

THE CRYSTAL STRUCTURE OF MURDOCHITE*

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ABSTRACT

The crystal structure of the new mineral murdochite, Cu_6PbO_8 , is shown to be of a new simple structure type. It is essentially a sodium chloride type with an ordered arrangement of the metal ions and vacant sites, and is the first crystal structure in which Cu^{++} is found to be octahedrally coordinated. The variable density found for murdochite and the occurrence of a second mineral of the same structure type, but with $\text{Pb} > \text{Cu}$, indicate a solid solution between Pb and Cu.

INTRODUCTION

Chemical analysis and x -ray structural studies have established as a new species a copper-lead oxide from Mammoth mine, Arizona. The new mineral has been named murdochite and is described by Fahey (see preceding article). Murdochite has a composition corresponding to the formula Cu_6PbO_8 , and its structure is a simple new type that is essentially an ordered NaCl arrangement (Christ, Clark, and Fahey, 1953; Christ and Clark, 1954). A second example of this structure type, a synthetic compound Mg_6MnO_8 , was discovered independently by Kasper and Prener (1954). A preliminary note on both these compounds has appeared (Kasper and Christ, 1953).

CRYSTAL STRUCTURE ANALYSIS

Preliminary investigations of murdochite were made through the use of Debye-Scherrer photographs. All reflections could be indexed for a cubic cell with $a_0 = 9.210 \pm 0.002 \text{ \AA}$, and systematic absences for hkl not all odd or all even were observed, indicating face centering. The special extinctions demanded by a spinel structure were not observed and this type of structure was therefore ruled out at the beginning of the analysis. X -ray powder data for murdochite are given in Table 1.

The length of the unit cell edge for murdochite is approximately twice, and the volume accordingly eight times, that expected for a simple NaCl structure. The data of the chemical analysis of Fahey (1955) yield the formula $\text{Cu}_{6.1}\text{Pb}_{0.93}\text{O}_{8.0}$, or ideally Cu_6PbO_8 . These facts indicate that the structure of murdochite is based on a NaCl structure, with a unit cell containing 32 oxygen atoms in essentially close-packed arrangement and with the metal ions placed in the octahedral interstices, the doubling of the cell edge being accounted for by a special kind of ordering of the metal ions.

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TABLE 1. X-RAY POWDER DATA FOR MURDOCHITE— Cu_6PbO_8
 CUBIC $Fm\bar{3}m$ (O_h^5); $a_0 = 9.210 \pm 0.002 \text{ \AA}^*$

Measured†		Calculated	
Cu/Ni	$\lambda = 1.5418 \text{ \AA}$		
<i>I</i>	d_{hkl}	d_{hkl}	<i>hkl</i>
10	5.30	5.318	111
7	4.59	4.605	200
8	3.25	3.257	220
8	2.776	2.777	311
10	2.659	2.659	222
9	2.303	2.303	400
9	2.109	2.113	331
7	2.059	2.059	420
5	1.880	1.880	422
7	1.772	1.773	511, 333
10	1.629	1.628	440
8	1.556	1.557	531
6	1.537	1.535	600, 442
4	1.457	1.456	620
4	1.404	1.405	533

Plus many additional lines.

* Lattice constant determined by the extrapolation method of Bradley and Jay (1932).

† Pattern corrected for shrinkage.

The postulated structure is appropriately described by the following crystallographic data:

4 Cu_6PbO_8 per unit cell

Space group: $Fm\bar{3}m(O_h^5)$

Atomic parameters:

$$(000; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0) +$$

$$4\text{Pb: } (a) 000$$

$$8 \text{ O}_I: (c) \frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{3}{4}\frac{3}{4}\frac{3}{4}$$

$$24 \text{ O}_{II}: (e) x00; 0x0; 00x; \bar{x}00; 0\bar{x}0; 00\bar{x}; x\frac{1}{2}\frac{1}{2}$$

The 24 Cu ions may alternatively be distributed over the 28 sites given by

$$4(b) \frac{1}{2}\frac{1}{2}\frac{1}{2}$$

$$24(d) 0\frac{1}{4}\frac{1}{4}; \frac{1}{4}0\frac{1}{4}; \frac{1}{4}\frac{1}{4}0; 0\frac{1}{4}\frac{3}{4}; \frac{3}{4}0\frac{1}{4}; \frac{1}{4}\frac{3}{4}0$$

or put into the 24(*d*) positions leaving four vacancies in the 4(*b*) positions. The model with the statistical distribution of Cu ions is designated the *disordered* structure, that with the ordered arrangement of Cu ions and holes, the *ordered* structure. Both models have been investigated.

Intensity measurements were first made by microphotometering Debye-Scherrer photographs. Although the agreement between the in-

tensities measured in this way and the intensities calculated from the postulated structure was sufficiently good to attest to the essential correctness of the structure, it was apparent that preferred orientation and particle size effects in the spindle sample were leading to poor data. Recourse was then made to single crystal patterns. Using a small crystal (ca. 0.2 mm. in largest dimension), multiple film Weissenberg patterns of the zero and second levels around [110] were prepared with Mo/Zr radiation. Intensities on these films were measured by comparing the densities of the reflections with those on a calibrated strip. The estimated intensities were converted to $|F_{hkl}|^2$ values through the use of the Lp chart of Cochran (1948). Structure factors, F_{hkl} , were calculated for both the disordered and the ordered structure models, setting the x parameter of the O_{II} atoms equal to $\frac{1}{4}$ in both cases. For these calculations the Hartree atomic scattering curve for O^- was used for the oxygen atoms. For Pb^{++++} and Cu^{++} , scattering curves corresponding to the Thomas-Fermi values for Pb and Cu for $(\sin \theta)/\lambda \geq 0.3 \text{ \AA}^{-1}$ and smoothed in to $f=78$ and $f=27$, respectively, for $(\sin \theta)/\lambda=0$ were used. All values of the scattering factors were taken from the International Tables (1935). An over-all temperature correction was made by multiplying the calculated structure factors by the modifying factor $\exp[-B(\sin^2\theta)/\lambda^2]$, according to the relationship $k|F_{obs.}| = |F_{calc.}| \exp[-B(\sin^2\theta)/\lambda^2]$, where k is a scaling constant. The values of k and B were found by plotting $\log(F_{calc.}/F_{obs.})$ vs. $(\sin^2\theta)/\lambda^2$, following the standard method of Wilson (1942). Corrections were not made for absorption effects in the crystal. The following expressions were used to calculate the structure factors:

I. h, k, l all odd

$$F_{hkl} = 4(f_{Pb} - 6/7f_{Cu}) \text{ disordered model}$$

$$F_{hkl} = 4f_{Pb} \text{ ordered model}$$

II. h, k, l all even

A. $h/2, k/2, l/2$ all even

$$F_{hkl} = 4(f_{Pb} + 6f_{Cu} + 8f_o) \text{ both models}$$

B. $h/2, k/2, l/2$ all odd

$$F_{hkl} = 4(f_{Pb} + 6f_{Cu} - 8f_o) \text{ both models}$$

C. $h/2, k/2, l/2$ mixed odd and even

$$F_{hkl} = 4(f_{Pb} - 6/7f_{Cu}) \text{ disordered model}$$

$$F_{hkl} = 4(f_{Pb} - 2f_{Cu}) \text{ ordered model}$$

A comparison of the calculated and observed structure factors for both models is given in Table 2. In order to assess the closeness of fit between the calculated and observed structure factors for each of the two models, discrepancy factors were calculated in several different ways. The discrepancy factor, R , is defined, as usual, as

$$R = \frac{\sum ||F_{obs.}| - |F_{calc.}||}{\sum |F_{obs.}|}$$

TABLE 2. COMPARISON OF CALCULATED AND OBSERVED CRYSTAL STRUCTURE FACTORS FOR MURDOCHITE

(I—disordered model, II—ordered model; $x = \frac{1}{4}$)

<i>hkl</i>	sin θ	I		II	
		<i>F</i> _{calc.}	<i>F</i> _{obs.}	<i>F</i> _{calc.}	<i>F</i> _{obs.}
111	.067	52	*	72	*
002	.077	51	*	24	*
220	.109	49	52	24	47
113	.128	48	55	65	50
222	.134	137	142	141	125
004	.154	221	181	219	165
331	.168	45	88	61	80
402	.173	45	48	23	44
224	.189	43	35	22	32
333	.201	43	36	57	33
115	.201	43	57	57	53
440	.218	186	198	182	180
315	.228	40	57	54	52
442	.232	40	27	21	24
006	.232	40	47	21	42
620	.244	39	27	21	24
335	.253	39	49	51	45
226	.256	121	153	118	139
444	.267	162	142	157	130
551	.276	37	49	48	46
117	.276	37	61	48	56
406	.278	37	17	20	16
624	.289	36	31	19	28
553	.297	35	53	45	48
317	.297	35	37	45	55
008	.309	144	137	139	125
337	.316	34	61	43	56
446	.318	34	40	18	36
660	.328	33	37	18	34
228	.328	33	24	18	17
555	.334	33	49	42	45
517	.334	33	40	42	36
662	.337	102	125	97	114
408	.345	131	110	125	100
119	.352	31	35	40	32
735	.352	31	45	40	41
842	.353	31	25	17	23
664	.362	31	<24†	17	<22
319	.368	31	40	38	36
448	.378	120	118	114	108
771	.384	30	53	37	48
557	.384	30	45	37	41
339	.384	30	37	37	34
0.0.10	.386	29	<26	16	<24
628	.394	29	<23	15	<21
519	.399	29	32	36	29
737	.399	29	23	36	21
666	.401	87	54	82	50
2.2.10	.401	87	90	82	82
953	.414	28	29	34	27

* Reflection not recorded.

† Values preceded by < are threshold values.

TABLE 2—(continued)

<i>hkl</i>	<i>sin</i> θ	I		II	
		<i>F</i> _{calc.}	<i>F</i> _{obs.}	<i>F</i> _{calc.}	<i>F</i> _{obs.}
4.0.10	.416	28	23	15	21
846	.416	28	<24	15	<22
880	.437	106	105	98	96
559	.442	27	29	32	36
3.1.11	.442	27	33	33	30
4.4.10	.444	27	28	15	25
882	.444	27	<29	14	<26
668	.450	26	<29	14	<26
10.6.0	.450	26	<24	14	<22
739	.455	26	35	31	31
6.2.10	.457	78	85	71	77
884	.463	99	80	90	73
0.0.12	.463	99	89	90	81
777	.468	25	29	30	27
5.1.11	.468	25	35	30	32
2.2.12	.476	25	<25	14	<23
10.6.4	.476	25	<24	14	<23
957	.481	25	24	29	22
4.0.12	.488	93	75	84	68
886	.495	24	<31	13	<28
6.6.10	.506	69	76	63	69
4.4.12	.512	89	65	80	59
7.3.11	.517	23	27	27	24
779	.517	23	32	27	29
8.4.10	.518	23	<27	13	<24
6.2.12	.523	23	<27	12	<24
888	.535	83	75	74	68
0.0.14	.540	22	<33	12	<30
10.6.8	.546	22	<29	12	<27
10.10.2	.551	62	76	55	69
2.2.14	.551	62	59	55	53
12.8.0	.557	80	59	70	53
4.0.14	.562	21	<29	11	<27
8.4.12	.578	76	61	66	56
10.10.6	.593	56	61	48	56
6.2.14	.593	56	56	48	51
0.0.16	.618	69	57	59	52
2.2.16	.627	18	<29	10	<27
6.6.14	.632	51	52	43	47
4.0.16	.637	66	55	56	50
8.8.12	.637	66	64	56	58
12.12.0	.655	63	52	52	47
2.2.18	.703	42	48	34	44

The over-all *R* for the ordered model is 0.17, whereas that for the disordered model is 0.18, if in both cases only the non-zero observed reflections are included. If, however, each reflection observed to be zero is assigned a value equal to one-half its threshold value, the ordered model yields an *R* equal to 0.18, and the disordered model, an *R* equal to 0.21.

A possibly more significant way to consider these data is to examine

R as a function of $\sin \theta$, as suggested by Luzzati (1952). In Luzzati's method R' , i.e. R for a chosen interval of $\sin \theta$, is plotted against the mid-point of that $\sin \theta$ interval, all $\sin \theta$ intervals for which there are data being plotted. The data for the disordered model together with the theoretical curve for a structure having a maximum mean absolute error in bond length of 0.05 \AA ($|\overline{\Delta r}| = 0.05$) as derived by Luzzati (1952), are shown in Fig. 1. It will be noted from this plot that for values of $\sin \theta < 0.35$, the R' increases with decreasing $\sin \theta$, in contradiction to the theoretical curve (the same effect holds for the ordered model, but in order to avoid confusion these data are not plotted). This deviation from the theoretical curve is undoubtedly due to absorption effects that are more important at smaller $\sin \theta$ values. It is therefore of interest to consider the R factors for reflections having $\sin \theta \geq 0.35$. For the ordered model, if only the non-zero values are included, R is 0.15; if one-half the threshold value is used for the zero-observed reflections, R is also 0.15. The corresponding cases for the disordered model yield $R = 0.16$ and $R = 0.22$, respectively. The values of R calculated by different methods are collected in Table 3.

The evidence from the foregoing considerations is in favor of the

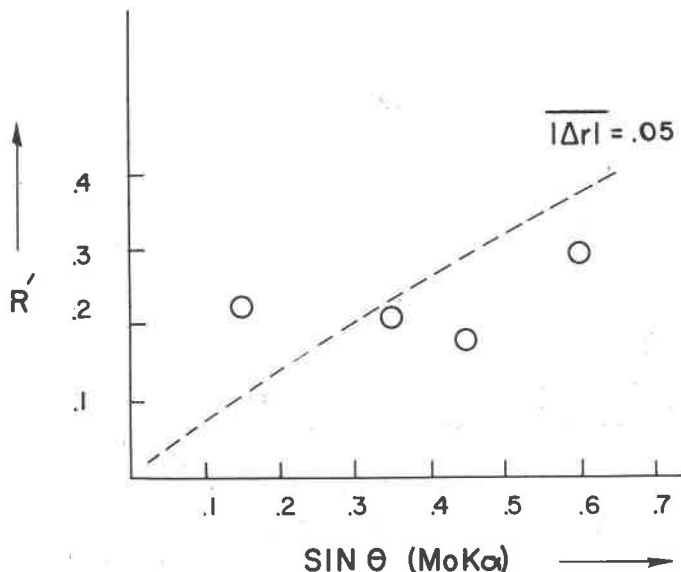


FIG. 1. Plot of R' vs. $\sin \theta$ for murdochite. The circles represent experimental points for the disordered structure. R' is calculated omitting the non-observed F_{obs} 's. The dashed line is the theoretical curve for a structure having a maximum mean error in bond length of 0.05 \AA .

TABLE 3. DISCREPANCY FACTORS FOR MURDOCHITE

Structure Model	R			
	I	II	III	IV
Ordered	0.17	0.18	0.15	0.15
Disordered	0.18	0.21	0.16	0.22

I—All reflections considered, $\Delta F = |F_{obs.}| - |F_{calc.}|$ omitted if $F_{obs.} = 0$.

II—All reflections considered, when $F_{obs.} = 0$ one-half its threshold value used.

III—Only reflections for which $\sin \theta \geq 0.35$ considered, otherwise same as I.

IV—Only reflections for which $\sin \theta \geq 0.35$ considered, otherwise same as II.

ordered model. This is in agreement with the findings of Kasper and Prener (1954) for Mg_6MnO_8 . It is also in agreement with the results of Bertaut (1953), who has shown from energy considerations that, in general, ionic substances with vacancies would be ordered.

DISCUSSION OF THE STRUCTURE

The postulated ordered structure of murdochite is illustrated in Fig. 2. Each Cu^{++} and each Pb^{++++} is surrounded octahedrally by eight O^- . No previous example of Cu^{++} in octahedral coordination is known, the usual coordination consisting of four oxygens equidistant from the Cu^{++} and lying in the same plane as the metal ion, as in tenorite, CuO (Tunell et al., 1935). Octahedrally coordinated Pb^{++++} occurs in Pb_3O_4 (Byström and Westgren, 1943).

On the basis of the parameterless model ($x = \frac{1}{4}$) all the $Cu-O$ and $Pb-O$ distances in murdochite are the same, namely 2.30 Å. In Pb_3O_4 the $Pb-O$ bond length is 2.15 Å. It is quite possible that in murdochite the oxygen ions depart from the ideal close-packed arrangement, corresponding to a deviation from $x = \frac{1}{4}$, as has been found for Mg_6MnO_8 , for which $x = 0.230$ (Kasper and Prener, 1954). For example, if $x = 0.235$, each Pb^{++++} would have six O^- neighbors at a distance of 2.16 Å, and each Cu^{++} two O^- neighbors at 2.30 Å and four at 2.33 Å. However, because of the lack of absorption corrections, the data at hand are not good enough to fix a more precise value of x . This point will be further investigated if it becomes possible to obtain sufficient material so that accurate intensities may be secured by the flat-plate reflection method of the diffractometer.

DENSITY AND SOLID SOLUTION

The calculated density for Cu_6PbO_8 is 6.1 gm. $cm.^{-3}$. The density of murdochite was measured in several ways. For the tube sample (0.4015

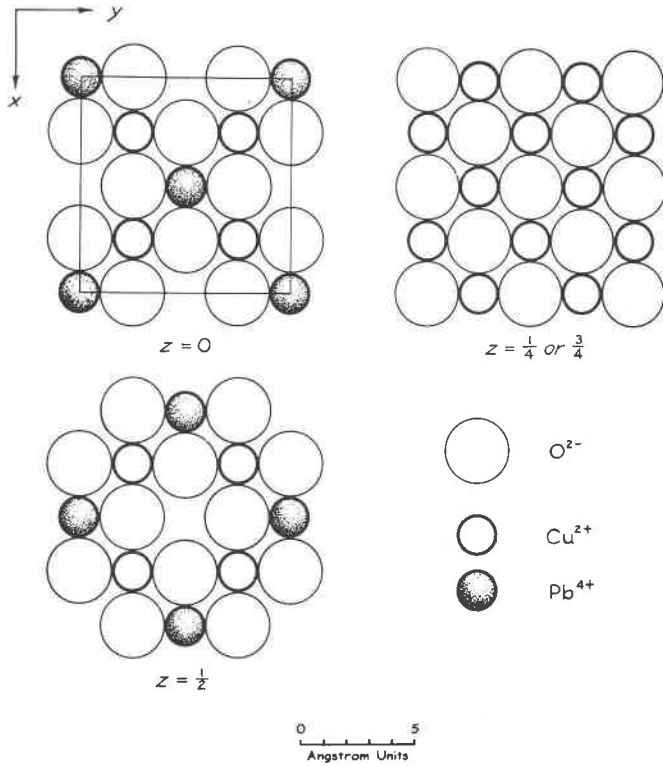


FIG. 2. Structure of murdochite, Cu_6PbO_8 .

gm.), Fahey (1955) found 6.47. H. T. Evans Jr., (private communication) using the Berman balance and hand-picked crystal fragments, obtained the following results.

Sample	A	B	C
Sample wt., mg.	9.68	5.41	6.77
Density	6.4	6.1	5.9

These latter results indicated that the density of the mineral varied according to the sample. In order to test this conclusion further, more accurate determinations using a micropycnometer were carried out by Frank Cuttitta (private communication), with the following results:

Sample	A	B	A+B
Sample wt., mg.	90.6	64.9	155.5
Density	6.7	6.0	6.3

It seems likely from the densities obtained that solid solution occurs in the mineral, probably with Pb^{++} substituting for Cu^{++} . At this stage

of the investigation only about 90 mg. of the mineral remained in existence, and it was decided not to destroy this in attempting to determine the Pb^{++} content. Attempts to synthesize murdochite and related compounds are being carried out in the U. S. Geological Survey laboratories at the present time. If these attempts are successful the problem of solid solution and other questions of interest can be dealt with more effectively.

The lattice constant herein reported for murdochite is given with a fairly high degree of precision ($9.210 \pm 0.002 \text{ \AA}$). For solid solution the lattice constant would be expected to vary as a function of chemical composition, hence the above figure applies only to the sample studied.

A second mineral of the murdochite type has been found at the Higgins mine, at Bisbee, Ariz. The mineral was first collected by a miner, from whom it was obtained by Mr. Arthur L. Flagg, a mining engineer of Phoenix, Ariz. Mr. Flagg then collected the material of interest remaining in the mine and submitted several specimens to the U. S. National Museum. The total quantity of this mineral available for study is quite limited.

The x -ray diffraction powder pattern of the mineral shows that it is of the same structural type as murdochite with $a_0 = 9.224 \pm 0.002 \text{ \AA}$. Spectrographic examination (K. J. Murata, private communication) shows, however, that it has a greater lead than copper content. This fact lends support to the hypothesis that lead and copper may occur in varying ratios to give the same murdochite structure type.

This second mineral is now under further investigation and will be described more completely in a future paper.

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Various colleagues in the U. S. Geological Survey helped in many ways: Fred A. Hildebrand took the first x -ray diffraction powder pattern of murdochite and found that it could not be identified with any known mineral; Joseph M. Axelrod drew our attention to the mineral from Bisbee; Howard T. Evans, Jr., and Frank Cuttitta made density measurements on murdochite; K. J. Murata made the spectrographic analyses. Drs. W. F. Foshag and George Switzer, of the U. S. National Museum furnished us with the mineral from Bisbee. We are greatly indebted to all of these persons.

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