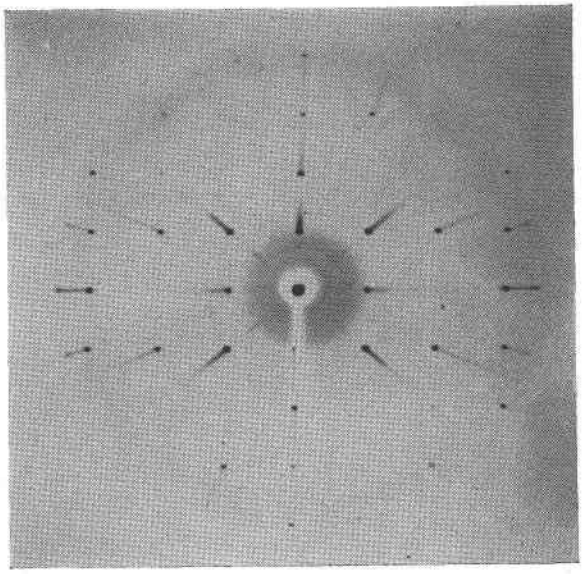

FIG. 3. Lindgrenite, *b* axis, zero level (Mo) (c^* horizontal)

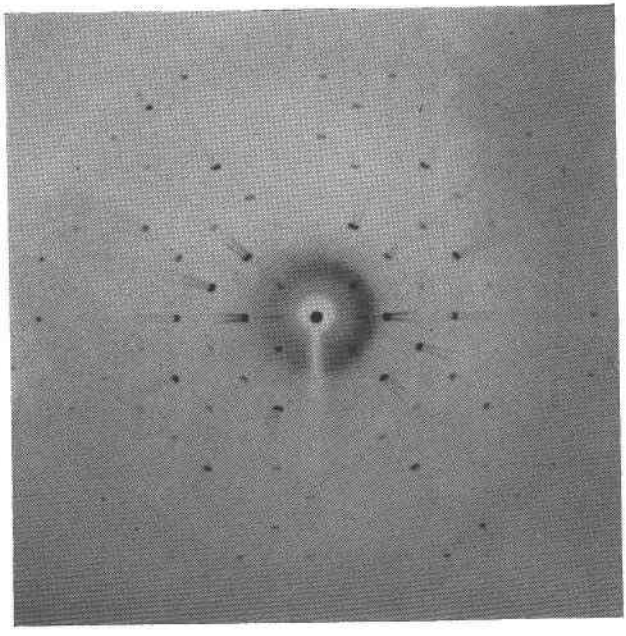

FIG. 4. Lindgrenite, *b* axis, first level (Mo) (c^* horizontal)

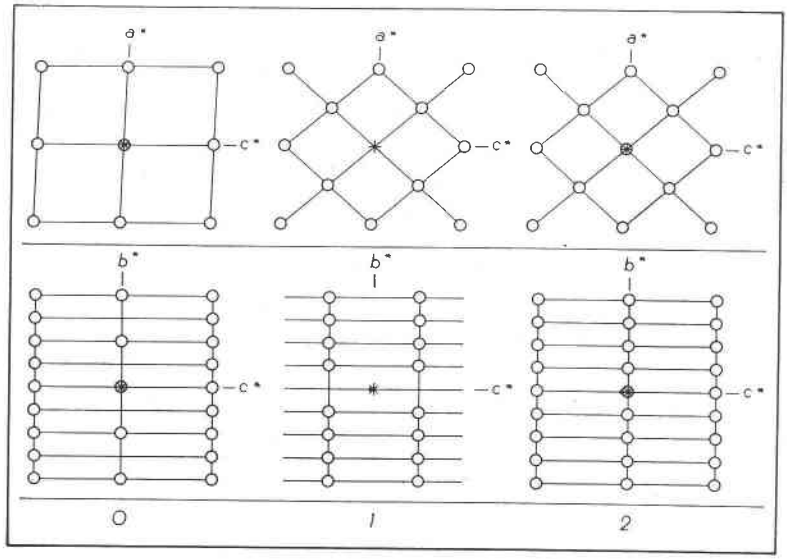

FIG. 5. 0,1,2 level reciprocal lattice nets shown by (upper row) b and (lower row) a axis precession photographs of lindgrenite. (Diffraction symbol $(2/M)B(2_1/c)$.

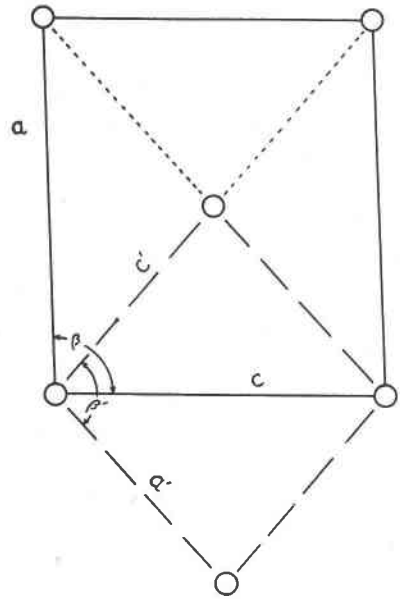

FIG. 6. Lindgrenite. Base of b-end centered cell (a, c, β), full lines, and base of primitive cell (a', c', β'), broken lines.

a and b axis levels are shown in Fig. 5, where the relative intensities of the diffraction spots on the photographs and extinctions not attributable to space group symmetry elements have been ignored. The center of each net is marked with a star and the intersection of the a axis with the b^*c^* nets of the first and second levels by a dot to the left of the center. The increasing off-set is due to the angle ($90-\beta^*$) between a and a^*.

The directions of the b^* and c^* axes (b^*c^* nets, Fig. 5) are at 90° whereas the directions of the a^* and c^* axes (a^*c^* nets, Fig. 5) are not. This confirms the system as monoclinic.

By inspection of the b^*c^* nets it is at once apparent that the direct cell as selected is b-end centered. The doubled translation along b^* in the zero level photograph indicates a 2_1 screw axis. The change from the rectangle-like a^*c^* zero level net to the diamond-like nets of the a^*c^* upper levels reveals a glide plane of component $c/2$ (or the equivalent $a/2$ since the cell is b-end centered). The a^*c^* nets are characterised by a center of symmetry only and the b^*c^* nets by two symmetry lines at right angles. The diffraction symmetry, therefore, is $2/m$ and the diffraction symbol is $(2/m)\ B(2_1/c)$.

Results for the reciprocal lattice spacings and β^* angle are shown in Table 1. Two zero level b axis films obtained from different crystals were measured.

TABLE 1

Precession axis	d_a^*	d_b^*	d_c^*	β^*
b	0.1853	—	0.2144	87°50′
b	0.1853	—	0.2142	87°43′
a	—	0.1099	0.2144	—
average	0.1853	0.1099	0.2143	87°46′

Taking λ (CuKα) as 1.5418 Å (4), the direct cell constants are

$$a = 1.5418/0.1853 = 8.321 \text{ Å}$$
$$b = 1.5418/0.1099 = 14.03 \text{ Å}$$
$$c = 1.5418/0.2143 = 7.195 \text{ Å}$$
$$\beta = (180 - \beta^*) = 92°14',$$
$$\text{Volume (V) of the unit cell} = abc \sin\beta = 839.19 \text{ Å}^3$$

With a specific gravity of 4.26, a formula weight (M) of 544.63 (3Cu, 190.71; 2Mo, 191.90; 10 O, 160.00; 2H, 2.016) chemical atomic mass units and using the density formula (4), $\rho = 1.6602\ ZM/V$, the number of formula units per cell,

$$Z = \frac{4.26 \times 839.19}{1.6602 \times 544.63} = 3.95 \approx 4.$$

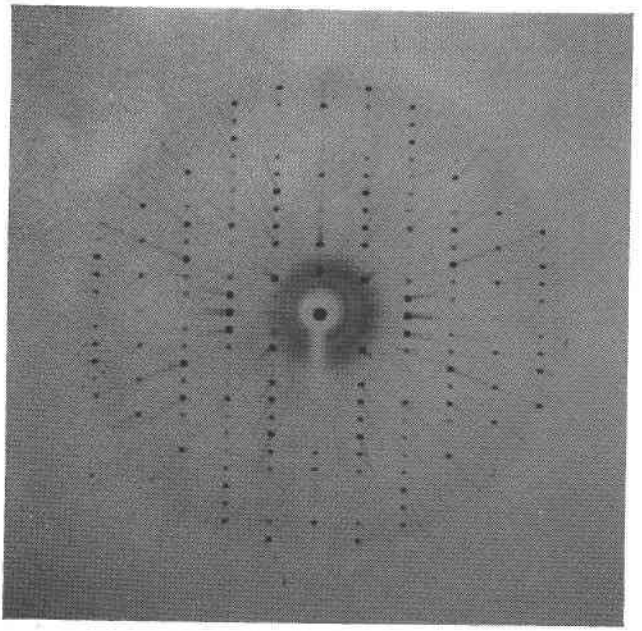

FIG. 7. Lindgrenite, new a axis, zero level (Mo) (new c^* horizontal)

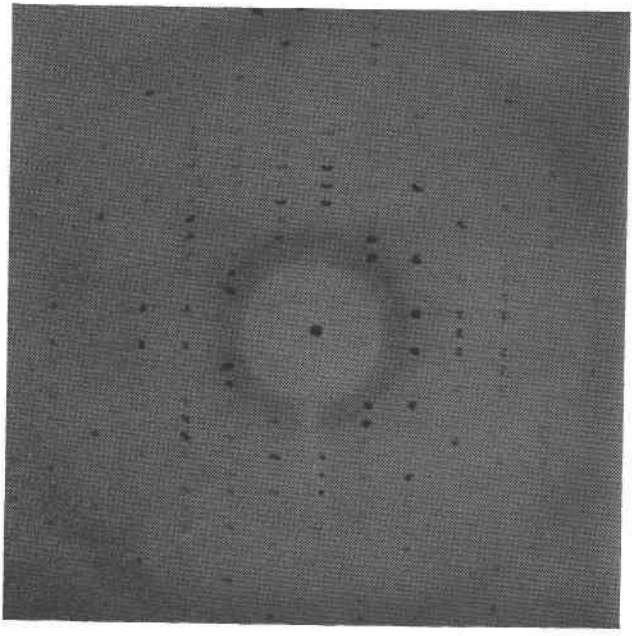

FIG. 8. Lindgrenite, new a axis, first level (Mo) (new c^* horizontal)

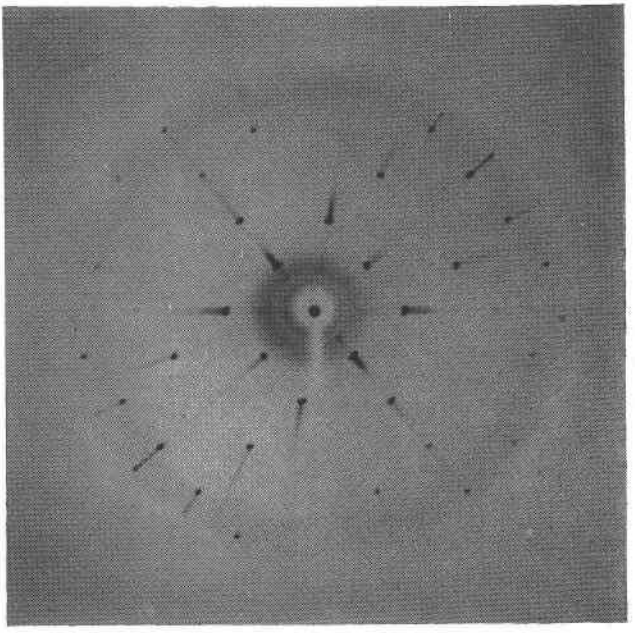

FIG. 9. Lindgrenite, *b* axis, zero level (Mo) (new c^* horizontal)

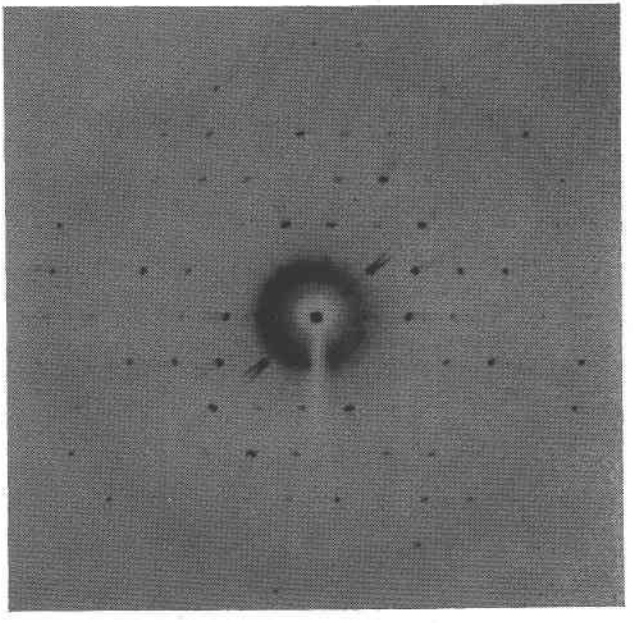

FIG. 10. Lindgrenite, *b* axis, first level (Mo) (new c^* horizontal)

However, since the foregoing cell is monoclinic and b-end centered, a primitive, and hence more desirable structural cell can be obtained by adopting the directions of the diagonals of the ac parallelogram as new a and c axes while retaining the original b axis, as shown in Fig. 6, where the base of the original cell (a, c, β) is represented by full lines and that of the new cell (a', c', β') by broken lines.

From the numerical data for the original cell it is, of course, a simple matter to compute corresponding data for the new (primitive) cell. As a

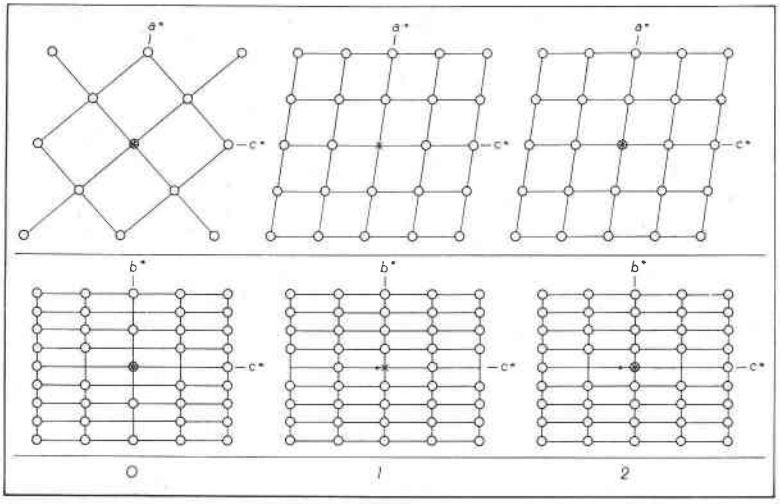

FIG. 11. 0, 1, 2 levels reciprocal lattice nets shown by (upper row) b and (lower row) a axis precession photographs of lindgrenite.
(New orientation, diffraction symbol $(2/M)P(2_1/n)$.

matter of interest in the precession camera, however, another lindgrenite crystal was mounted and precession photographs about the b axis (new orientation of a and c axes) and the new a axis were obtained for the zero, first and second reciprocal lattice levels in each case. Some of these are reproduced in Figs. 7, 8, 9, 10. A diagram of the plane nets is shown in Fig. 11. Simple inspection confirms the cell as primitive; the a^*c^* nets indicate an n glide plane (component, a/2+c/2) perpendicular to b; the doubled translation along b^* in the b^*c^* net of the a axis zero level again reveals the 2_1 screw axis along b. The diffraction symmetry of the new cell, therefore, is $2/m$, the diffraction symbol is $(2/m)P(2_1/n)$ and the space group is $P2_1/n$.

The constants of the new reciprocal lattice (obtained from direct

measurement of the zero level a and b axis films) are $d_a^*=0.2747$, $d_b^*=0.1096$, $d_c^*=0.2853$, $\beta^*=81°37'$.

The constants of the new cell derived by computation from the original unit and by direct measurement are listed in Table 2.

TABLE 2

	Old Cell	New Cell	
		Computed	Observed‡
a	8.321 Å	5.604 Å	5.613 Å
b	14.03 Å	14.03 Å	14.07 Å
c	7.195 Å	5.393 Å	5.405 Å
β	92°14′	98°19′	98°23′
$a:b:c$	0.5931:1:0.5128	0.3994:1:0.3844	0.3989:1:0.3842

‡ The values for a, b, and c differ slightly from those reported at the 1947 meeting of The Crystallographic Society of America (5) because they have been recomputed from the measured values of d^* in terms of the currently accepted Ångström unit instead of the kX unit.

The agreement between the observed and computed values for the unit cell dimensions demonstrates that results obtained with the precession instrument are reproducible to 0.2% or 0.3% or better.

A precision measurement of the b translation to be described in another communication shows that 14.03 Å is the more probable value of b. This makes $a:b:c=0.4001:1:0.3852$. The number of formula units per cell is $1.984\approx 2$ and the calculated density is 4.295 g./cc.

The following transformation converts indices from the old to the new axes:

Old		*New*
$\frac{1-h}{2}$	=	H
k	=	K
$\frac{1+h}{2}$	=	L

ACKNOWLEDGMENTS

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