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CRYSTALLOGRAPHIC TABLES FOR THE RHOMBOHEDRAL CARBONATES

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ABSTRACT

Cell constants are given for $CaCO_3$, $MgCO_3$, $CaMg(CO_3)_2$, $MnCO_3$, $FeCO_3$, $ZnCO_3$, $CoCO_3$, $NiCO_3$, and $CdCO_3$, together with listings of all possible *d*-values for powder diagrams taken with $CuK\alpha_1$ radiation. Less complete information is presented for $CuCO_3$, $Mg_3Ca(CO_3)_4$, $CaMn(CO_3)_2$, $CdMg(CO_3)_2$, and the hypothetical end member, $CaFe(CO_3)_2$. Samples of some of these materials prepared at or near room temperature have unit cells distinctly larger than those of equivalent samples prepared at higher temperature.

Amplitude contributions to the structure factors of calcite and dolomite powder reflections are given, based upon recently refined parameters cited in the literature. Front reflection intensities, based upon a simplified model essentially involving spherical neutral atoms at rest, are computed for a number of carbonates.

INTRODUCTION

The rhombohedral carbonate solid solutions, because of their widespread occurrence in a variety of geochemical environments, are important in evaluating the conditions under which various rocks formed. They are also of theoretical interest in a variety of solid-state studies. *X*-ray diffraction probably is the single most valuable technique for characterizing these materials. The change of unit-cell size among rhombohedral CaMg and CaMn carbonate solid solutions has been shown to be sufficient to allow the positions of suitably located individual back reflections on films taken with standard 114.59 mm. diameter powder cameras to be used as accurate measures of composition (Goldsmith, Graf and Joensuu, 1955; Goldsmith and Graf, 1957; Goldsmith and Graf, 1958b; Goldsmith, Graf, and Heard, 1961). The Debye-Scherrer method is particularly suitable for samples too small to utilize the maximum potential accuracy of the diffractometer.

Such back reflection measurements will yield useful information regardless of the indices of the particular reflection. Major advantages, however, are derived from considering the indices of the various back reflections:

1) More accurate values of the cell constants, a_0 and c_0, may be obtained by making extrapolations using reflections having, respectively, very large *a*-axis and *c*-axis components. Because reflections of this nature are limited in number, the procedure is most effective when various characteristic *X*-radiations may be utilized in order to bring the desired reflections as close as possible to $2\theta = 180°$;

2) The change in $c\!:\!a$ ratio between some pairs of carbonates is great enough to cause appreciable differential shifts in the positions of nearby reflections. The change of separation of such reflections becomes in itself an accurate measure of the extent of solid solution; film shrinkage can be

ignored over such a small portion of the film and errors varying with θ can be assumed to affect the two reflections equally and thus to cancel. The differential shift will be a maximum if one of the reflections has a strong *c*-axis component and the other, a strong *a*-axis component;

3) The spacings of reflections with strong *c*-axis components from carbonates with mixed-layer progressions along the *c*-axis (Graf, Blyth, and Stemmler, 1957; Goldsmith and Graf, 1958*b*; Graf, Blyth, and Stemmler, 1958) are altered because of this arrangement, and compositional measurements of such materials are best carried out using reflections with little or no *c*-axis component.

The back reflections of the rhombohedral carbonates are numerous enough so that interference or superposition of two or more reflections is not uncommon. Reliable unit-cell and *d*-spacing values for pure, well crystallized end members and ordered 1:1 compounds are, therefore, a prerequisite if diffraction diagrams of intermediate solid solutions and poorly crystallized materials are to yield maximum information. Tables 1 and 2 are a somewhat expanded version of a compilation of these quantities which has proved its usefulness. The accurate values given in Table 3 of the angles between [c] and the various plane normals of $CaMg(CO_3)_2$ may be used to estimate the orientation of planes in the other carbonates.

Intensities are important in evaluating cation and anion disorder and in estimating compositions of solid solutions between carbonates whose cations are very similar in size, such as $ZnCO_3$ and $CoCO_3$, and the ferroan dolomites, $Ca(Mg, Fe)(CO_3)_2$. The amplitude contributions of the several kinds of atoms to the structure factor are presented in Table 3 for the various reflections of $CaCO_3$ and $CaMg(CO_3)_2$, the only two rhombohedral carbonates for which variable parameters have been determined. These values were used in calculating the relative intensities of calcite and dolomite reflections out to $\{00\cdot12\}$ which are given in Table 4. The parameter approximations made in calculating analogous intensities for the other carbonates of Table 4 are discussed in a later section of the paper.

Measurements of reflection profiles and of the amounts of carbonates present in mixtures typically utilize low-angle reflections. Table 5 gives the 2θ values for such reflections from the more common rhombohedral carbonates for $CuK\alpha_1$ radiation.

Unit-Cell Dimensions

Table 6 summarizes the methods used in preparing the various materials for which unit-cell dimensions were determined. It also gives spectro-

TABLE 1. PREFERRED CELL CONSTANTS FOR THE RHOMBOHEDRAL CARBONATES*

Material	a_0	c_0	c_0/a_0	a_{rh}	α
$CaCO_3$					
20° C.	4.9900	17.061_5	3.4191	6.3753	46° 4.6′
26° C.	4.9899	17.064	3.4197	6.3760	46° 4.3′
$CaMg(CO_3)_2$ (ordered)	4.8079	16.010	3.3299	6.0154	47° 6.6′
$Ca_{50}Mg_{50}$†	4.8114_5	16.039_5	3.3336	6.0251	47 4.0′
$MgCO_3$	4.6330	15.016	3.2411	5.6752	48° 10.9′
$MnCO_3$	4.7771	15.664	3.2790	5.9050	47° 43.1_5′
$CaMn(CO_3)_2$ (disordered)	4.8797	16.367	3.3541		
$Ca_{50}Mn_{50}$†	4.8835	16.364	3.3509	6.1402_5	46° 51.8_5′
$FeCO_3$	4.6887	15.373	3.2787	5.7954	47° 43.3′
$Ca_{50}Fe_{50}$†	4.8393	16.218_5	3.3514	6.0855	46° 51.5′
$ZnCO_3$	4.6528	15.025	3.2292	5.6833	48° 19.6′
$CdCO_3$	4.9204	16.298	3.3123	6.1306	47° 19.1_5′
$CoCO_3$	4.6581	14.958	3.2112	5.6650_5	48° 33.1′
$Cd_{50}Mg_{50}$†	4.7767	15.657	3.2778	5.9028_5	47° 44.0′
$CdMg(CO_3)_2$ (ordered)	4.7770 ±0.0009‡	15.641 ±0.003‡	3.2742		
$CdMg(CO_3)_2$ (disordered)	4.7746 ±0.0009‡	15.678 ±0.03‡	3.2836		
$NiCO_3$	4.5975	14.723	3.2024	5.5795	48° 39.7′

* Pistorius (1960) has synthesized what appear to be mixtures of malachite and the anhydrous rhombohedral cupric carbonate, $CuCO_3$. Seven powder diffraction lines of the latter material give, from least square analysis, $a_0=4.796\pm0.005$ Å, $c_0=15.48\pm0.01$ Å, $c_0/a_0=3.227$, $\alpha=48°11'$, $a_{rh}=5.856$ Å.

† Hypothetical solid solutions with a_0 and c_0 midway between those of the two end members.

‡ The ranges given for a_0 and c_0 of ordered and disordered $CdMg(CO_3)_2$ indicate only the uncertainty that would result from a misreading of line position on the films (taken with a Guinier-type focusing camera) by the smallest unit measured, 0.05 mm. The procedure used in obtaining these $CdMg(CO_3)_2$ values is summarized in Table 7.

graphic analyses of those cations considered most likely to enter into solid solution in the carbonates. The analyses are computed with all cations as carbonates in solid solution, the most severe assumption possible inasmuch as some of the impurities may be present as traces of other compounds. Of the impurities detected, the 0.38 mol percent $CaCO_3$ in the $MgCO_3$ is the most significant, both because of the absolute amount and because the large size difference between Ca^{++} and Mg^{++} results in maximum spacing change. Assuming a linear relation between cell size

TABLE 2. POSSIBLE *X*-RAY REFLECTIONS FOR THE RHOMBOHEDRAL CARBONATES IN DEBYE-SCHERRER DIAGRAMS TAKEN WITH CuK_{α_1} RADIATION

$hk \cdot l$	$h_rk_rl_r$	$MgCO_3$	$CaMg(CO_3)_2$	$Ca_{50}Mg_{50}$*	$CaCO_3$ (26° C.)	$Ca_{50}Fe_{50}$*	$FeCO_3$	$Ca_{50}Mn_{50}$*	$MnCO_3$	$ZnCO_3$	$CdCO_3$	$CoCO_3$	$NiCO_3$
00·3	111		5.3366	5.3645		5.4062		5.4547					
10·1	100		4.0297	4.0330		4.0577		4.0947					
01·2	110	3.5387	3.6939	3.6975	3.8551	3.7233	3.5903	3.7570	3.6581	3.5509	3.7761	3.5505	3.5021
10·4	211	2.7412	2.8855	2.8893	3.0359	2.9141	2.7912	2.9404	2.8440	2.7476	2.9449	2.7424	2.7028
00·6	222	2.5027	2.6683	2.6733	2.8440	2.7031	2.5622	2.7273	2.6107	2.5042	2.7163	2.4930	2.4538
01·5	221		2.5382	2.5419		2.5651		2.5883					
11·0	$10\bar{1}$	2.3165	2.4039	2.4057	2.4949	2.4197	2.3443	2.4417	2.3886	2.3264	2.4602	2.3291	2.2988
11·3	210	2.1023	2.1918	2.1939	2.2848	2.2085	2.1318	2.2286	2.1721	2.1099	2.2411	2.1102	2.0817
02·1	$11\bar{1}$		2.0645	2.0661		2.0782		2.0972					
20·2	200	1.9832	2.0149	2.0165	2.0946	2.0288	1.9629	2.0473	2.0000	1.9460	2.0613	1.9474	1.9217
10·7	322		2.0046	2.0078		2.0277		2.0460					
02·4	220	1.7693	1.8470	1.8488	1.9275	1.8616	1.7952	1.8785	1.8290	1.7754	1.8880	1.7752	1.7511
01·8	332	1.7002	1.8037	1.8067	1.9127	1.8250	1.7369	1.8414	1.7698	1.7023	1.8380	1.6964	1.6705
11·6	321	1.7000	1.7860	1.7882	1.8755	1.8029	1.7296	1.8192	1.7623	1.7044	1.8235	1.7019	1.6776
00·9	333		1.7789	1.7822		1.8021		1.8182					
20·5	311		1.7454	1.7473		1.7601		1.7761					
21·1	$20\bar{1}$	1.5088	1.5662	1.5674	1.6259	1.5765	1.5271	1.5909	1.5559	1.5152	1.6028	1.5169	1.4971
12·2	$21\bar{1}$	1.4865	1.5442	1.5454	1.6042	1.5547	1.5050	1.5688	1.5334	1.4926	1.5800	1.4940	1.4744
02·7	331		1.5396	1.5415		1.5541		1.5682					
10·10	433	1.4063	1.4943	1.4969	1.5872	1.5125	1.4377	1.5261	1.4649	1.4078	1.5223	1.4025	1.3809
21·4	310	1.4061	1.4646	1.4659	1.5253	1.4754	1.4253	1.4889	1.4522	1.4114	1.4978	1.4119	1.3930
20·8	422	1.3706	1.4428	1.4447	1.5180	1.4570	1.3956	1.4702	1.4220	1.3728	1.4724	1.3712	1.3514
11·9	432	1.3538	1.4300	1.4320	1.5096	1.4453	1.3805	1.4583	1.4066	1.3563	1.4584	1.3529	1.3328
12·5	320	1.3537	1.4124	1.4137	1.4733	1.4234	1.3732	1.4363	1.3991	1.3585	1.4439	1.3585	1.3400
03·0	$11\bar{2}$	1.3374	1.3879	1.3889	1.4404	1.3970	1.3535	1.4097	1.3790	1.3432	1.4204	1.3447	1.3272

* Hypothetical solid solutions with a_0 and c_0 midway between those of the two end members.

$hk\cdot l$	$h_rk_rl_r$	$MgCO_3$	$CaMg(CO_3)_2$	$Ca_{50}Mg_{50}$*	$CaCO_3$ (26° C.)	$Ca_{50}Fe_{50}$*	$FeCO_3$	$Ca_{50}Mn_{50}$*	$MnCO_3$	$ZnCO_3$	$CdCO_3$	$CoCO_3$	$NiCO_3$
01·11	443		1.3739	1.3763		1.3908		1.4034					
{30·3, 03·3}	{300, 22$\bar{1}$}		1.3432	1.3443		1.3526		1.3649					
00·12	444	1.2513	1.3342	1.3366	1.4220	1.3515	1.2811	1.3637	1.3053	1.2521	1.3582	1.2465	1.2269
21·7	421	1.2383	1.2965	1.2979	1.3569	1.3076	1.2580	1.3195	1.2817	1.2421	1.3246	1.2412	1.2239
02·10	442	1.2021	1.2691	1.2709	1.3391	1.2826	1.2256	1.2942	1.2488	1.2044	1.2945	1.2015	1.1837
12·8	431	1.1796	1.2371	1.2385	1.2968	1.2482	1.1992	1.2595	1.2219	1.1829	1.2634	1.1816	1.1650
{30·6, 03·6}	{411, 330}	1.1796	1.2313	1.2325	1.2850	1.2410	1.1968	1.2523	1.2194	1.1836	1.2587	1.1835	1.1674
22·0	20$\bar{2}$	1.1583	1.2020	1.2029	1.2475	1.2098	1.1722	1.2209	1.1943	1.1632	1.2301	1.1645	1.1494
20·11	533		1.1929	1.1946		1.2058		1.2167					
10·13	544		1.1810	1.1830		1.1957		1.2065					
22·3	31$\bar{1}$	1.1284	1.1726	1.1735	1.2185	1.1806	1.1427	1.1914	1.1642	1.1330	1.1997	1.1340	1.1191
11·12	543	1.1010	1.1665	1.1684	1.2354	1.1799	1.1242	1.1906	1.1454	1.1025	1.1890	1.0990	1.0824
13·1	21$\bar{2}$	1.1098	1.1518	1.1527	1.1956	1.1594	1.1232	1.1700	1.1444	1.1145	1.1787	1.1157	1.1012
31·2	30$\bar{1}$	1.1008	1.1430	1.1439	1.1869	1.1506	1.1143	1.1611	1.1353	1.1054	1.1696	1.1065	1.0921
21·10	532	1.0670	1.1223	1.1238	1.1799	1.1332	1.0861	1.1435	1.1066	1.0696	1.1456	1.0678	1.0524
13·4	32$\bar{1}$	1.0669	1.1096	1.1105	1.1539	1.1174	1.0807	1.1275	1.1011	1.0712	1.1351	1.0719	1.0577
01·14	554	1.0362	1.1027	1.1047	1.1731	1.1166	1.0600	1.1266	1.0801	1.0371	1.1230	1.0328	1.0168
22·6	420	1.0511	1.0959	1.0969	1.1424	1.1043	1.0659	1.1143	1.0860	1.0549	1.1206	1.0551	1.0409
{03·9, 30·9}	{441, 522}		1.0943	1.0955		1.1041		1.1141					
31·5	410	1.0435	1.0863	1.0873	1.1308	1.0942	1.0575	1.1042	1.0774	1.0475	1.1111	1.0480	1.0340
12·11	542	1.0146	1.0685	1.0700	1.1248	1.0792	1.0333	1.0890	1.0528	1.0169	1.0904	1.0148	1.0001
00·15	555		1.0673	1.0693		1.0812		1.0909					
02·13	553		1.0600	1.0616		1.0720		1.0816					

TABLE 2—(*continued*)

$hk\cdot l$	$h_r k_r l_r$	$MgCO_3$	$CaMg(CO_3)_2$	$Ca_{50}Mg_{50}$*	$CaCO_3$ (26° C.)	$Ca_{50}Fe_{50}$*	$FeCO_3$	$Ca_{50}Mn_{50}$*	$MnCO_3$	$ZnCO_3$	$CdCO_3$	$CoCO_3$	$NiCO_3$
40·1	$11\bar{3}$		1.0387	1.0395		1.0456		1.0551					
04·2	$22\bar{2}$	.99424	1.0322	1.0330	1.0718	1.0391	1.0064	1.0486	1.0254	.99842	1.0563	.99947	.98641
13·7	430	.98781	1.0309	1.0319	1.0756	1.0390	1.0021	1.0484	1.0210	.99125	1.0538	.99119	.97772
40·4	400	.96908	1.0074	1.0082	1.0473	1.0144	.98147	1.0237	.99998	.97298	1.0307	.97372	.96087
20·14	644	.94587	1.0023	1.0039	1.0616	1.0138	.96585	1.0230	.98412	.94720	1.0216	.94414	.92987
31·8	521	.95723	1.0002	1.0012	1.0449	1.0084	.97162	1.0175	.98996	.96040	1.0223	.96008	.94690
22·9	531	.95146	.99593	.99701	1.0421	1.0045	.96649	1.0136	.98473	.95438	1.0175	.95371	.94045
04·5	$33\bar{1}$		.98994	.99078		.99702		1.0061					
11·15	654	.91893	.97550	.97713	1.0351	.98716	.93905	.99604	.95682	.92001	.99392	.91670	.90269
10·16	655	.91383	.97292	.97466	1.0354	.98525	.93499	.99410	.95269	.91455	.99071	.91073	.89656
21·13	643	.91889	.96987	.97125	1.0232	.98010	.93672	.98895	.95443	.92067	.98930	.91844	.90491
{30·12 {03·12	633} 552}	.91375	.96184	.96310	1.0120	.97135	.93041	.98014	.94799	.91586	.98163	.91415	.90093
32·1	$30\bar{2}$	.91876	.95353	.95424	.98972	.95979	.92984	.96855	.94738	.92267	.97583	.92371	.91168
23·2	$31\bar{2}$	.91365	.94850	.94922	.98476	.95479	.92478	.96350	.94222	.91750	.97062	.91847	.90648
40·7	511		.94743	.94831		.95467		.96336					
13·10	541	.89406	.93659	.93764	.98078	.94478	.90849	.95335	.92564	.89671	.95677	.89594	.88341
32·4	$41\bar{1}$	.89400	.92914	.92988	.96565	.93553	.90533	.94406	.92241	.89763	.95061	.89837	.88654
12·14	653	.87568	.92512	.92647	.97685	.93508	.89303	.94352	.90991	.87728	.94348	.87498	.86202
04·8	440	.88467	.92348	.92438	.96377	.93079	.89758	.93925	.91452	.88772	.94402	.88762	.87553
01·17	665		.91856	.92021		.93023		.93858					
23·5	$42\bar{1}$	.88008	.91537	.91612	.95203	.92183	.89152	.93023	.90834	.88355	.93638	.88413	.87242
14·0	$21\bar{3}$	.87556	.90861	.90928	.94300	.91454	.88608	.92289	.90279	.87929	.92987	.88030	.86885
31·11	632	.86253	.90465	.90570	.94843	.91281	.87690	.92109	.89346	.86494	.92392	.86398	.85180
02·16	664	.85008	.90186	.90334	.95635	.91250	.86847	.92071	.88490	.85114	.91900	.84819	.83527
{14·3 {41·3	$32\bar{2}$} $40\bar{1}$}	.86246	.89572	.89640	.93030	.90173	.87312	.90996	.88959	.86605	.91654	.86689	.85554

$hk\cdot l$	$h_r k_r l_r$	$MgCO_3$	$CaMg(CO_3)_2$	$Ca_{50}Mg_{50}$*	$CaCO_3$ (26° C.)	$Ca_{50}Fe_{50}$*	$FeCO_3$	$Ca_{50}Mn_{50}$*	$MnCO_3$	$ZnCO_3$	$CdCO_3$	$CoCO_3$	$NiCO_3$
22·12	642	.85001	.89301	.89411	.93777	.90143	.86479	.90960	.88113	.85219	.91173	.85095	.83881
00·18	666	.83422	.88944	.89109	.94801	.90103	.85405	.90911	.87022	.83472	.90545	.83099	.81794
32·7	520	.84590	.88144	.88224	.91835	.88805	.85759	.89613	.87377	.84902	.90136	.84924	.83783
40·10	622	.83409	.87269	.87363	.91278	.88007	.84711	.88806	.86310	.83671	.89171	.83620	.82461
23·8	530	.82646	.86206	.86288	.89903	.86873	.83824	.87663	.85406	.82939	.88136	.82943	.81820
{41·6 14·6}	{510 43$\bar{1}$}	.82644	.86011	.86084	.89508	.86630	.83741	.87420	.85321	.82964	.87975	.83007	.81902
20·17	755		.85805	.85948		.86827		.87609					
04·11	551		.84668	.84762		.85406		.86181					
{03·15 30·15}	{663 744}		.84608	.84729		.85505		.86277					
21·16	754	.79804	.84439	.84568	.89299	.85380	.81438	.86150	.82978	.79932	.86089	.79698	.78506
13·13	652	.80140	.84239	.84345	.88508	.85045	.81553	.85815	.83093	.80340	.85997	.80213	.79065
11·18	765	.78488	.83417	.83560	.88619	.84438	.80246	.85198	.81764	.78567	.84972	.78267	.77061
05·1	22$\bar{3}$		.83163	.83224		.83708		.84472					
50·2	11$\bar{4}$	.79792	.82828	.82890	.85987	.83375	.80761	.84136	.82284	.80129	.84761	.80216	.79169
10·19	766		.82589	.82738		.83643		.84394					
32·10	631	.78477	.82031	.82116	.85722	.82706	.79699	.83458	.81173	.78733	.83834	.78701	.77618
05·4	33$\bar{2}$	.78473	.81529	.81593	.84706	.82084	.79456	.82833	.80954	.78796	.83419	.78866	.77830
31·14	743	.77226	.81257	.81363	.85459	.82053	.78620	.82795	.80106	.77408	.82936	.77270	
{14·9 41·9}	{540 621}	.77529	.80916	.80995	.84433	.81553	.78655	.82295	.80139	.77798	.82719	.77792	
12·17	764		.80812	.80937	.85519	.81725	.77910	.82462	.79384		.82380		
50·5	500		.80594	.80659		.81154		.81893					
33·0	30$\bar{3}$	.77217	.80131	.80191	.83164	.80655	.78145	.81392	.79618	.77546	.82007	.77635	

TABLE 2—(*continued*)

$hk\cdot l$	$h_rk_rl_r$	$MgCO_3$	$CaMg(CO_3)_2$	$Ca_{50}Mg_{50}$*	$CaCO_3$ (26° C.)	$Ca_{50}Fe_{50}$*	$FeCO_3$	$Ca_{50}Mn_{50}$*	$MnCO_3$	$ZnCO_3$	$CdCO_3$	$CoCO_3$	$NiCO_3$
23·11	641		.79859	.77945	.83537	.80537	.77513	.81268	.78977		.81598		
22·15	753		.79809	.79918	.84057	.80619	.77154	.81348	.78613		.81435		
40·13	733		.79500	.79595		.80233		.80960					
33·3	$41\bar{2}$		.79243	.79303	.82290	.79772	.77252	.80500	.78709		.81088		
01·20	776		.78610	.78752	.83705	.79616		.80331			.80040		
24·1	$31\bar{3}$		.78593	.78651	.81572	.79108		.79830	.78086		.80431		
42·2	$40\bar{2}$		.78310	.78369	.81294	.78827		.79546	.77797		.80139		
05·7	$44\bar{1}$		.78250	.78317		.78820		.79538					
02·19	775		.78108	.78240		.79053		.79764					
24·4	$42\bar{2}$		.77210	.77270	.80209	.77733		.78442			.79001		
04·14	662			.77074	.80847	.77707		.78411			.78590		
50·8	611				.80101	.77460		.78165			.78622		
33·6	$52\bar{1}$				.79822	.77288		.77993			.78507		
00·21	777					.77231		.77924					
42·5	511				.79424			.77643			.78178		
13·16	763				.79674			.77087			.77158		
20·20	866				.79358								
{30·18 03·18	855} 774				.79189								
32·13	742				.79110						.77092		
21·19	865				.78698								
{41·12 14·12	732} 651				.78590								
51·1	$21\bar{4}$				.77534								
24·7	$53\bar{1}$				.77436								
15·2	$32\bar{3}$				.77295								
11·21	876				.77263								
05·10	550				.77102								

TABLE 3. AMPLITUDE CONTRIBUTIONS TO STRUCTURE FACTORS, AND ANGLES BETWEEN [c] AND PLANE NORMALS, FOR CALCITE AND DOLOMITE

$hk\cdot l$	$h_rk_rl_r$	Amplitude contributions* to structure factors, F, for calcite			Amplitude contributions* to structure factors, F, for dolomite				Angle between plane normal and [c], for dolomite, in degrees
		f_{Ca}	f_C	f_O	f_{Ca}	f_{Mg}	f_C	f_O	
00·3	111				+1	−1	−0.2444	−0.6771	0
10·1	100				+1	−1	+0.0817	−0.3761	75.422
01·2	110	+2	−2	−1.8040	+1	+1	−1.9933	−1.7952	62.519
10·4	211	+2	+2	+1.8040	+1	+1	+1.9734	+1.8801	43.869
00·6	222	+2	−2	−6.0000	+1	+1	−1.9402	−5.8472	0
01·5	221				+1	−1	+0.4056	+0.7814	37.562
11·0	$10\bar{1}$	+2	+2	−2.1864	+1	+1	+2.0000	−2.1095	90
11·3	210			+4.1910	+1	−1	−0.2444	+4.1187 −3.6426	65.751
02·1	$11\bar{1}$				+1	−1	+0.0817	+1.6286	82.591
20·2	200	+2	−2	+1.9808	+1	+1	−1.9933	+1.9509	75.422
10·7	322				+1	−1	−0.5640	−0.0482	28.782
02·4	220	+2	+2	−1.9808	+1	+1	+1.9734	−2.3185	62.518
01·8	332	+2	+2	+1.8040	+1	+1	+1.8942	+1.6189	25.672
11·6	321	+2	−2	+2.1864	+1	+1	−1.9402	+1.1798 +2.9316	47.985
00·9	333				+1	−1	+0.7187	+1.9969	0
20·5	311				+1	−1	+0.4056	−2.0689	56.969
21·1	$20\bar{1}$			+3.7802	+1	+1	+0.0817	−4.4674 +2.7560	84.386
12·2	$21\bar{1}$	+2	−2	+1.7954	+1	+1	−1.9933	+0.6004 +2.8753	78.878
02·7	331				+1	−1	−0.5640	−1.1053	47.689
10·10	433	+2	−2	−1.8040	+1	+1	−1.8355	−1.8692	21.036
21·4	310	+2	+2	−1.7954	+1	+1	+1.9734	−1.8669 −1.2224	68.535
20·8	422	+2	+2	−1.9808	+1	+1	+1.8942	−1.4839	43.867
11·9	432			+4.1910	+1	−1	+0.7187	−4.3850 +3.0204	36.499
12·5	320			+3.7802	+1	−1	+0.4056	−2.8915 +3.8184	63.826
03·0	$11\bar{2}$	+2	+2	+2.5860	+1	+1	+2.0000	+1.9259	90
01·11	443				+1	−1	−0.8686	−1.1467	19.271
30·3 03·3	300 $22\bar{1}$				+1	−1	−0.2444	+0.8776 −1.3123	75.422
00·12	444	+2	+2	+6.0000	+1	+1	+1.7646	+5.3964	0
21·7	421			+3.7802	+1	−1	−0.5640	+4.8888 −2.4801	55.468

* The amplitude contributions have been divided by 6 in order to obtain expressions corresponding to the contents of the rhombohedral unit cell.

TABLE 3—(*continued*)

$hk\cdot l$	$h_rk_rl_r$	Amplitude contributions* to structure factors, F, for calcite			Amplitude contributions* to structure factors, F, for dolomite				Angle between normal and normal and [c], for dolomite, in degrees
		f_{Ca}	f_C	f_O	f_{Ca}	f_{Mg}	f_C	f_O	
02·10	442	+2	−2	+1.9808	+1	+1	−1.8355	+2.5679	37.562
12·8	431	+2	+2	−1.7954	+1	+1	+1.8942	+0.0523 −3.7372	51.818
30·6 03.6	411 330	+2	−2	−2.5860	+1	+1	−1.9402	−2.1240 −1.6297	62.519
22·0	20$\bar{2}$	+2	+2	−2.0192	+1	+1	+2.0000	−1.1830	90
20·11	533				+1	−1	−0.8686	+2.4039	34.955
10·13	544				+1	−1	+1.0127	+0.4701	16.470
22·3	31$\bar{1}$			−0.7811	+1	−1	−0.2444	−0.2913 +0.5583	77.307
11·12	543	+2	+2	−2.1864	+1	+1	+1.7646	−0.1901 −3.6045	29.035
13·1	21$\bar{2}$			−0.3704	+1	−1	+0.0817	+0.0978 −1.0696	85.875
31·2	30$\bar{1}$	+2	−2	−2.1566	+1	+1	−1.9933	+0.4957 −4.4963	81.791
21·10	532	+2	−2	+1.7954	+1	+1	−1.8355	+0.7635 +1.7822	45.493
13·4	32$\bar{1}$	+2	+2	+2.1566	+1	+1	+1.9734	+4.4742 −0.2543	73.905
01·14	554	+2	−2	−1.8040	+1	+1	−1.6819	−1.3600	15.365
22·6	420	+2	−2	+2.0192	+1	+1	−1.9402	+1.2488 +1.0570	65.751
03·9 30·9	441 522				+1	−1	+0.7187	+1.6801 −0.3982	52.036
31·5	410			−0.3704	+1	−1	+0.4056	+0.9577 +0.9170	70.169
12·11	542			+3.7802	+1	−1	−0.8686	+2.8797 −2.9749	42.766
00·15	555				+1	−1	−1.1500	−3.2150	0
02·13	553				+1	−1	+1.0127	+0.5257	30.603
04·$\bar{1}$	11$\bar{3}$				+1	−1	+0.0817	+0.3301	86.280
04·2	22$\bar{2}$	+2	−2	−5.9232	+1	+1	−1.9933	−4.8835	82.591
13·7	430			−0.3704	+1	−1	−0.5640	−1.1077 +1.1270	63.209
40·4	400	+2	+2	+5.9232	+1	+1	+1.9734	+4.8089	75.422
20·14	644	+2	−2	+1.9808	+1	+1	−1.6819	+0.9413	28.782
31·8	521	+2	+2	+2.1566	+1	+1	+1.8942	−0.7119 +4.2893	60.014
22·8	531			−0.7811	+1	−1	+0.7187	+0.0095 −0.7969	60.155
04.5	33$\bar{1}$				+1	−1	+0.4056	+0.7721	71.991

TABLE 3—(*continued*)

$hk \cdot l$	$h_r k_r l_r$	Amplitude contributions* to structure factors, F, for calcite			Amplitude contributions* to structure factors, F, for dolomite				Angle between plane normal and [*c*], for dolomite, in degrees
		f_{Ca}	f_C	f_O	f_{Ca}	f_{Mg}	f_C	f_O	
11·15	654			+4.1910	+1	−1	−1.1500	+4.4279 −2.1673	23.942
10·16	655	+2	+2	+1.8040	+1	+1	+1.5880	+1.7631	13.514
21·13	643			+3.7802	+1	−1	+1.0127	−5.0611 +2.0778	38.045
30·12 03·12	633 552	+2	+2	+2.5860	+1	+1	+1.7646	+2.2139 +1.2505	43.868
32·1	$30\bar{2}$			−4.1145	+1	−1	+0.0817	+4.9874 −1.8593	86.586
23·2	$31\bar{2}$	+2	−2	+2.1826	+1	+1	−1.9933	+0.0903 +2.5584	83.195
40·7	511				+1	−1	−0.5640	−1.4156	65.528
13·10	541	+2	−2	−2.1566	+1	+1	−1.8355	−4.2242 −0.0001	54.197
32·4	$41\bar{1}$	+2	+2	−2.1826	+1	+1	+1.9734	−3.6841 +0.3294	76.577
12·14	653	+2	−2	+1.7954	+1	+1	−1.6819	−0.7023 +4.4086	36.005
04·8	440	+2	+2	+5.9232	+1	+1	+1.8942	+4.7092	62.519
01·17	665				+1	−1	+1.2797	+1.4537	12.745
23·5	$42\bar{1}$			−4.1145	+1	−1	+0.4056	+1.8389 −5.5649	73.389
14·0	$21\bar{3}$	+2	+2	+1.3784	+1	+1	+2.0000	+3.4131 −0.8908	90
31·11	632			−0.3704	+1	−1	−0.8686	−0.7970 −1.8852	51.570
02·16	664	+2	+2	−1.9808	+1	+1	+1.5880	−2.6866	25.671
14·3 41·3	$32\bar{2}$ $40\bar{1}$			+0.4469	+1	−1	−0.2444	+0.2011 +1.8240 −1.6229 −0.9715	80.338
22·12	642	+2	+2	−2.0192	+1	+1	+1.7646	−1.2509 −0.8771	47.984
00·18	666	+2	−2	−6.0000	+1	+1	−1.4835	−4.6708	0
32·7	520			−4.1145	+1	−1	−0.5640	−4.1559 +1.7849	67.332
40·10	622	+2	−2	−5.9232	+1	+1	−1.8355	−4.4894	56.969
23·8	530	+2	+2	−2.1826	+1	+1	+1.8942	−0.5054 −1.3023	64.484
41·6 14·6	510 $43\bar{1}$	+2	−2	−1.3784	+1	+1	−1.9402	+1.2571 −3.1938 −3.4585 +0.4791	71.196

TABLE 3—(*continued*)

$hk\cdot l$	$h_rk_rl_r$	Amplitude contributions* to structure factors, F, for calcite			Amplitude contributions* to structure factors, F, for dolomite				Angle between plane normal and [c], for dolomite, in degrees
		f_{Ca}	f_C	f_O	f_{Ca}	f_{Mg}	f_C	f_O	
20·17	755				+1	−1	+1.2797	−2.6163	24.341
04·11	551				+1	−1	−0.8686	−1.8350	54.428
03·15 30·15	663 744				+1	−1	−1.1500	−1.9624 −0.1016	37.561
21·16	754	+2	+2	−1.7954	+1	+1	+1.5880	+0.3789 −2.2512	32.450
13·13	652			−0.3704	+1	−1	+1.0127	+2.0612 −1.1270	46.842
11·18	765	+2	−2	+2.1864	+1	+1	−1.4835	−0.8094 +4.0937	20.306
05·1	22$\bar{3}$				+1	−1	+0.0817	+2.0959	87.023
05·$\bar{2}$	11$\bar{4}$	+2	−2	−1.0296	+1	+1	−1.9933	−0.5718	84.061
10·19	766				+1	−1	−1.4008	−0.8681	11.441
32·10	631	+2	−2	+2.1826	+1	+1	−1.8355	+4.6221 −0.7322	59.178
05·4	33$\bar{2}$	+2	+2	+1.0296	+1	+1	+1.9734	+0.0988	78.247
31·14	743	+2	−2	−2.1566	+1	+1	−1.6819	+0.8918 −3.8638	44.720
14·9 41·9	540 621			+0.4469	+1	−1	+0.7187	+0.5795 −1.9321 +1.3391 +1.6923	62.944
12·17	764			+3.7802	+1	−1	+1.2797	−2.7212 +1.9798	30.897
50·5	500				+1	−1	+0.4056	−1.9669	75.422
33·0	30$\bar{3}$	+2	+2	−1.3282	+1	+1	+2.0000	−1.7691	90
23·11	641			−4.1145	+1	−1	−0.8686	−1.7248 +5.8588	56.723
22·15	753			−0.7811	+1	−1	−1.1500	+0.2729 +0.9949	41.605
40·13	733				+1	−1	+1.0127	+2.4289	49.794
33·3	41$\bar{2}$			−3.3772	+1	−1	−0.2444	−1.6477 +2.0470	81.460
01·20	776	+2	+2	+1.8040	+1	+1	+1.3691	+1.0319	10.883
24·1	31$\bar{3}$			+0.7735	+1	−1	+0.0817	−3.3813 −2.4627	87.186
42·2	40$\bar{2}$	+2	−2	+1.9430	+1	+1	−1.9933	+1.3808 +2.1764	84.386
05·7	44$\bar{1}$				+1	−1	−0.5640	+1.7233	69.993
02·19	775				+1	−1	−1.4008	+0.0808	22.036

TABLE 3—(*continued*)

$hk\cdot l$	$h_rk_rl_r$	Amplitude contributions* to structure factors, F, for calcite			Amplitude contributions* to structure factors, F, for dolomite				Angle between plane normal and [c], for dolomite, in degrees
		f_{Ca}	f_C	f_O	f_{Ca}	f_{Mg}	f_C	f_O	
24·4	$42\bar{2}$	+2	+2	−1.9430	+1	+1	+1.9734	−1.4132 −0.8250	78.878
04·14	662	+2	−2	−5.9232					48.448†
50·8	611	+2	+2	+1.0296					67.943†
33·6	$52\bar{1}$	+2	−2	+1.3282					73.700†
42·5	$51\bar{1}$			+0.7735					76.543†
13·16	763	+2	+2	+2.1566					41.664†
20·20	866	+2	+2	−1.9808					21.546†
30·18 03·18	855 774	+2	−2	−2.5860					33.350†
32·13	742			−4.1145					52.937†
21·19	865			+3.7802					28.805†
41·12 14·12	732 651	+2	−2	−1.3784					56.449†
15·$\bar{1}$	$21\bar{4}$			+4.5175					87.396†
24·7	$53\bar{1}$			+0.7735					71.479†
15·2	$32\bar{3}$	+2	−2	+2.4974					84.802†
11·21	876			+4.1910					18.040†
05·10	550	+2	−2	−1.0296					63.138†

† These angles are for calcite (26° C.).

and composition, 0.38 mol percent substituted $CaCO_3$ in $MgCO_3$ would produce a change of 0.0005 Å in a 1 Å basal reflection and 0.0003 Å in a 1 Å reflection with no c-axis component. These differences would be readily measurable in the back reflection region of films taken with a 114.59 mm. diameter powder camera such as that used in this work.*

The other impurities in Table 6, where they are greater than the limit of detection, would probably not produce detectable spacing changes. The Li_2CO_3 used to facilitate recrystallization of some of these samples in runs made with a squeezer-type apparatus (Griggs and Kennedy, 1956) has never been observed to lead to changed spacings in cases where carbonates were initially well crystallized and careful comparisons of back-reflection spacings before and after the run could be made.

* The slight equilibrium substitution of $CaCO_3$ in $MgCO_3$ at higher temperatures (Harker and Tuttle, 1955) suggests that the 0.38 mol percent $CaCO_3$ here computed is probably not all present in solid solution.

TABLE 4. COMPUTED RELATIVE INTENSITIES OF FRONT REFLECTIONS IN POWDER DIAGRAMS OF THE RHOMBOHEDRAL CARBONATES AND THE HYPOTHETICAL END MEMBER, $CaFe(CO_3)_2$, FOR COPPER RADIATION

$h_r k_r l_r$	$MgCO_3$	$Mg_3Ca(CO_3)_4$		$CaMg(CO_3)_2$	$CaCO_3$	$CaMn(CO_3)_2$	$CaFe(CO_3)_2$	$MnCO_3$	$FeCO_3$	$CoCO_3$	$NiCO_3$	$CuCO_3$	$ZnCO_3$	$CdMg(CO_3)_2$	$CdCO_3$
111				.021		(14.2)†	(16.4)†							67.6	
100				2.46		(9.17)	(12.7)							141	
110	.689	4.05	$11\bar{1}$*	3.38	17.3	42.1	48.1	75.4	90.1	105	122	136	154	125	565
211	78.9	196	200	146	213	231	231	246	243	246	249	323	296	342	779
222	9.73	17.9	111	6.65	4.96	1.59	1.15	.145	.0020	.0864	.346	.712	1.27	.817	28.0
221				7.20		(.039)	(.0052)							68.0	
$10\bar{1}$	5.17	22.7	$20\bar{2}$	17.0	30.2	40.2	41.3	50.7	52.7	58.1	61.8	82.3	80.3	87.6	267
210	39.4			34.9	44.6	43.4	42.5	41.6	40.4	39.4	38.6	41.2	39.5	97.7	47.2
$11\bar{1}$				6.07		(.465)	(.229)							45.2	
200	10.3	18.3	$3\bar{1}\bar{1}$	20.2	33.2	40.8	41.6	48.0	48.9	52.5	54.3	71.8	69.2	73.2	201
322				.260		(1.64)	(2.02)							20.5	
220	4.29	6.88	$22\bar{2}$	6.48	14.6	1.97	20.9	25.1	26.9	29.5	32.0	40.0	41.2	37.3	126
332	14.7	36.3	220	26.8	45.9	48.2	48.0	49.3	48.5	48.3	48.7	66.7	62.7	70.3	181
321	18.9	35.8	$31\bar{1}$	28.6	48.4	59.6	61.5	69.5	72.8	76.7	80.5	101	102	101	275
333				1.86		(.360)	(.247)							10.4	
311				.273		(3.64)	(4.09)							7.73	
$20\bar{1}$	4.09			6.95	8.98	7.78	6.72	5.88	5.06	4.38	3.71	6.11	4.33	23.7	7.94
$21\bar{1}$	6.24	6.94	$31\bar{3}$	14.9	21.4	28.6	28.9	33.0	33.2	35.9	37.3	52.6	49.9	57.9	163
331				.0416		(1.65)	(1.92)							6.21	
433	.324	.846	311	.782	2.15	3.93	4.40	5.69	6.64	7.29	8.29	10.7	11.7	11.7	46.7
310	5.17	7.34	$40\bar{2}$	8.46	13.6	18.7	19.8	21.9	25.9	28.6	31.1	38.6	40.3	41.4	121
422	1.76	3.62	400	4.00	6.20	8.14	8.50	9.89	10.6	11.4	12.4	16.1	16.6	19.1	56.1
432	5.85			5.05	7.92	6.74	7.05	6.42	6.17	5.73	5.52	6.18	5.81	19.1	7.00
320	2.50			4.78	5.74	4.61	4.23	3.63	2.91	2.65	2.24	3.70	2.63	22.3	4.90
$11\bar{2}$	11.2	7.81	$4\bar{2}\bar{2}$	10.4	17.7	21.5	22.2	25.1	26.4	28.4	30.0	34.6	35.7	30.6	81.6
443				.0534		(1.26)	(1.42)							4.02	
300, $22\bar{1}$				.455		(.970)	(1.14)							12.3	
444	4.18	10.7	222	5.77	10.1	9.95	9.93	9.62	9.53	9.17	9.22	12.0	11.5	12.4	30.1

* The calcite rhombohedral cell, on the basis of which the intensities in this table are computed, contains only $\frac{1}{2}$ $Mg_3Ca(CO_3)_4$ and is thus a pseudo-cell for huntite. The huntite reflections listed here may be indexed on this pseudo-cell; the corresponding index in the true huntite rhombohedral cell is given immediately after each huntite relative intensity value (see Graf and Bradley, in press).

† The intensities in parentheses were computed for a dolomite-type structure, the other $CaMn(CO_3)_2$ and $CaFe(CO_3)_2$ intensities, for a calcite-type structure (see text).

TABLE 5. VALUES OF 2θ FOR LOW-ANGLE *X*-RAY REFLECTIONS OF THE COMMON RHOMBOHEDRAL CARBONATES, COMPUTED FOR $CuK\alpha_1$ RADIATION

$hk\cdot l$	$h_r k_r l_r$	$MgCO_3$	$CaMg(CO_3)_2$	$CaCO_3$ (26° C.)	$FeCO_3$	$MnCO_3$	$ZnCO_3$
00·3	111		16.597				
10·1	100		22.039				
01·2	110	25.143	24.071	23.051	24.777	24.310	25.056
10·4	211	32.637	30.964	29.394	32.038	31.428	32.561
00.6	222	35.850	33.557	31.427	34.989	34.319	35.827
01·5	221		35.331				
11·0	$10\bar{1}$	38.841	37.376	35.965	38.363	37.625	38.670
11·3	210	42.985	41.148	39.402	42.362	41.539	42.822
02·1	$11\bar{1}$		43.812				
20·2	200	46.832	44.950	43.152	46.208	45.302	46.633
10·7	322		45.193				
02·4	220	51.614	49.295	47.107	50.815	49.812	51.424
01·8	332	53.877	50.560	47.494	52.650	51.597	53.806
11·6	321	53.884	51.096	48.496	52.889	51.835	53.733
00·9	333		51.315				
20·5	311		52.374				
21·1	$20\bar{1}$	61.395	58.918	56.555	60.581	59.346	61.108
12·2	$21\bar{1}$	62.417	59.841	57.391	61.567	60.309	62.135
02·7	331		60.039				
10·10	433	66.420	62.056	58.063	64.789	63.448	66.340
21·4	310	66.431	63.459	60.660	65.423	64.065	66.149
20·8	422	68.386	64.533	60.983	66.996	65.595	68.204
11·9	432	69.354	65.182	61.359	67.828	66.405	69.210
12·5	320	69.360	66.097	63.042	68.239	66.806	69.081
03·0	$11\bar{2}$	70.329	67.419	64.654	69.372	67.911	69.981
01·11	443		68.199				
30·3 03·3	300 $22\bar{1}$		69.981				
00·12	444	75.986	70.523	65.595	73.917	72.327	75.928

Table 6 also gives the a_0 and c_0 values obtained from $\cos^2\theta$ and

$$\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$$

extrapolations for various samples of $MgCO_3$, $FeCO_3$, $MnCO_3$, $CoCO_3$, $CdCO_3$, $NiCO_3$, $ZnCO_3$, and $CaMn(CO_3)_2$, together with measurements of $CdMg(CO_3)_2$ samples made on films taken with a Guinier-type focusing camera. The comparable information for $CaCO_3$ and $CaMg(CO_3)_2$ has been given in Goldsmith and Graf (1958*b*), together with a discussion of the extrapolation procedure, which involves successive approximations.

In making spacing measurements, film shrinkage and camera radius

TABLE 6. METHOD OF PREPARATION, PURITY, AND CELL CONSTANTS OF VARIOUS RHOMBOHEDRAL CARBONATE SAMPLES

$MgCO_3$, No. G-1219; basic Mg carbonate+CO_2+H_2O, 15 hours in Morey bomb at 300° C.; 0.38±0.06% $CaCO_3$, 0.01±0.003% $FeCO_3$, <0.003% $MnCO_3$, <0.04% $CdCO_3$, <0.007% $CoCO_3$, <0.25% $ZnCO_3$.

$a_0=$ 4.6330 Å, Cu radiation
$c_0=$15.016 Å (Goldsmith and Graf, 1958*b*)
$c_0/a_0=$ 3.2411

$MnCO_3$, reagent grade chemical; 0.1_1±0.03% $CaCO_3$, 0.02±0.01_5% $CdCO_3$, <0.02% $CoCO_3$, <0.01% $FeCO_3$, 0.1±0.05% $MgCO_3$, <0.2% $ZnCO_3$. H_2O (−110° C.), 0.85%*; H_2O (+110° C.), 3.32%*.

$a_0=$ 4.792 Å, $\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ extrapolation, Fe radiation
$c_0=$15.71 Å, $\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ extrapolation, Fe radiation
$c_0/a_0=$ 3.278

$MnCO_3$, No. G-738; reagent grade $MnCO_3$+CO_2, 3 hours at 722° C. in cold-seal bomb; 0.09±0.02% $CaCO_3$, 0.1±0.05% $MgCO_3$, 0.01±0.008% $FeCO_3$, <0.02% $CdCO_6$, <0.02% $CoCO_3$, <0.2% $ZnCO_3$.

$a_0=$ 4.7771 Å, Fe radiation
$a_0=$ 4.7772 Å, Cu radiation
$c_0=$15.664 Å, Fe radiation
$c_0/a_0=$ 3.2790

$FeCO_3$, No. G-613; $FeSO_4$+Na_2CO_3+CO_2+H_2O, 20 hours at 143° C. in Morey bomb;

$a_0=$ 4.690_2 Å, Co radiation
$c_0=$15.369 Å, Co radiation
$c_0/a_0=$ 3.276_8

$FeCO_3$, No. G-1219; $FeSO_4$+Na_2CO_3+CO_2+H_2O, 15 hours at 300° C. in Morey bomb; 0.038±0.020% $CaCO_3$, 0.072±0.014% $MgCO_3$, 0.13±0.013% $MnCO_3$, <0.08% $CdCO_3$, 0.008±0.002% $CoCO_3$, 0.18±0.04% $ZnCO_3$.

$a_0=$ 4.6887 Å, Co radiation
$a_0=$ 4.6888 Å, Fe radiation
$c_0=$15.373 Å, Co radiation
$c_0/a_0=$ 3.2787

$FeCO_3$, material from No. G-1219+$NaHCO_3$, 3 hours in squeezer-type apparatus (Griggs and Kennedy, 1956), 14 kb, 659° C.

$a_0=$ 4.6889 Å, Fe radiation
$c_0=$15.373 Å, Fe radiation
$c_0/a_0=$ 3.2786

$CdCO_3$, reagent grade chemical; <0.09% $CaCO_3$, <0.06% $CoCO_3$, 0.01_2±0.009% $FeCO_3$,

Unless otherwise noted, impurities reported in spectrographic analyses by Juanita Witters as weight per cent metal have been recalculated to mol per cent carbonate. Cell constants were obtained by $\cos^2\theta$ extrapolations unless otherwise noted. The ranges given for a_0 and c_0 of ordered and disordered $CdMg(CO_3)_2$ indicate only the uncertainty that would result from a misreading of line position on the films by the smallest unit measured, 0.05 mm.

* Analyst, L. D. McVicker.

TABLE 6—(*continued*)

$0.03_8 \pm 0.02_5\%$ $MgCO_3$, $0.06 \pm 0.03\%$ $MnCO_3$, $<0.08\%$ $ZnCO_3$. H_2O ($-110°$ C.), 0.23%*; H_2O ($+110°$ C.), 2.87%*.

$a_0 = 4.936$ Å, $\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ extrapolation, Fe radiation

$c_0 = 16.29$ Å, $c_0/a_0 = 3.300$ $\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ extrapolation, Fe radiation

$CdCO_3$, No. G-1321; $CdSO_4 + Na_2CO_3 + CO_2 + H_2O$, 15 hours at 255° C. in Morey bomb; $0.09 \pm 0.07\%$ $CaCO_3$, $<0.01_5\%$ $MgCO_3$, $0.009 \pm 0.007\%$ $FeCO_3$, $0.003 \pm 0.002_5\%$ $MnCO_3$, $<0.06\%$ $CoCO_3$, $<0.08\%$ $ZnCO_3$.

$a_0 = 4.9207$ Å, Co radiation
$c_0 = 16.295$ Å, Co radiation
$c_0/a_0 = 3.3115$

$CdCO_3$, material from No. G-1321 plus Li_2CO_3 in squeezer-type apparatus for 3 hours at 10 kb, 500° C.

$a_0 = 4.9204$ Å, Co radiation
$c_0 = 16.298$ Å, Co radiation
$c_0/a_0 = 3.3123$

$ZnCO_3$, No. G-1316; reagent grade chemical $+H_2O + CO_2$, 15 hours at 250° C. in Morey bomb; $0.19 \pm 0.04\%$ $CaCO_3$, $0.01 \pm 0.008\%$ $MgCO_3$, $0.040 \pm 0.020\%$ $FeCO_3$, $0.002 \pm 0.001_5\%$ $MnCO_3$, $<0.02\%$ $CdCO_3$, $<0.02\%$ $CoCO_3$; H_2O ($-110°$ C.), 0.54%†; H_2O ($+110°$ C.), 3.73%†.

$a_0 = 4.6528$ Å, Cu radiation
$a_0 = 4.6525$ Å, Co radiation
$c_0 = 15.025$ Å, Cu radiation
$c_0 = 15.024$ Å, Co radiation
$c_0/a_0 = 3.2292$

$ZnCO_3$, transparent crystal from Broken Hill, Rhodesia; $0.03 \pm 0.01_5\%$ $CaCO_3$, $0.92 \pm 0.09\%$ $FeCO_3$, $0.30 \pm 0.03\%$ $MgCO_3$, $0.041 \pm 0.004\%$ $MnCO_3$, $<0.02\%$ $CdCO_3$, $<0.04\%$ $CoCO_3$, $<0.004\%$ $NiCO_3$.

$a_0 = 4.6534$ Å, Co radiation
$c_0 = 15.027$ Å, Co radiation
$c_0/a_0 = 3.2293$

$NiCO_3$ (prepared by Thelma Isaacs), $NiCl_2 \cdot 6H_2O + NaHCO_3 + H_2O + CO_2$, 2.5 months at 250° C. in Morey bomb; $0.06 \pm 0.03\%$ $CaCO_3$, $0.04 \pm 0.02\%$ $FeCO_3$, $0.01_5 \pm 0.008\%$ $MgCO_3$, $0.04 \pm 0.02\%$ $MnCO_3$, $0.09 \pm 0.05\%$ $ZnCO_3$, 0.02 wt % Cu, 0.2 wt % Na, 0.02 wt % Si. Infrared absorption curve shows no water in excess of that for the KBr blank.

$a_0 = 4.5975$ Å, Co radiation
$c_0 = 14.723$ Å, Co radiation
$c_0/a_0 = 3.2024$

$CoCO_3$, No. G-1319; "Specpure" $Co_3O_4 + KHSO_4 \xrightarrow{25°\text{ C.}}$ Co sulfate; Co sulfate + "Specpure" $Na_2CO_3 \xrightarrow{25°\text{ C.}}$ basic Co carbonate; basic Co carbonate $+H_2O + CO_2$ for 15 hours at 255° C. in Morey bomb; $<0.1_5\%$ $CaCO_3$, $0.04 \pm 0.03_5\%$ $MgCO_3$, 0.01

† Microanalyst, D. R. Dickerson.

TABLE 6—(*continued*)

$\pm 0.008\%$ $FeCO_3$, $<0.004\%$ $MnCO_3$, $<0.1\%$ $CdCO_3$, $<0.002\%$ $NiCO_3$, $<0.09\%$ $ZnCO_3$. H_2O ($-110°$ C.), none†; H_2O ($+110°$ C.), 8.10%†.

$a_0 = 4.6620$ Å, Co radiation
$c_0 = 14.975$ Å, Co radiation
$c_0/a_0 = 3.2121$

$CoCO_3$, material from No. G-1319+Li_2CO_3, 2 hours in squeezer-type apparatus at 10 kb., 60° C.

$a_0 = 4.6581$ Å, Co radiation
$c_0 = 14.958$ Å, Co radiation
$c_0/a_0 = 3.2112$

$CdMg(CO_3)_2$, ordered; Li_2CO_3 added to equimolar mixture of $CdCO_3$ and $MgCO_3$, treated in cold-seal bomb for 23 hours under 27,000 psi CO_2 at 600° C.

$d_{\{444\}}$ and $d_{\{11\bar{2}\}}$ measured on film taken with $FeK\alpha_1$ radiation, using a Guinier-type focusing camera, and calibrated against the closely similar $d_{\{444\}}$ and $d_{\{11\bar{2}\}}$ values of synthetic $MnCO_3$ run on the adjoining strip of the same film.

$a_0 = 4.7770 \pm 0.0009$ Å
$c_0 = 15.641 \pm 0.003$ Å
$c_0/a_0 = 3.2742$

$CdMg(CO_3)_2$, disordered; equimolar mixture of $CdCO_3$ and $MgCO_3$ treated at 10 kb. and 900° C. for 1.5 hours in sealed-tube gas system; spacing measurements made as for the ordered material.

$a_0 = 4.7746 \pm 0.0009$ Å
$c_0 = 15.678 \pm 0.003$ Å
$c_0/a_0 = 3.2836$

$CaMn(CO_3)_2$, disordered; equimolar mixture of $CaCO_3$ and $MnCO_3$ reacted in cold-seal bomb at 706–710° C. under 14,000 psi CO_2 pressure for 22 hours.

Line coincidence of {400} and {644} used to obtain accurate c_0/a_0 ratio, followed by a_0 and c_0 extrapolations of back reflections on film taken with Fe radiation. $I_{\{400\}}:I_{\{644\}}$ is computed to be about 3, and observed as such on films of CaMn carbonate solid solutions containing 40 and 60 mol per cent $MnCO_3$, for which the two reflections are resolved. Departure from coincidence in the $CaMn(CO_3)_2$ sample would thus readily be observable as line broadening relative to the line breadths of neighboring reflections.

$a_0 = 4.8797$ Å
$c_0 = 16.367$ Å
$c_0/a_0 = 3.3541$

errors were taken into account by using the Straumanis film mount and correction procedure. Reflections in the range $\theta = 60°–90°$ were used for the $\cos^2\theta$ extrapolations, in accordance with the finding of Taylor and Sinclair (1945) that almost linear extrapolation curves which simultaneously eliminate eccentricity and absorption errors are obtained within this angular range.

COMPARISON OF CELL CONSTANTS WITH PUBLISHED VALUES

Cell constants cited in this paper are compared in Table 7 with values obtained from the literature. For most of the carbonates, the agreement is excellent. The newly determined values for coarsely crystalline synthetic $NiCO_3$ are preferred over those of Pistorious (1959), and there is a small discrepancy for $CdCO_3$.

The range of a_0 values reported in Table 7 for several $CdCO_3$ samples, 4.9204 to 4.936 Å, includes the values published by Swanson *et al.* (1957) and Ramdohr and Strunz (1941), but the range of c_0 values, 16.298 to 16.29 Å, is clearly distinct from their 16.27 Å. Mr. Swanson (personal communication) finds $a_0 = 4.9279$ Å and $c_0 = 16.284$ Å on repeating the least squares calculation for his $CdCO_3$ sample.

The several sets of $CdCO_3$ values in Tables 6 and 7 suggest that a_0 increases and c_0 decreases with decreasing temperature of formation, although some of these differences are near the limit of error, and that Swanson's sample was made at fairly low temperature.

Enlarged Unit Cells of Lower Temperature Preparations

Effects analogous to the change in cell size of $CdCO_3$ prepared at lower temperatures are noted for other carbonates (Table 6). There is a considerable increase in both a_0 and c_0 of $CoCO_3$ prepared at 255° C., compared with that made at 600° C. Reagent-grade chemical $MnCO_3$ as received has a markedly enlarged cell compared with that of material crystallized at 722° C. Saint Léon Langlès (1952) reported values for two $NiCO_3$ preparations that indicate the higher temperature product has a smaller cell. Graf *et al.* (1961) have described a magnesite from the Lake Bonneville sediments of Quaternary age in the Great Salt Lake Desert, Utah, which has $a_0 = 4.669$ Å, $c_0 = 15.21$ Å, compared with $a_0 = 4.6330$ Å and $c_0 = 15.016$ Å given in Table 7 for material prepared at 250° C. The impurity content which could conceivably be in solid solution in the magnesite of the Utah sample, 0.7 wt% Fe, 0.01 wt% Mn, and about 0.2 wt% Ca (spectrographic analysis by Juanita Witters), fails by an order of magnitude to explain the change in cell size.

Calculations by Verwey (1946) for several alkali halides, which should be similar enough to the rhombohedral carbonates for order-of-magnitude comparison, indicated that near-surface shifts of position of positive and negative ions and their electron clouds should occur, but only for one or two atomic layers below the surface. The effect would thus be insignificant for particles of the order of 1 micron diameter such as those making up the lowest-temperature carbonate preparations. Rymer's recent (1957) review indicates extensive disagreement as to the size and magnitude of the effect of small particle-size *per se* on cell constants.

Lehovec (1953) computed that the space-charge zone in NaCl particles, which causes an electrostatic potential between the bulk and the surface of the crystal and affects the concentration of point defects, should extend inward from the surface about 0.013 micron at 627° C.,

TABLE 7. COMPARISON WITH PUBLISHED VALUES OF CELL CONSTANTS

Material	c_0 in Å	a_0 in Å	Reference	Remarks
$CaCO_3$	17.064	4.9900, 4.9896	Goldsmith and Graf (1958*b*)	Extrapolated values; spectrographic standard $CaCO_3$
	17.064 (26° C.)	4.9899 (26° C.)	See discussion in Graf and Lamar (1955)	Calculated from spectrometer measurements of α and $d_{\{211\}}$ of single crystals
	17.060±0.005 (18° C.)	4.9898±0.0003 (18° C.)	Andrews (1950)	Spectrographic standard $CaCO_3$
	17.063_6 (26° C.)	4.9896 (26° C.)		Andrews' values recalculated to 26° C. using thermal expansion data of Austin *et al.* (1940)
	17.062 (26° C.)	4.989 (26° C.)	Swanson and Fuyat (1953)	0.01–0.1% Sr is major residual impurity after purification
$MgCO_3$	15.016	4.6330	Goldsmith and Graf (1958*b*)	
	15.015	4.6332	Swanson *et al.* (1957)	Sample heated four days at 120,000 psi and 280° C.; 0.01–0.1% Ca
$MnCO_3$	15.664	4.7768	Goldsmith and Graf (1957)	
	15.67	4.777	Swanson *et al.* (1957)	Ppt. from solutions of $MnSO_4$ and $NaHCO_3$, heated in CO_2 atmosphere 3 days at 400° C.
	15.664	4.7771	This paper	Recrystallized at 722° C. (see Table 6)
$FeCO_3$	15.370±0.003	4.690±0.002	Sharp (1960)	$NaHCO_3$ and $FeSO_4 \cdot 7H_2O$ reacted at 200° C. under 500 bars (CO_2+H_2O) pressure, then held at 600° C. under 15 lb. pressure in squeezer apparatus of Griggs and Kennedy (1956); least squares treatment of diffractometer data
	15.373	4.6887	This paper	Prepared at 300° C. (see Table 6)

Material	c_0 in Å	a_0 in Å	Reference	Remarks
$ZnCO_3$	15.028 (25° C.)	4.6533 (25° C.)	Swanson *et al.* (1959)	U.S.N.M.#96155, Broken Hill, Rhodesia; 0.01–0.1% of Cd, Fe, Mg, and Pb; 0.001–0.01% of Ca, Mn, and Si; 0.0001–0.001% Cu.
	15.027	4.6534	This paper	Small transparent smithsonite crystals from Broken Hill, Rhodesia, supplied by C. S. Hurlbut, Jr. (see Hurlbut, 1954); spectographic analysis calculates to 0.92 mol per cent $FeCO_3$, 0.30 mol per cent $MgCO_3$ content
	15.024	4.6531	This paper	Previous entry corrected for $FeCO_3$ and $MgCO_3$, assuming straight-line relation between cell constants and composition in systems $ZnCO_3$-$FeCO_3$ and $ZnCO_3$-$MgCO_3$
	15.025	4.6528	This paper	Recrystallized at 250° C. (see Table 6)
$NiCO_3$	14.744±0.003 (25° C.)	4.602±0.001 (25° C.)	Pistorius (1959)	Ppt. from mixed $NiSO_4$ and $NaHCO_3$ solns. treated 15 min. at 500° C. and 2 kb. pressure in squeezer apparatus of Griggs and Kennedy (1956); 0.001% Fe, 0.01% Co, 0.005% Cu, <0.005% Pb
	14.723	4.5975	This paper	Prepared at 250° C. (see Table 6)
$CdCO_3$	16.27	4.92	Ramdohr and Strunz (1941)	Schering's (chemical) $CdCO_3$; kX values here converted to Å
	16.27	4.930	Swanson *et al.* (1957)	Fine-grained material; 0.001–0.01% of Cr, Ni, and Pb; 0.0001–0.001% of Ca, Cu, Fe, Mg, and Si
	16.298	4.9204	This paper	Recrystallized at 500° C. (see Table 6)
$CoCO_3$	14.957	4.659	Swanson *et al.* (1960)	$CoCl_2 \cdot 6H_2O$, $NaHCO_3$, and H_2CO_3 reacted in Morey bomb; 0.01–0.1% of Mo, Ni; 0.001–0.01% of Ba, Cu, Mg, Si, and Ag
	14.958	4.6581	This paper	Recrystallized at 600° C. (see Table 6)

0.22 micron at 327° C. However, the vacancy concentrations observed in the alkali halides even at high temperature hardly seem adequate to explain the larger of the cell-size anomalies described in this paper.

Some of the samples prepared at lower temperatures include several percent of H_2O or OH^- that is not released in 12 to 15 hours at 110° C. (Table 6). The remarkably high value reported for $CoCO_3$ is from a microanalysis that totals poorly and may be in error, but there is no reason to doubt the results given for $ZnCO_3$, $CdCO_3$, and $MnCO_3$. The structural location of this H_2O or OH^- (it may, of course, only be tightly adsorbed) and its possible effect upon cell constants will be discussed in a subsequent communication.

It is possible that some of the cell enlargement of dolomite in fine-grained precipitates formed at room temperature, hitherto attributed exclusively to excess calcium (Graf and Goldsmith, 1956; Goldsmith and Graf, 1958*a*), may actually result from structurally incorporated H_2O or OH^-. Such a hydration effect is, of course, ruled out for other dolomites with enlarged cells which were formed by high-temperature synthesis in an anhydrous system.

The Unit Cell of Huntite, $Mg_3Ca(CO_3)_4$

Graf and Bradley (In press) gave for the unit cell of huntite $a_0=9.505$ Å, $c_0=7.821$ Å, obtained from a powder diffraction film of huntite from Currant Creek, Nevada, by making a least squares analysis involving a drift error term of the form

$$\sin^2\theta\left(\frac{1}{\sin\theta}-\frac{1}{\theta}\right).$$

Their cell was of principal value in demonstrating the close agreement between observed and calculated d-spacings of front reflections. A more accurate a_0 value can be obtained by combining the c/a ratio obtained from the least squares analysis with measurements on a film taken with iron radiation of the positions of the $\{71\cdot3\}$ and $\{72\cdot2\}$ reflections, at $2\theta\cong149°$ and 168°, respectively, to make a two-point $\cos^2\theta$ extrapolation. Then c_0 is calculated from $d_{\{00\cdot6\}}$, the latter first corrected by the amount that the measured spacing of the adjacent $\{25\cdot0\}$ reflection differs from the value calculated from a_0. Varying the c/a ratio by an amount corresponding to a_0 fixed at 9.4980 Å and c_0 changing from 7.81 to 7.82 Å changes the extrapolated a_0 value by only ±0.0003 Å.

Measurements for three huntite samples, all very fine-grained naturally-occurring materials, are given in Table 8. The cell constants of the two samples from Currant Creek, Nevada, are identical within the general limits of error observed in such extrapolations for the other rhombohedral carbonates. The sample from Tea Tree Gully has a significantly larger cell. Graf and Bradley estimated that the a_0 of the Currant Creek huntite was 0.61% greater than predicted from a straight-line interpolation between the values for magnesite and calcite; c_0, 0.75% larger. The corresponding values for the more accurately determined unit cells in Table 8 are a_0, 0.57–0.61%, c_0 0.66–0.70%.

Coarsely crystalline huntite will have to be found in nature or synthesized before it will be possible to attribute a particular cell size to

TABLE 8. UNIT CELL DIMENSIONS OF THE HEXAGONAL STRUCTURE CELL OF HUNTITE

Sample	a_0 by extrapolation	c_0		
		Using a_0 and the c/a ratio of the least squares analysis	From $d_{\{00\cdot6\}}$ corrected against $d_{\{25\cdot0\}}$	
			Diffractometer	Film
Currant Creek, Nevada (Collected by D. L. Graf)	9.4981	7.815_5	7.815_8	
Currant Creek, Nevada (Collected by G. T. Faust)	9.4979	7.815_5		7.815_0
Tea Tree Gully, South Australia	9.5020	7.818_7		7.818_5

material of strictly 3:1 molar $MgCO_3$: $CaCO_3$ composition, free of hydration effects.

EFFECT OF CATION ORDER ON CELL SIZE

Small but measurable changes in cell size take place with cation disordering of the 1:1 compounds. Comparison of a_0 and c_0 values for the ordered and disordered cells with those predicted by taking a_0 and c_0 values midway between those of the two end members is interesting. Thus far, the only composition for which all three sets of values are available is $CdMg(CO_3)_2$ (Goldsmith, 1958). The crystallinity of these preparations is not ideal, and back reflection measurements are therefore not of the highest quality. The most accurate data available are those obtained from films taken with a Guinier-type focusing camera. The change in a_0 on disordering is -0.0024 Å, that in c_0, $+0.037$ Å (Table 1). One might suspect that these slight differences resulted from a sampling or mixing error—it need involve only about 0.2 mol percent $CdCO_3$—were it not for the fact that the two axial lengths change in opposite directions and that comparable effects, discussed below, are observed for dolomite. Actually, Goldsmith's mixing was achieved by prolonged hand mulling of small portions under alcohol, a method that leaves little reason to distrust the stated compositions.

The a_0 and c_0 cited for dolomite in Table 1 and used in computations elsewhere in this paper, 4.8079 and 16.010 Å, respectively, are those derived by Goldsmith and Graf (1958*b*) from study of several analyzed single-crystal dolomite samples. Goldsmith and Graf have discussed the relations between these values and those derived by averages of the a_0 values and of the c_0 values for calcite and magnesite. These averages also are included in Table 1.

The most probable Δa_0 and Δc_0 values for largely but not completely disordered materials having essentially the composition $CaMg(CO_3)_2$ are respectively, -0.003 Å and $+0.03_5$ Å (Goldsmith *et al.*, 1961). Most of the measurements were made on films taken with a Guinier-type focusing camera; the uncertainty in Δa_0 resulting from a possible Guinier measurement error on each pattern of the smallest unit recorded, 0.05 mm, is ± 0.0018 Å, and in c_0 is ± 0.006 Å.

The agreement among Δa_0 and Δc_0 values for the various $CaMg(CO_3)_2$ and $CdMg(CO_3)_2$ samples is good, in view of the difficulty in making accurate measurements on imperfectly crystallized materials and the fact that neither the compositions of the several dolomite samples nor the amounts of residual order remaining in them after quenching from temperatures near 1125° C. are precisely the same. Any variation that may exist in Δa_0 and Δc_0 with slight departures from equimolar composition is masked by the experimental uncertainty.

No 1:1 ordered calcium iron carbonate has yet been described, but a_0 and c_0 values predicted from those for $FeCO_3$ and $CaCO_3$ are presented in Table 1 because of their possible usefulness in studies of ferroan dolomite. The ordered compound $CaMn(CO_3)_2$, kutnahorite, is present in nature in well crystallized specimens, but none of the single-phase samples yet studied is sufficiently free of Mg and Fe in solid solution to permit precise comparison with predicted values. Order reflections for this composition can be detected with certainty only in single-crystal *x*-ray diagrams, so that it has not proved possible to determine whether ordered synthetic powders have been prepared. However, at a sufficiently high temperature, by analogy with single-crystal experiments (Goldsmith and Graf, unpublished data), one can be certain that such a powder is disordered, and values are given in Table 1 for a sample of this kind.

Reliability of Cell Constants

The extrapolated cell constants presented here and by Goldsmith and Graf (1958*b*) for materials recrystallized at high temperatures appear to differ from comparable published data, and also among themselves where measurements of the same constant were made with several radiations, by from 0.0001 to 0.0003 Å in a_0 and by 0.001 or 0.001_5 Å in c_0, or from 2.5 to 10 parts per 100,000. The maximum uncertainty in the temperature for which cell constants are valid is $26 \pm 3°$ C., the range of temperature encountered in the laboratory where the films were taken, which is air-conditioned in summer. The correction for these materials for a temperature difference of 5° C., based upon available thermal expansion data, would be about 0.0001 Å in a_0 and about 0.002 Å in c_0, values comparable with the differences mentioned above.

The cell constants presented here should be satisfactory for most geochemical and mineralogical purposes, but they may not be adequate for some studies of defects in these solids. The extent to which they can be further refined appears to be limited by poor crystallinity for materials formed at moderate temperatures. Less than perfect cation ordering in 1:1 compounds such as dolomite appears, in principle, to be present in greater or lesser amount at all temperatures (Goldsmith and Graf, 1958*b*), and places a further limit on the accuracy with which cell constants can be obtained for these materials.

Interplanar Spacings

The a_0 and c_0 values selected for use in calculating d-values, typically those for well crystallized high-temperature materials giving the most accurate $\cos^2 \theta$ extrapolations, are given in Table 1 together with a_{rh} and α values for the rhombohedral cells.

Table 2 includes all possible reflections of the carbonates listed there using $CuK\alpha_1$ radiation. A list of such reflections was first prepared for a hypothetical dolomite-type structure having the a_0 and c_0 of $CaCO_3$. Deletions from this list were then made of reflections forbidden for calcite-type structures, and of reflections with $d < 0.77025$ for the carbonates with smaller cells. The spacings listed for $CaCO_3$ by Andrews (1950) and Swanson and Fuyat (1953), for $CaMg(CO_3)_2$ by Howie and Broadhurst (1958), for $MnCO_3$ by Goldsmith and Graf (1957) and Swanson *et al.* (1957), for $CdCO_3$ and $MgCO_3$ by Swanson *et al.* (1957), for $ZnCO_3$ by Swanson *et al.* (1959) and for $CoCO_3$ by Swanson *et al.* (1960) indicate which of the possible reflections for these compounds have sufficient intensity to be readily observed in routine diffraction analyses.

Structure Factors

Calcite belongs to space group $R\bar{3}c$, dolomite to $R\bar{3}$, and the huntite model proposed by Graf and Bradley (In press) to $R32$. The unit cells of these materials contain, respectively, $2CaCO_3$, $Ca{>}Mg(CO_3)_2$, and $Mg_3Ca(CO_3)_4$. All $\{h_r k_r l_r\}$ are possible reflections for dolomite and for huntite, but for calcite reflections having $h_r+k_r+l_r$ odd are forbidden unless $h_r \neq k_r \neq l_r$.

Structure factor computations like those which follow are simplified considerably by using the rhombohedral cell. The amplitude contributions to the calcite structure factors, obtained by substituting in the appropriate expression (International Tables for X-ray Crystallography, volume 1, 1952, p. 473) for each atom in the rhombohedral unit cell and summing, fall into three types that may be represented by greatly simplified expressions. The types are defined using sign changes of amplitude contributions from atoms whose coordinates do not involve variable parameters, and the zero or non-zero character of amplitude contributions in general. Further definitions involving variable parameters which are very nearly equal to simple fractions could be made, but would break down for higher order reflections. The letter-designated subdivisions are not distinct types, but will be useful in a comparison of calcite, dolomite, and huntite reflection types which follow.

The calcite types are:

1. $(h_r+k_r+l_r)$ divisible by 4
   $2f_{Ca}+2sf_C+2f_O[\cos 2\pi x(h-k)+\cos 2\pi x(k-l)+ \cos 2\pi x(l-h)]$
   (1a. Two or three indices alike)
   (1b. $h \neq k \neq l$)
2. $(h_r+k_r+l_r)$ even, but not divisible by 4
   $2f_{Ca}-2f_C-2f_O[\cos 2\pi x(h-k)+\cos 2\pi x(k-l)+\cos 2\pi x(l-h)]$
   (2a. Two or three indices alike)
   (2b. $h \neq k \neq l$)
3. $(h_r+k_r+l_r)$ odd, $h \neq k \neq l$
   $2f_O[\sin 2\pi x(h-k)+\sin 2\pi x(k-l)+\sin 2\pi x(l-h)]$.

These expressions are analogous to those presented by Tahvonen (1947) for the isostructural $NaNO_3$, but with calcium rather than the anion at the origin. Like the amplitude contributions which follow for dolomite and huntite, those for calcite have been divided by an appropriate constant so that they refer to the contents of one unit cell.

From the expression for the dolomite space group, given on page 463 of volume 1 of the International Tables for X-ray Crystallography, with calcium at the origin, three simplified expressions for the various types of dolomite reflections may be obtained:

1. $(h_r+k_r+l_r)$ even
   $f_{Ca}+f_{Mg}+2f_C[\cos 2\pi x(h+k+l)]$ $2f_O[\cos 2\pi(hx+ky+lz)+\cos 2\pi(kx+ly+hz)+\cos 2\pi(lx+hy+kz)]$
   (1a. $(h_r+k_r+l_r)$ divisible by 4; 2 or 3 indices alike)
   (1b. $(h_r+k_r+l_r)$ divisible by 4; $h \neq k \neq l$)
   (1c. $(h_r+k_r+l_r)$ even but not divisible by 4; 2 or 3 indices alike)
   (1d. $(h_r+k_r+l_r)$ even but not divisible by 4; $h \neq k \neq l$)

2. $(h_r+k_r+l_r)$ odd, two or three indices alike
$f_{Ca}-f_{Mg}+2f_C[\cos 2\pi x(h+k+l)]+2f_O[\text{as in } 1]$
3. $(h_r+k_r+l_r)$ odd, $h\neq k\neq l$
$f_{Ca}-f_{Mg}+2f_C[\cos 2\pi x(h+k+l)]+2f_O[\cos 2\pi(hx+ky+lz)+\cos 2\pi(kx+ly+hz)+\cos 2\pi(lx+hy+kz)]$;
$f_{Ca}-f_{Mg}+2f_C[\cos 2\pi x(h+k+l)]+2f_O[\cos 2\pi(kx+hy+lz)+\cos 2\pi(hx+ly+kz)+\cos 2\pi(lx+ky+hz)]$

Dolomite reflections of type 2, a consequence of cation ordering, are forbidden in calcite. Those of dolomite type 3 are in calcite contributed to exclusively by oxygen.

From the expressions for the space group of the Graf-Bradley huntite model, given on page 466 of volume 1 of the International Tables for X-ray Crystallography, with calcium at the origin, the following four simplified expressions for the various types of reflections may be obtained. Lengthy trigonometric expressions which appear within the brackets have been omitted; those indicated by asterisks include both sines and cosines, the others, only cosines:

1. $(h+k+l)$ even, 2 or 3 indices the same
$f_{Ca}+f_{C_I}+1/3[\ ]f_{C_{II}}+1/3[\ ]f_{Mg}+1/3[\ ]f_{O_I}+1/3[\ ]f_{O_{II}}+2/3[\ ]f_{O_{III}}$
(a. h, k, l all even numbers)
(b. Only one even index)
2. $(h+k+l)$ even, $h\neq k\neq l$
$\sqrt{A^2+B^2}$, where
$A=$the expression given under 1
$B=1/3[*]f_{C_{II}}+1/3[*]f_{Mg}+1/3[*]f_{O_I}+1/3[*]f_{O_{II}}+2/3[*]f_{O_{III}}$
(2a. h, k, l all even numbers)
(2b. Only one even index)
3. $(h+k+l)$ odd, 2 or 3 indices the same
$f_{Ca}-f_{C_I}+\cdots$ remainder as in 1
(3a. h, k, l all odd numbers)
(3b. Only one odd index)
4. $(h+k+l)$ odd, $h\neq k\neq l$
$\sqrt{A^2+B^2}$, where
$A=f_{Ca}-f_{C_I}+\cdots$ remainder as in 1
B as in 2
(4a. h, k, l all odd numbers)
(4b. Only one odd index)

Table 9 gives correlations among the several groups of reflections which have been described for calcite, dolomite, and huntite.

The number of cooperating planes for the various types of calcite and huntite powder reflections, expressed in hexagonal indices, is (See Internationale Tabellen, 1935, p. 502): $\{hkil\}$, $2\cdot 12$; $\{hh2\bar{h}l\}$, 12; $\{0k\bar{k}l\}$, $2\cdot 6$; $\{hki0\}$, 12; $\{hh2\bar{h}0\}$, 6; $\{0k\bar{k}0\}$, 6; $\{000l\}$, 2. For dolomite powder reflections the analogous values are: $\{hkil\}$, $4\cdot 6$; $\{hh2\bar{h}l\}$, $2\cdot 6$; $\{0k\bar{k}l\}$, $2\cdot 6$; $\{hki0\}$, $2\cdot 6$; $\{hh2\bar{h}0\}$, 6; $\{0k\bar{k}0\}$, 6; $\{000l\}$, 2. The $4\cdot 6$ and $2\cdot 6$

entries for dolomite indicate that atoms in general positions, namely, oxygens, will scatter with a different amplitude for some of the co-operating planes of a given $\{hkil\}$, $\{hh2\bar{h}l\}$, or $\{hki0\}$ reflection than for others.

Zero amplitudes result for particular sets of planes whose hexagonal indices do not transform to whole-number rhombohedral indices. Thus, there are for dolomite only two non-zero oxygen amplitudes for $\{21\cdot4\}$ and only one for $\{02\cdot7\}$. These relations are somewhat more simply stated in terms of rhombohedral indices: two non-zero oxygen amplitudes

TABLE 9. CORRELATION OF POWDER REFLECTION TYPES FOR THREE RHOMBOHEDRAL STRUCTURE CELLS (see text)

Calcite	Dolomite	Huntite
1*a*	1*a*	1*a*
1*b*	1*b*	2*a*
2*a*	1*c*	3*a*
2*b*	1*d*	4*a*
	2	
3	3	
		1*b*
		2*b*
		3*b*
		4*b*

result for all dolomite $\{h_rk_rl_r\}$ in which $h_r \neq k_r \neq l_r$, except for $\{h0\bar{h}\}$ reflections, which have a unique oxygen amplitude. The occurrence of zero amplitudes for calcite and huntite is such that there is only one non-zero oxygen amplitude for each $\{h_rk_rl_r\}$.

The amplitude contributions for calcite given in Table 3 have been calculated by using the value of $x=0.2578$ (corresponding to a C—O distance of 1.286 Å) given by Chessin and Post (1958). Sass *et al.* (1957) obtained closely similar values, $x=0.2593\pm0.0008$ and C—O$=1.294\pm0.004$ Å. The amplitude contributions for dolomite derive from Steinfink and Sans' (1959) oxygen parameters, $x=0.2374\pm0.0068$, $y=-0.0347\pm0.0068$, and $z=0.2440\pm0.00017$, and their value of $z=0.2435\pm0.00031$ for carbon, all in terms of the hexagonal unit cell. The corresponding values for the rhombohedral unit cell upon which the discussion in this paper is based are $x_0=0.4814$, $y_0=-0.0281$, $z_0=0.2787$, and $x_c=0.2435$. The C—O distance for dolomite corresponding to these parameters is 1.283 Å, in particularly good agreement with Chessin and Post's value. All three of the parameter determinations are based upon single-crystal measurements. Those for calcite involve oxygen-only reflections, and those for dolomite are based on some 500 reflections of all types.

The variable parameters used for the other calcite structures (Table 10) were calculated by assuming that the C—O bond length remains constant at 1.286 Å; the parameter $x = \text{C—O}/a_0$. The dolomite x and y hexagonal unit-cell parameters were multiplied by the ratio of a_0 for $CaMg(CO_3)_2$ to that of a_0 for $CdMg(CO_3)_2$, so as to retain in $CdMg(CO_3)_2$ the same C—O value of 1.283 Å found for dolomite. In the absence of evidence for making other assumptions, the dolomite z parameters for

TABLE 10. ESTIMATED VARIABLE PARAMETERS USED IN INTENSITY CALCULATIONS

$MgCO_3$	$x=0.2776$		$CdCO_3$	$x=0.2614$
$MnCO_3$	$x=0.2692$		$CoCO_3$	$x=0.2761$
$FeCO_3$	$x=0.2743$		$NiCO_3$	$x=0.2797$
$ZnCO_3$	$x=0.2764$		$CuCO_3$	$x=0.2681$*
$CaMn(CO_3)_2$	$x=0.2635$		$CaFe(CO_3)_2$	$x=0.2657$
$CaMn(CO_3)_2$	$x_O=0.4779$,	$y_O=-0.0241$,	$z_O=0.2782$,	$x_C=0.2435$
$CaFe(CO_3)_2$	$x_O=0.4799$,	$y_O=-0.0264$,	$z_O=0.2785$,	$x_C=0.2435$
$CdMg(CO_3)_2$	$x_O=0.4829$,	$y_O=-0.0298$,	$z_O=0.2789$,	$x_C=0.2435$

* Using the a_0 value given by Pistorius (1960).

oxygen and carbon were retained for $CdMg(CO_3)_2$, as was the slight rotation of the carbonate group relative to the hexagonal a axes, and the parameters for the hexagonal cell were then converted to values for the rhombohedral cell. Coplanarity of carbon with the oxygens of its carbonate group is not required by symmetry for the dolomite structure as is the case for calcite. The reality of the 0.0005 difference between the Steinfink and Sans z parameters for oxygen and carbon is indeterminate, because the uncertainty ranges attached to these values are just great enough to allow for coplanarity at $z=0.2438$. The intensity difference for this shift of carbon by about 0.01 Å is, in any event, insignificant compared with other sources of error.

Parameter assumptions of the same type as those for $CdMg(CO_3)_2$ were used in calculating the values given in Table 10 for dolomite structures having the compositions $CaMn(CO_3)_2$ and $CaFe(CO_3)_2$. These parameters involve a further approximation because, as discussed earlier, the a_0 values available for the calculations were not measured on ordered compounds. The a_0 available for $CaMn(CO_3)_2$ is that for disordered material, that for $CaFe(CO_3)_2$, merely the mean of the values for calcite and siderite. However, these parameters are the best that can be derived at present for making intensity estimates for order reflections. Parameter estimates for calcite-type structures having the compositions $CaMn(CO_3)_2$ and $CaFe(CO_3)_2$ are also shown in Table 10.

The variable parameters given by Graf and Bradley (In press) for a huntite structure model derived from powder x-ray diffraction data are, for the rhombohedral unit cell, $x_{Mg}=0.541$, $x_{C_{II}}=-0.039$, $x_{O_I}=0.365$, $x_{O_{II}}=0.096$, $x_{O_{III}}=-0.033$, $y_{O_{III}}=0.180$, $z_{O_{III}}=0.371$.

Intensities

Intensities of front reflections in powder diagrams of the rhombohedral carbonates, computed for copper radiation, are given in Table 4. The change of intensities in the solid solution series between $CaMg(CO_3)_2$ and the hypothetical end member, $CaFe(CO_3)_2$, is shown graphically in Fig. 1. Estimated changes in cell size with composition have been considered in the ferroan dolomite computations, but these computations do not allow for departure of $CaCO_3$ content from 50 mol percent.

These intensities are simply the products of F^2 times multiplicity times the combined Lorentz and polarization correction for Debye-Scherrer lines on a cylindrical film,

$$\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}.$$

Absorption and temperature factors have not been considered, but could be added as corrective multipliers suitable for a given experimental situation. The scattering factors given by Berghius *et al.* (1955) were used for C, O, Ca, and Mg^{++}, all self-consistent field data with exchange, with the curve for Mg^{++} at $(\sin \theta/\lambda) < 0.25$ diverted toward the value for the neutral Mg atom at $\sin \theta/\lambda = 0$. Watson and Freeman (1961) give self-consistent field data with exchange for Mn, Fe, Co, Ni, and Cu^+; the latter curve at $(\sin \theta/\lambda) < 0.25$ has been diverted toward the value for the neutral Cu atom at $\sin \theta/\lambda = 0$.

The curve of Berghius *et al.* for Zn, based on self-consistent field data *without* exchange, gives expectably low values relative to the curves computed with exchange; it is essentially coincident with the Cu curve over part of the $\sin \theta/\lambda$ range. The values for Zn used in this paper were taken from a curve drawn, at each $\sin \theta/\lambda$ value, the same distance above the Cu curve as the separation between the Cu and Ni curves at that point. The scattering factor curve used for Cd, the only recent one available, was computed by Thomas and Umeda (1957) from the Thomas-Fermi-Dirac model.

These scattering factor curves fall off in generally concordant fashion and make it possible to observe the effect of progressively heavier cations upon the relative intensities of the various carbonate reflections. These

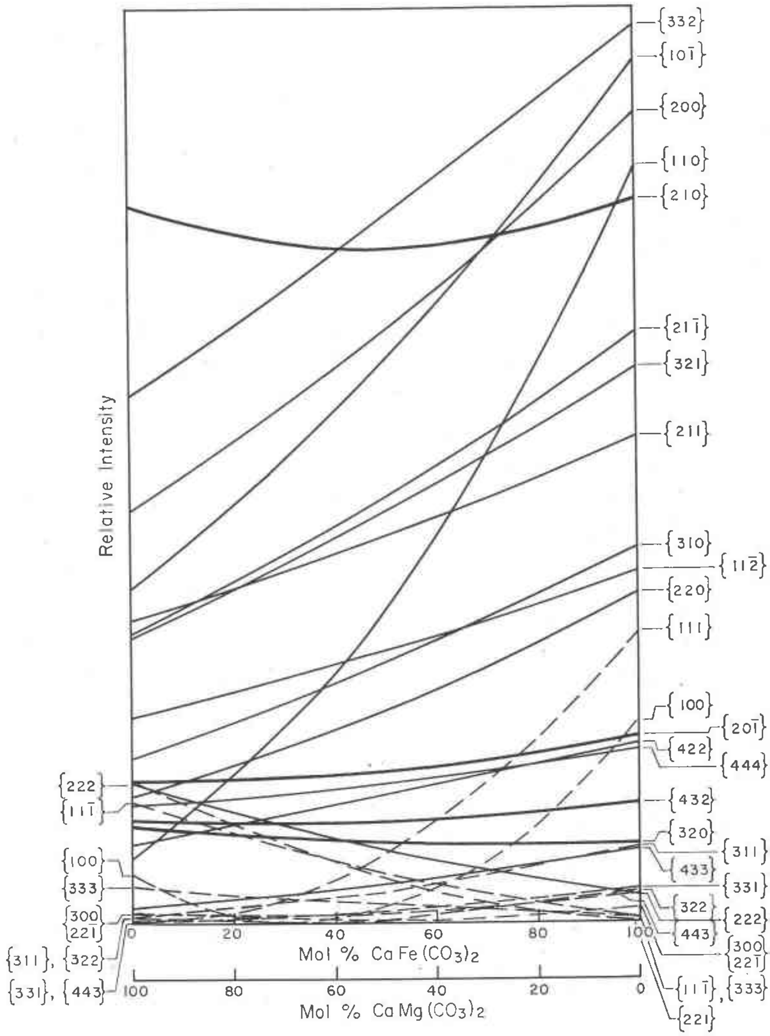

FIG. 1. Computed relative intensities for powder reflections in the front reflection region, using copper radiation, for the solid solution series between $CaMg(CO_3)_2$ and the hypothetical end-member, $CaFe(CO_3)_2$. Order reflections are shown by dashed lines, strong oxygen reflections by heavy lines. The intensity of the very strong {211} reflection is plotted reduced by a factor of ten relative to those of the other reflections; that of {321}, reduced by a factor of two.

relations are modified somewhat by differences in atomic arrangement in the related calcite, dolomite, and huntite structures. The increase in intensity of the $CdMg(CO_3)_2$ order reflections relative to those of the other ordered 1:1 carbonates is noteworthy.

The computed intensities of Table 4 and Fig. 1 are based upon a simplified model essentially involving spherical neutral atoms at rest, in accord with the empirical observation that observed intensities are better explained using neutral-atom scattering factor curves than those for ions. The radically different solubility rates of, for example, $CaCO_3$ and $NiCO_3$ in HCl solution indicate that an error is introduced for reflections at $(\sin \theta/\lambda) < 0.25$ by this uniform bonding approximation. The determination of scattering factor curves appropriate for specific carbonate structures is, however, beyond the scope of this paper. The third figure given in the computed intensities is obviously not generally significant, but may have meaning, for example, in computing an intensity ratio for two reflections of the same compound which lie at about the same 2θ angle and have similar structure factors.

It should be noted, in comparing observed intensities of two or more carbonates with the equivalent computed values in Table 4, that the observed values must be suitably corrected so that they all represent intensity diffracted from the same number of unit cells.

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References

Andrews, K. W. (1950), An x-ray examination of a sample of pure calcite and of solid-solution effects in some natural calcites: *Mineral. Mag.*, **29**, 85–89.

Austin, J. B., Saini, H., Weigle, J., and Pierce, R. H. H. (1940), Direct comparison on a crystal of calcite of the x-ray and optical interferometer methods of determining linear thermal expansion: *Phys. Rev.*, **57**, 931–933.

Berghius, J., Jbertha, I., Haanappel, M., Potters, M., Loopstra, B. O., McGillavry, C. H., and Veenendall, A. L. (1955), New calculation of atomic scattering factors: *Acta Cryst.*, **8**, 478–483.

Chessin, Henry, and Post, Ben (1958), Positional parameter and thermal motions of oxygen atoms in calcite (Abst.): Annual Meeting of the American Crystallographic Association, Milwaukee, Wisconsin, June 23–27, 1958.

FREEMAN, A. J. (1959), Atomic scattering factors for spherical and aspherical charge distributions: *Acta Cryst.*, **12,** 261–271.

FREEMAN, A. J., AND WOOD, J. H. (1959), An atomic scattering factor for iron: *Acta Cryst.*, **12,** 271–273.

GOLDSMITH, J. R. (1958), Cadmium-dolomite and the system $CdCO_3$—$MgCO_3$: *Geol. Soc. Amer. Bull.*, **69,** 1570–1571.

GOLDSMITH, J. R., AND GRAF, D. L. (1957), The system CaO—MnO—CO_2: solid solution and decomposition relations: *Geochim. et Cosmochim. Acta*, **11,** 310–334.

GOLDSMITH, J. R., AND GRAF, D. L. (1958a), Structural and compositional variations in some natural dolomites: *Jour. Geology*, **66,** 678–693.

GOLDSMITH, J. R., AND GRAF, D. L. (1958b), Relation between lattice constants and composition of the Ca-Mg carbonates: *Am. Mineral.*, **43,** 84–101.

GOLDSMITH, J. R., GRAF, D. L., AND HEARD, H. C. (1961), Cell constants of the calcium magnesium carbonates: *Am. Mineral.*, **46,** 453–457.

GOLDSMITH, J. R., GRAF, D. L., AND JOENSUU, O. I. (1955), The occurrence of magnesian calcites in nature: *Geoch. et Cosmoch. Acta*, **7,** 212–230.

GRAF, D. L., BLYTH, C. R., AND STEMMLER, R. S. (1957), Mixed-layer effects in the rhombohedral carbonates: *Geol. Soc. Amer. Bull.*, **68,** 1737–1738.

GRAF, D. L., BLYTH, C. R., AND STEMMLER, R. S. (1958), Mixed-layer computations using ILLIAC: The three-layer case: *Geol. Soc. Amer. Bull.*, **69,** 1572.

GRAF, D. L., AND BRADLEY, W. F., The crystal structure of huntite, $Mg_3Ca(CO_3)_4$: In Press, *Acta Cryst.*

GRAF, D. L., EARDLEY, A. J., AND SHIMP, N. F. (1961), A preliminary report on magnesium carbonate formation in glacial Lake Bonneville: *Jour. Geology*, **69,** 219–223.

GRAF, D. L., AND GOLDSMITH, J. R. (1956), Some hydrothermal syntheses of dolomite and protodolomite: *Jour. Geology*, **64,** 173–186.

GRAF, D. L., AND LAMAR, J. E. (1955), Properties of calcium and magnesium carbonates and their bearing on some use of carbonate rocks: *Econ. Geol.*, **Fiftieth Anniversary Volume,** 639–713.

GRIGGS, D. T., AND KENNEDY, G. C. (1956), A simple apparatus for high pressures and temperatures: *Amer. Jour. Sci.*, **254,** 722–735.

HARKER, R. I., AND TUTTLE, O. F. (1955), Studies in the system CaO—MgO—CO_2: Part 2. Limits of solid solution along the binary join, $CaCO_3$—$MgCO_3$: *Amer. Jour. Sci.*, **253,** 274–282.

HOWIE, R. A., AND BROADHURST, F. M. (1958), *X*-ray data for dolomite and ankerite: *Am. Mineral.*, **43,** 1210–1214.

HURLBUT, C. S. (1954), Smithsonite from Broken Hill Mine, Rhodesia: *Am. Mineral.*, **39,** 47–50.

INTERNATIONAL TABLES FOR *X*-RAY CRYSTALLOGRAPHY (1952), The Kynoch Press, Birmingham, England, vol. I.

INTERNATIONALE TABELLEN ZUR BESTIMMUNG VON KRISTALLSTRUKTUREN (1935), Gebrüder Borntraeger, Berlin, vol. II.

LEHOVEC, KURT (1953), Space-charge layer and distribution of lattice defects at the surface of ionic crystals: *Jour. Chem. Physics*, **21,** 1123–1128.

PISTORIUS, C. W. F. T. (1959), High pressure preparation and structure of crystalline nickelous carbonate: *Experientia*, **15,** 328–329.

PISTORIUS, C. W. F. T. (1960), Synthesis at high pressure and lattice constants of normal cupric carbonate: *Experientia*, **16,** 447–448.

RAMDOHR, P., AND STRUNZ, H. (1941), Isomorphie von Otavite mit Kalkspat: *Zentralbl. Min.*, **A,** 97–98.

Rymer, T. B. (1957), The lattice constants of small crystals: *Nuovo Cimento*, **VI** (Suppl.), 294–305.

Saint Léon Langlès, René de (1952), Préparation et structure du carbonate neutre de nickel anhydre cristallisé: *Ann. chim. (Paris), ser. 12*, **7**, 568–583.

Sass, R. L., Vidale, R., and Donohue, J. (1957), Interatomic distances and thermal anisotropy in sodium nitrate and calcite: *Acta Cryst.*, **10**, 567–570.

Sharp, W. E. (1960), The cell constants of artificial siderite: *Am. Mineral.*, **45**, 241–243.

Steinfink, H., and Sans, F. J. (1959), Refinement of the crystal structure of dolomite: *Am. Mineral.*, **44**, 679–682.

Swanson, H. E., Cook, M. I., Evans, E. H., and de Groot, J. H. (1960), Standard *x*-ray diffraction powder patterns: *U. S. National Bureau of Standards, Circ. 539*, **10**.

Swanson, H. E., and Fuyat, R. K. (1953), Standard *x*-ray diffraction powder patterns: *U. S. National Bureau of Standards, Circ.* 539, 2.

Swanson, H. E., Gilfrich, N. T., and Cook, M. I. (1957), Standard *x*-ray diffraction powder patterns: *U. S. National Bureau of Standards, Circ. 539*, **7**.

Swanson, H. E., Gilfrich, N. T., Cook, M. I., Stinchfield, Roger, and Parks, P. C. (1959), Standard *x*-ray diffraction powder patterns: *U. S. National Bureau of Standards, Circ. 539*, **8**.

Tahvonen, P. E. (1947), (The crystal structure of sodium nitrate and the atom form-factors of the atoms in the nitrate group): *Annales Acad. Scientiarum Fennicae*, **1** (Mathematica-Physica), 3–25.

Taylor, A., and Sinclair, H. (1945), On the determination of lattice parameters by the Debye-Scherrer method: *Proc. Phys. Soc. London*, **57**, 126–135.

Thomas, L. H., and Umeda, K. (1957), Atomic scattering factors calculated from the TFD atomic model: *Jour. Chem. Physics*, **26**, 293–303.

Verwey, E. J. W. (1946), Lattice structure of the free surface of alkali halide crystals: *Rec. trav. chim.*, **65**, 521–528.

Watson, R. E., and Freeman, A. J. (1961), Hartree-Frock atomic scattering factors for the iron transition series: *Acta Cryst.*, **14**, 27–37.

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