TABLE 2

TEMPER-ATURE ABS.	LOG K_{O_2} L AND R, p. 485	LOG K_{O_2} B AND R, p. 96	LOG K_{OH_B}	LOG K_{OH} B AND R, p. 96	LOG K_{OH_V}	LOG K_{1_B}	LOG K_{1_V}	LOG K_{4_B}	LOG K_{4_V}
1000	-19.8	-20.1	-21.8	-21.1	-15.5	$+1.95$	-4.35	$+2.74$	-3.55
1300	-13.9	-14.01	-15.2	-14.3	-10.34	$+1.31$	-3.53	$+0.30$	-4.54
1500	-11.2	-11.42	-12.24	-11.4	-8.05	$+1.03$	-3.16	-0.79	-4.98
1705	-9.13	-9.28	-9.95	-9.0	-6.26	$+0.81$	-2.87	-1.66	-5.35
1900	-7.55	-7.6 interp.	-8.21	-7.2	-4.90	$+0.65$	-2.66	-2.29	-5.60
2155	-5.94	-6.08	-6.42	-5.5	-3.50	$+0.48$	-2.43	-2.99	-5.91
2505	-4.27	-4.31	-4.59	-3.5	-2.08	$+0.32$	-2.19	-3.67	-6.18

$$2OH \longrightarrow H_2 + O_2 + 14,000 \text{ cal. } (B)$$
$$2OH \longrightarrow H_2 + O_2 - 15,000 \text{ cal. } (V)$$
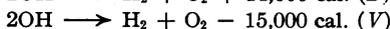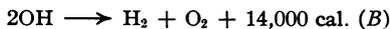
[1] Villars, *J. Am. Chem. Soc.*, **51**, 2374-7 (1929).

[2] Dr. Langmuir has kindly pointed out that the knowledge of such equilibrium constants will be extremely useful in investigating the possibility of the direct formation of hydroxyl during the combustion of hydrogen and oxygen at high temperatures, an investigation which he is at present carrying on.

[3] *Z. physik. Chem.*, **139A**, 75-97 (1928).

[4] *Z. Physik*, **49**, 465.

[5] Cf. Rodebush's chapter XVII, p. 1202, in Taylor, *A Treatise on Physical Chemistry*, D. Van Nostrand, **1925**.

[6] Lewis and Gibson, *J. Am. Chem. Soc.*, **39**, 2554 (1917).

[7] Mulliken, *Phys. Rev.*, **32**, 186.

[8] *J. Am. Chem. Soc.*, **50**, 3221.

[9] These PROCEEDINGS, **15**, 678-680 (1929).

[10] Rodebush, loc. cit., obtained this value and showed that the experimental method used to determine the entropy of hydrogen is theoretically unsound.

[11] Prof. Rodebush has shown independently that this relation must obtain.

ON THE CRYSTAL STRUCTURE OF THE CHLORIDES OF CERTAIN BIVALENT ELEMENTS

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In 1925 Bruni and Ferrari[1] reported that the lines on a powder photograph of the hexagonal crystal $MgCl_2$ could be accounted for on the basis of a rhombohedral (pseudocubic) unit of structure with $a = 5.08$ Å and $\alpha = 90°$ containing 2 $MgCl_2$. Later they announced[2] that $ZnCl_2$, $CdCl_2$, and $MnCl_2$ have the same structure, with values of α a few degrees larger than $90°$. Ferrari[3] then added $CoCl_2$ and $NiCl_2$ to the group; certain weak lines occurring on the powder photographs of these substances require the value of a to be doubled, giving a rhombohedral unit with $\alpha = 90°$

and $a = 10.02$ Å and 10.00 Å, respectively, containing 16 $M^{++}Cl_2$. Gold-schmidt[4] has also reported that unpublished powder photographic data obtained by Oftedal in his laboratory show that $RuCl_2$, $RhCl_2$, $PdCl_2$, $IrCl_2$, and $PtCl_2$ are to be assigned the same structure as $NiCl_2$.

None of these investigators succeeded in deducing the atomic arrangement in these crystals; the utilization of Bruni and Ferrari's data to this end is described in the following paragraphs.

Bruni and Ferrari published reproductions[2] of Laue photographs of $CdCl_2$, $MgCl_2$ and $MnCl_2$, taken in order to determine the axial ratios for these crystals. I have assigned indices to the spots appearing on the best of these photographs, that of $CdCl_2$, with the aid of a gnomonic projection made from a tracing. The forms producing these spots and values of $n\lambda$ calculated for a unit with $\alpha = 94°$ and $a = 10.2$ Å (an estimated value, about equal to that for $ZnCl_2$) are given in the first and second columns of table 1.

Only a few forms show $n\lambda$ values below 0.4 Å, indicating first-order reflections. It is, indeed, possible to account for the production of all of the spots on the photograph on the basis of a much smaller unit, a rhombohedron with $a = 6.35$ Å and $\alpha = 36° 40'$, containing $1MCl_2$. This unit has lattice points at the face-centered positions of the rhombohedron which is itself formed by the face-centered positions of the original pseudo-cubic unit. Inasmuch as values of $n\lambda$ calculated for this unit (fourth column of table 1) in no case fall below the short wave-length limit, the unit may be accepted as the true one.

The presence of a three-fold axis and three planes of symmetry in the Laue photograph taken with the incident beam normal to the basal plane requires that the crystal be isomorphous with one of the point-groups C_{3v}, D_3 and D_{3d}. The fundamental lattice has been found to be rhombohedral. The only ways of placing $1CdCl_2$ in the unit compatible with these restrictions are

I Cd at 000, 2 Cl at uuu, ūūū; D_3^7 and D_{3d}^5;

II Cd at $\frac{111}{222}$, 2 Cl at uuu, ūūū; D_3^7 and D_{3d}^5;

III Cd at uuu, Cl_I at vvv, Cl_{II} at www; C_{3v}^5.

In the absence of any evidence requiring it, the three-parameter structure III need not be considered.

Structures I and II are identical. The data are not sufficient for an accurate determination of the value of the chlorine parameter u. The fact that the powder photograph of $MgCl_2$ is nearly identical with that of LiCl indicates that the chlorine atoms are in nearly the same positions in the two crystals, namely, at the points of a face-centered cubic lattice. This corresponds to a value of u of $^1/_4$. Further evidence that the chloride

ions are in approximate cubic close-packing is provided by the considera-
tion of interionic distances.   With a crystal radius of 1.81 Å,[5] 32 chloride
ions would occupy a cube 10.24 Å on an edge; this approximates closely
the values reported for the various bivalent chlorides.

TABLE 1

DATA FROM BRUNI AND FERRARI'S LAUE PHOTOGRAPH OF CADMIUM CHLORIDE

PSEUDOCUBIC UNIT $a = 10.2$ Å $\alpha = 94°$		TRUE UNIT $a = 6.36$ Å, $\alpha = 36°40'$		ESTIMATED INTENSITY*	STRUCTURE FACTOR
{hkl}	$n\lambda$	{hkl}	$n\lambda$		
33$\bar{5}$	0.33 Å	11$\bar{1}$	0.33 Å	m.	$\overline{Cd} - 2\overline{Cl}$
3$\bar{3}$1	0.68	21$\bar{1}$	0.34	w.	$\overline{Cd} - 2\overline{Cl}$
55$\bar{7}$	0.40	22$\bar{1}$	0.40	m.	$\overline{Cd}$
12$\bar{2}$	1.44	32$\bar{1}$	0.36	m.s.	$\overline{Cd} + 2\overline{Cl}$
77$\bar{9}$	0.32	33$\bar{1}$	0.32	v.w.	$\overline{Cd}$
3$\bar{2}$0	1.04	411	0.26	v.w.	$\overline{Cd} - 2\overline{Cl}$
7$\bar{3}$1	0.72	631	0.36	v.w.	$\overline{Cd} - 2\overline{Cl}$
41$\bar{1}$	1.52	611	0.38	m.	$\overline{Cd} + 2\overline{Cl}$
4$\bar{3}$2	1.40	750	0.35	m.w.	$\overline{Cd} + 2\overline{Cl}$
61$\bar{1}$	1.40	10.3.3	0.35	v.v.w.	$\overline{Cd} + 2\overline{Cl}$
11$\bar{1}$	4.44	110	2.22	m.	
31$\bar{1}$	1.38	100	1.38	s.	
3$\bar{1}$0	2.64	521	0.66	m.	
3$\bar{2}$1	2.02	530	0.50	m.w.	
51$\bar{1}$	1.52	411	0.76	v.v.w.	
5$\bar{3}$1	1.20	210	1.20	w.	
7$\bar{5}$3	0.80	320	0.80	m.w.	

* v.s. = very strong, m = medium, w = weak, etc.

Structure factors calculated for structure I with $u = 0.25$ are included
in table 1 for forms giving first-order reflections.   (These forms are ar-
ranged in order of decreasing interplanar distance.)   These are in satis-
factory agreement with intensities estimated from the reproduction of
the photograph.   Similar agreement is obtained with the powder photo-
graph intensities for $MgCl_2$, $ZnCl_2$, $CoCl_2$ and $NiCl_2$ reported by Bruni
and Ferrari.[6]

The structure found for this series of divalent chlorides is shown in the
figure.   It is a layer structure closely related to that of cadmium iodide.
Each cation is surrounded by six chloride ions approximately at the
corners of a regular octahedron, six edges of which are shared with other
octahedra in such a way as to form a layer.   In the cadmium iodide
structure these layers are superimposed in such a way that each cation
is directly above a cation in the layer below, whereas in the cadmium
chloride structure each cation is directly above an anion in the layer
below, and below an anion in the layer above.   It is probable that the
cadmium chloride structure is stable for substances MX_2 in which the
cation M has a coördination number 6 and the anion has an appreciable
but not great polarizability.

I propose to carry on the experimental investigation of some of these crystals in order to obtain accurate values for the parameter. The discussion of interionic distances can be postponed until the results of this study are reported in the *Zeitschrift für Kristallographie*.
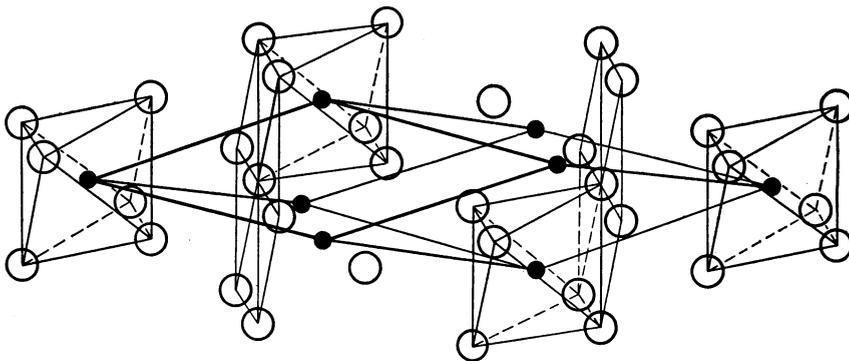

FIGURE I

The structure of cadmium chloride and other bivalent chlorides. Large open circles represent chloride ions, small closed circles cadmium ions. Heavy lines mark the rhombohedral unit of structure, and light lines the coördinated octahedron formed by six chloride ions about each cadmium ion.

Summary.—With the aid of data obtained from a reproduction of a Laue photograph published by Bruni and Ferrari, it is shown that the unit of structure of $CdCl_2$ is a rhombohedron with $\alpha = 36° 40'$ and $a = 6.35$ Å, about, containing $1CdCl_2$, Cd at 000, 2Cl at uuu, $\bar{u}\bar{u}\bar{u}$, with $u = 1/4$. The isomorphous crystals $MgCl_2$, $CoCl_2$, and $NiCl_2$ have $\alpha = 33° 36'$ and $a = 6.21$, 6.14 and 6.13 Å, respectively. Other representatives of the structure are $MnCl_2$, $ZnCl_2$, $RuCl_2$, $RhCl_2$, $PdCl_2$, $IrCl_2$ and $PtCl_2$.

[1] G. Bruni and A. Ferrari, *Rendiconti Acc. dei Lincei*, **2**, 457 (1925).
[2] G. Bruni and A. Ferrari, *Ibid.*, **4**, 10 (1926).
[3] A. Ferrari, *Ibid.*, **6**, 56 (1927).
[4] V. M. Goldschmidt, *Geochemische Verteilungsgesetze der Elemente*, VIII, p. 147.
[5] L. Pauling, *J. Am. Chem. Soc.*, **49**, 765 (1927).
[6] One line of small intensity, assigned indices {422} by Ferrari, is not compatible with the unit containing $1MCl_2$.