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The Crystal Structure of Boleite—A Mineral Containing Silver Atom Clusters

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The mineral boleite, $Pb_{26}Ag_9Cu_{24}Cl_{62}(OH)_{48}$, is cubic, space group $Pm3m$, with $a = 15.29$ Å. Lead and silver atoms form a distorted body-centered array leading to octahedral groupings of these atoms. The silver atoms and their coordinating chlorines form $Ag_6Cl_8Cl_6$ groups similar to those in the metal cluster compounds $MoCl_2$ and WCl_2. Lead and copper atoms are in distorted square antiprismatic and tetragonal bipyramidal coordination, respectively.

Introduction

Boleite is a lead copper oxychloride mineral which occurs as deep blue crystals of cubic form. These cubes are zoned and consist of an optically isotropic or quasi-isotropic core and a birefringent outer rim of complex structure. The cube faces are sometimes occupied by epitaxial overgrowths of the related species pseudoboleite and cumengite. Boleite has been studied in detail by Mallard and Cumenge (*1*), Friedel (*2*), and Hocart (*3*). They all considered the birefringent material to be tetragonal and untwinned and the isotropic core to be pseudocubic due to twinning. Hadding (*4*) and Gossner (*5*), however, concluded that boleite was truly cubic. Ito (*6*) proposed a tetragonal structure based upon twinning of cubic units at the unit cell level. The tetragonal twinned cell has a "twinned space group" $I4/mmm$ and parameters $a = 15.27$ and $c = 60.94$ Å. It consists of four cubic cells stacked along [001] and related by mirror planes at $z = \frac{1}{4}$ and $\frac{3}{4}$ and by a glide plane at $z = \frac{1}{2}$.

In a restudy of the boleite group Winchell (*7*) concluded that the outer rim of boleite is either an intergrowth of two species (perhaps boleite and pseudoboleite) or consists of boleite lamellae having different orientations. He also performed heating stage experiments on boleite between 25 and 265°C where crystal decomposition began. Between 80 and 180°C the color changed gradually from blue to green, while the birefringent rim and the quasi-isotropic core merged into an apparently homogeneous, isotropic phase. Upon cooling, the blue color returned but the isotropy persisted. From these and other observations Winchell proposed that boleite undergoes an inversion from a pseudocubic form to a cubic one with increasing temperature.

Symmetry and Composition

To determine the true symmetry of boleite, isotropic cleavage fragments were examined by the author using the Weissenberg and precession methods and Cu$K\alpha$ and Mo$K\alpha$ radiation. As reported by (*4*) and (*5*), isotropic boleite is cubic, space group $Pm3m$, with no evidence of twinning. The unit cell parameter, as determined from Bradley–Jay extrapolations of single-crystal diffractometer data, is $a = 15.29$ Å. Unit cell contents calculated from the chemical analysis of isotropic boleite reported in (*2*) are

$$Pb_{25.88}Ag_{9.16}Cu_{23.54}Cl_{61.58}O_{49.87}H_{52.65}.$$

A qualitative chemical analysis with the electron microprobe showed Pb, Ag, Cu, and Cl as the only elements present. Oxygen was not determined due to instrumental limitations. The above results accord well with the formula $Pb_{26}Ag_9Cu_{24}Cl_{62}(OH)_{48}$ determined by crystal structure analysis. The observed and calculated densities are 5.054 and 5.062 g/cm^3, respectively.

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TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

h	F_{obsd}	F_{calc}	h	F_{obsd}	F_{calc}	h	F_{obsd}	F_{calc}	h	F_{obsd}	F_{calc}	h	F_{obsd}	F_{calc}
(0, 0)			(4, 0)			(1, 1)			(5, 1)			(3, 2)—*(continued)*		
3	748	683	4	2388	2392	2	161	90	5	855	655	7	111	89
4	2295	2413	5	1001	929	3	356	246	6	283	244	8	506	471
5	1762	1707	6	1082	947	4	280	233	7	100	21	9	97	15
6	1606	1639	7	102	29	5	117	42	8	540	538	10	370	457
7	837	800	8	730	724	6	567	474	9	598	596	11	399	423
8	1935	2046	9	109	188	7	338	275	10	82	34	12	526	566
9	287	333	10	931	964	8	254	252	11	281	294	13	314	370
10	1967	2062	11	217	152	9	805	794	12	72	54	(4, 2)		
11	211	251	12	1143	1185	10	70	49	13	946	1023	4	1144	1010
12	975	1078	13	119	76	11	552	536				5	219	202
13	192	200				12	218	157	(6, 1)			6	564	471
			(5, 0)			13	383	424	6	714	623	7	242	226
(1, 0)			5	773	732				7	432	365	8	523	469
2	178	207	6	187	43	(2, 1)			9	94	70	9	638	554
3	444	406	7	642	597	2	648	604	10	291	223	10	648	694
4	112	28	8	110	61	3	285	231	11	241	278	11	86	116
5	104	52	9	235	217	4	459	353	12	159	132	12	80	87
6	114	54	10	604	637	5	367	261				13	324	336
7	80	16	11	255	251	6	994	828	(7, 1)			(5, 2)		
8	314	323	12	81	124	7	568	502	7	983	916	5	1067	981
9	430	402	13	529	586	8	202	188	8	258	265	6	298	282
10	452	441				9	167	132	9	107	142	7	707	661
11	234	228	(6, 0)			10	459	421	10	102	88	8	340	315
12	325	320	6	1604	1616	11	79	55	11	640	649	9	438	404
13	349	381	7	607	579	12	75	16	12	419	438	10	325	348
			8	105	111	13	171	207				11	79	30
(2, 0)			9	107	103	14	237	211	(8, 1)			12	79	24
3	570	430	10	838	810				8	112	78	(6, 2)		
4	405	409	11	277	285	(3, 1)						6	1642	1491
5	1044	954	12	80	34	3	998	934	(9, 1)			7	398	348
6	114	26	13	248	263	4	491	403	9	876	924	8	125	148
7	91	81				5	919	776	10	180	184	9	328	266
8	959	938	(7, 0)			6	107	5				10	859	890
9	104	47	7	666	595	7	1101	969	(2, 2)			11	636	704
10	710	646	8	335	301	8	99	58	2	1806	2094	12	220	255
11	152	141	9	205	219	9	94	24	3	682	681	(7, 2)		
12	143	111	10	700	689	10	257	268	4	1079	1057	7	379	319
13	398	421	11	81	19	11	470	473	5	631	495	8	824	843
14	470	390	12	154	173	12	180	171	6	1458	1285	9	105	44
			13	333	354	13	256	228	7	901	787	10	222	274
(3, 0)									8	1439	1371	11	480	504
3	733	568	(8, 0)			(4, 1)			9	163	54	12	527	595
4	120	161	8	1961	2110	4	582	495	10	228	274	13	172	206
5	920	846	9	103	173	5	637	512	11	376	410	(8, 2)		
6	594	540	10	177	162	6	221	190	12	990	1057	8	297	214
7	468	456	11	261	260	7	98	105	13	435	575	9	385	371
8	886	807	12	792	858	8	118	51				10	103	103
9	388	421				9	467	459	(3, 2)			11	84	108
10	576	633	(9, 0)			10	518	516	3	205	222	12	489	522
11	81	102	9	457	464	11	146	70	4	214	178			
12	210	205	10	311	284	12	80	30	5	583	549			
13	307	311				13	341	351	6	252	257			

TABLE I—*continued*

h	F_{obsd}	F_{calc}	h	F_{obsd}	F_{calc}	h	F_{obsd}	F_{calc}	h	F_{obsd}	F_{calc}	h	F_{obsd}	F_{calc}
(9, 2)			(5, 3)—(*continued*)			(4, 4)—(*continued*)			(9, 4)			(6, 6)—(*continued*)		
9	114	137	12	266	238	8	1167	1028	9	432	438	10	364	363
			13	225	158	9	569	565	10	543	529	11	491	550
(3, 3)			(6, 3)			10	1203	1284	(5, 5)			(7, 6)		
3	1312	1343	6	673	610	11	149	200	5	507	400	7	856	723
4	188	150	7	480	434	12	312	376	6	394	341	8	276	263
5	1447	1424	8	121	28	(5, 4)			7	954	859	9	120	35
6	415	387	9	125	179	5	460	421	8	846	816	10	371	351
7	836	784	10	394	439	6	211	146	9	1171	1117	11	263	276
8	295	285	11	197	177	7	373	330	10	96	142	(8, 6)		
9	311	270	12	84	152	8	441	366	11	510	481	8	257	254
10	404	400	13	188	205	9	563	506	12	332	370	9	120	9
11	1310	1456	(7, 3)			10	394	365	(6, 5)			10	354	354
12	327	350	7	954	861	11	211	271	6	117	102	(7, 7)		
13	169	106	8	331	332	12	152	147	7	120	101	7	1038	931
(4, 3)			9	438	427	13	401	404	8	478	442	8	124	102
4	647	581	10	455	452	(6, 4)			9	126	182	9	320	353
5	721	670	11	1026	1075	6	388	300	10	309	320	10	599	582
6	348	318	12	124	97	7	448	406	11	410	485	11	1034	1090
7	115	7	(8, 3)			8	368	313	12	470	472	(8, 7)		
8	483	441	8	108	95	9	230	186	(8, 5)			8	418	406
9	383	360	9	163	60	10	102	60	8	919	863	10	105	116
10	91	22	10	440	507	11	91	64	9	471	442	(9, 7)		
11	197	199	11	227	335	(7, 4)			10	406	426	9	285	344
12	88	94	12	307	372	7	309	274	11	301	305	(8, 8)		
13	74	133	(9, 3)			8	342	288	(9, 5)			8	474	482
(5, 3)			9	113	228	9	176	97	9	614	684	9	355	341
5	1011	926	10	175	221	10	200	148	10	122	201	10	846	853
6	108	62	11	227	250	11	88	5	11	190	200	(9, 8)		
7	825	690	(4, 4)			(8, 4)			(6, 6)			9	336	335
8	416	393	4	671	560	8	439	409	6	885	811			
9	668	667	5	931	814	9	257	251	7	606	591			
10	655	726	6	824	698	10	364	363	8	120	46			
11	266	240	7	521	473	11	243	206	9	283	236			

[a] The indices for (k, l) are given in parentheses above each grouping.

Structure Determination

Using an isotropic cleavage fragment of dimensions $0.08 \times 0.14 \times 0.40$ mm and equi-inclination Weissenberg geometry, a total of 1560 intensities were measured on an automated single-crystal diffractometer. Graphite flat-crystal mono-chromated Cu$K\alpha$ radiation and pulse height analysis were employed. The data were corrected for Lorentz, polarization, and absorption effects. Symmetrically equivalent reflections were then averaged to obtain the final set of 360 $|F|_{obsd}$ values.

The data were then used to calculate the Patterson function of boleite. Interatomic vectors were also calculated from the atomic positions in Ito's untwinned cubic structure. Comparison of the two vector sets showed that two of the five cation sites in Ito's structure were occupied by heavy atoms. Starting with these two atoms, the rest were located by means of successive electron density syntheses.

Refinement of the structure was carried out by the method of least-squares using the IBM 360 program SFLSQ5 written by C. T. Prewitt.

TABLE II

POSITIONAL AND THERMAL PARAMETERS IN BOLEITE[a]

Atom	x	y	z	B (Å^2)
Pb(1)	0.2269(5)	½	½	1.4(2)
Pb(2)	0.3030(2)	0.3030	0.3030	1.0(1)
Pb(3)	0.2734(3)	½	0	1.4(1)
Ag(1)	0	0.1561(10)	0	2.2(3)
Ag(2)	0	½	0	3.2(5)
Cu	0.2563(5)	0.2563	0.0925(7)	0.7(2)
Cl(1)	0.1233(16)	0.1233	0.1233	2.4(8)
Cl(2)	0.3864(10)	0.3864	0.1218(15)	2.0(4)
Cl(3)	0	0.3354(32)	0	2.0(9)
Cl(4)	0.1311(14)	½	0.1311	1.9(7)
Cl(5)	0.3282(14)	½	0.3282	1.9(6)
OH(1)	0	0.3218(30)	0.2060(30)	0.2(10)
OH(2)	0.1831(28)	0.1831	0.3300(43)	3.3(14)

[a] Standard errors to the least significant digit are shown in parentheses.

TABLE III

INTERATOMIC DISTANCES[a] (IN Å)

Pb(1)–4 Cl(2)	2.94(2)	Cl(1)–3 OH(2)	3.41(8)
4 Cl(5)	3.05(1)	3 Cl(1)	3.77(5)
Pb(2)–3 OH(2)	2.63(6)	6 OH(1)	3.79(4)
3 Cl(5)	3.06(1)	Cl(2)–2 OH(2)	3.36(4)
3 Cl(2)	3.31(2)	2 OH(1)	3.47(4)
Pb(3)–2 OH(1)	2.91(5)	2 Cl(2)	3.47(3)
2 Cl(4)	2.96(1)	2 Cl(5)	3.71(2)
4 Cl(2)	3.08(1)	Cl(2)	3.72(5)
2 Pb(3)	4.900(7)	Cl(3)–4 OH(1)	3.16(5)
2 Pb(1)	4.903(6)	4 Cl(4)	3.79(4)
Ag(1)–4 Cl(1)	2.71(3)	4 OH(2)	3.96(6)
Cl(3)	2.74(5)	Cl(4)–2 OH(2)	2.83(6)
4 Ag(1)	3.38(2)	4 OH(1)	3.57(4)
Ag(2)–2 Cl(3)	2.52(5)	2 Cl(4)	4.01(4)
4 Cl(4)	2.83(3)	Cl(5)–4 Cl(5)	3.71(3)
Cu–2 OH(1)	1.90(3)	OH(1)– OH(1)	2.50(9)
2 OH(2)	2.11(4)	2 OH(2)	2.82(4)
Cl(2)	2.85(2)	OH(2)–2 OH(2)	3.18(11)
Cl(1)	2.91(3)		
Cu	2.83(2)		
Pb(2)	3.37(1)		
2 Cu	3.54(2)		

[a] Standard errors in parentheses.

Scattering factors for Pb^+ and $Ag^{+1/2}$ were obtained from Cromer and Waber (*8*), Cu^+ and $Cl^{-1/2}$ from Doyle and Turner (*9*), and O^- from the "International Tables for X-ray Crystallography" (*10*). Anomalous dispersion corrections for Pb, Ag, Cu, and Cl were taken from Cromer (*11*). Refinement was carried out using isotropic atomic temperature factors. All reflections, excluding $F_{obsd} < F_{min}$, were equally weighted. The final R value is 10.5% for all reflections or 8.9% if the unobserved reflections are excluded. Table I contains a list of structure factors and Table II, the refined atomic parameters. Interatomic distances and their standard errors (Table III) were calculated with the program ORFFE of Busing, Martin, and Levy (*12*) using the variance–covariance matrix for atomic coordinates.

Structure and Bonding

Although the unit cell of boleite corresponds to that found by Ito, his proposed crystal structure is quite different from the one described here. Before giving a detailed description of this complex structure, it is desirable to provide a brief overview.

The structure of boleite is based upon a distorted body-centered framework of lead and silver atoms. Only the three Ag(2) atoms are not part of the body-centered array. Since an octahedron may be inscribed within a pair of body-centered cubic cells, this arrangement leads to octahedral groupings of lead and silver atoms in boleite. Coordinated to the faces and vertices of the metal polyhedra are chlorine atoms. These chlorines are shared with $Ag(2)Cl_6$ and $Cu(OH)_4Cl_2$ distorted octahedra such that the anion polyhedra form bridges between the metal polyhedra. Individual lead atoms are coordinated by distorted square antiprisms of chlorine and hydroxyl ions. These antiprisms are linked in a complex fashion by shared faces and vertices. The octahedra around the copper atoms are likewise linked by shared edges.

Looking at the structure in detail, the Ag(1) atoms form a regular octahedron centered at the unit-cell origin. Eight Cl(1) atoms are located above the faces of the octahedron and six Cl(3) atoms lie adjacent to the six octahedral vertices (Fig. 1). This is the same configuration found in the well-known metal cluster compounds $NbI_{1.83}$, $MoCl_2$, WCl_2, and their derivatives (*13*). By analogy, boleite is a metal cluster compound, the first reported involving silver and a halogen. Silver(I) dipropyldithiocarbamate contains a distorted Ag_6 octahedron (*14*), but the silver–anion arrangement is unrelated to that in boleite.

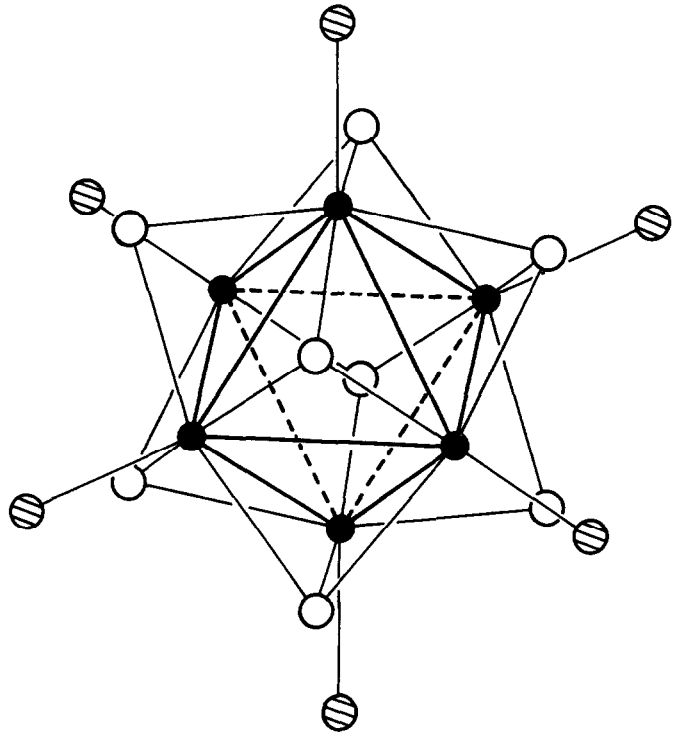

FIG. 1. The $Ag_6Cl_8Cl_6$ group in boleite.

Within the Ag_6 octahedron of boleite the Ag–Ag distance is 3.38 Å. This is longer than in silver metal (2.89 Å) and no claim is made here for the existence of metal–metal bonds in boleite. The Ag(1) octahedron, which is centered at 000, shares Cl(3) atoms with three $Ag(2)Cl_6$ tetragonal bipyramids. The latter are centered at $\frac{1}{2}00$ and equivalent positions. Along the unit cell edges the sequence of polyhedra is therefore Ag_6 octahedron—$AgCl_6$ bipyramid—Ag_6 octahedron. Ag(1) is coordinated by four chlorine atoms at 2.71 Å and one more at 2.74 Å. These Ag–Cl distances are comparable to that in AgCl (2.77 Å) and to the sum of the covalent radii, 2.78 Å (*15*). Ag(2) is coordinated by two chlorine atoms at 2.52 Å and another four at 2.83 Å. Analogously, in $Cs_2AgAuCl_6$ (*16*), there are distorted $AgCl_6$ octahedra which have two Ag–Cl distances of 2.36 Å and four more of 2.92 Å. The two short bonds result from the tendency of Ag^I to form pairs of linear covalent bonds.

Also of interest are the nearly regular Pb_6 octahedra centered at $\frac{1}{2}\frac{1}{2}0$ and equivalent positions. Here the Pb–Pb distances are 4.900 and 4.903 Å, which are much greater than in lead metal (3.50 Å). Above each octahedron face is a Cl(2) atom, but there are no anions adjacent to the vertex metal atoms as in the silver octahedron.

Pb(1), Pb(2), and Pb(3) are coordinated by distorted square antiprisms of chlorine and/or hydroxyl ions much as in diaboleite, $Pb_2Cu(OH)_4Cl_2$ (*17*). The antiprism around Pb(2) is grossly distorted and includes a ninth ligand. Pb–OH distances in these polyhedra are 2.63 and 2.91 Å, and Pb–Cl distances range from 2.94 to 3.31 Å. These are typical of distances in ionic lead oxychlorides (*17*). The Pb(1) and Pb(2) antiprisms share faces to form an eight-membered ring, and the Pb(3) antiprisms share edges to form a separate four-membered ring. Both rings are centered around the axis $\frac{1}{2}\frac{1}{2}z$ and are joined by shared vertices.

Copper atoms are coordinated by two OH groups at 1.90 Å, another two at 2.11 Å, and two chlorine atoms at 2.85 and 2.91 Å. Together they form a distorted tetragonal bipyramid around the Cu^{+2} ion. Each $Cu(OH)_4Cl_2$ bipyramid shares edges and a common vertex (A in Fig. 2) with two others to form a trimer around the [111] axis. Next, each trimer shares edges (BC and DE) with two other trimers. These two then share edges with a fourth to form a four-membered ring of trimers around the axis

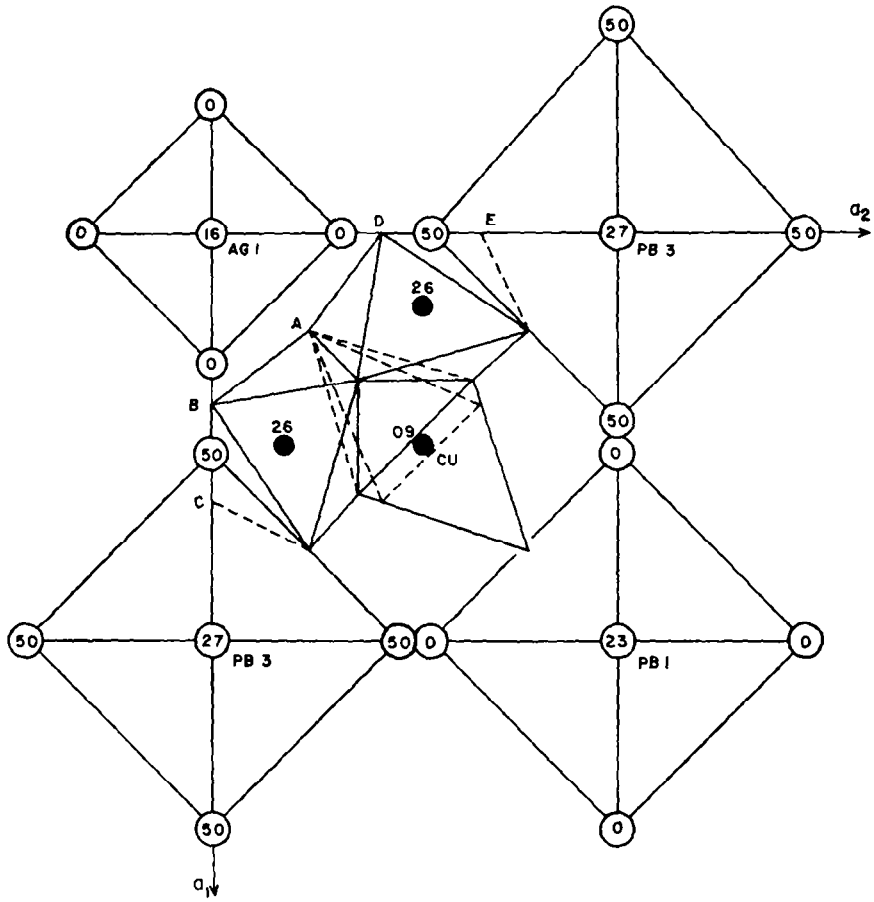

FIG. 2. Projection on (001) of $\frac{1}{8}$ of the unit cell. Some atoms are omitted for clarity. The Ag_6 and Pb_6 octahedra are shown along with a trimer of Cu coordination polyhedra. Numerals are heights of atoms in $z \times 100$.

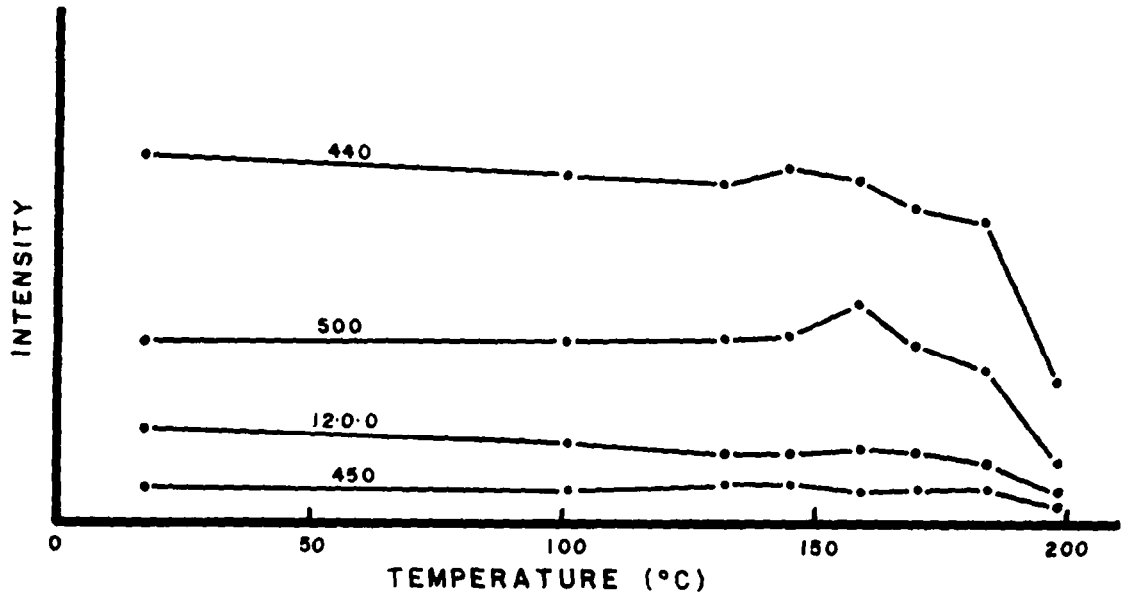

FIG. 3. Plot of integrated intensity vs temperature for several reflections.

00z. Since the basal plane of the unit cell is a mirror plane, the ring is duplicated by reflection in the next unit-cell down. Thus, there are two rings, each composed of four trimers. These two rings are also joined by shared edges. Cu–Cu distances across these shared edges are very short (2.83 Å) compared to those within an individual trimer (3.54 Å). The very short OH(1)–OH(1) separation of 2.50 Å is the edge shared between trimers. To the author's knowledge, this configuration of copper coordination polyhedra is unique.

High Temperature Study

In order to check the conclusions of (7) with respect to polymorphism in boleite, a cleavage fragment was mounted in a high temperature furnace attached to a single-crystal diffractometer. The intensities of four reflections were monitored (Fig. 3) as the crystal was slowly heated from 17 to 251°C. The average heating rate was about 9°C/hr. No significant change occurred until ~160°C when the intensities of all reflections began to decrease noticeably. When the crystal was examined by eye at 198°C, its color had changed from blue to black. After heating to 251°C and cooling, an X-ray powder photograph of the crystal was obtained. It showed only lines due to $PbCl_2$, AgCl, and CuO. In summary, no evidence was found for an inversion in boleite. The intensity change above 160°C is due to crystal decomposition, the black coating being CuO. It should be noted that the heating rate in (7) was between 1° and 4°C/min, hence equilibrium was probably not attained. The blue to green color change may have been due simply to small changes in bond lengths within the copper coordination polyhedron producing changes in the crystal field splittings. The attainment of complete isotropy probably resulted from the relief of strain in a cubic crystal.

Acknowledgments

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