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The Crystal Structure of $CsMgCl_3$

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ABSTRACT. The crystal structure of $CsMgCl_3$ has been determined by Weissenberg technique. The crystals are hexagonal, with two molecules per unit cell of dimensions: a = 7.26(2)Å, c = 6.18(1)Å. Cs, Mg and Cl atoms are located at the special positions 2(d), 2(a) and 6 (h) respectively of the space group $P6_3/mmc$. After several cycles of least square refinement the reliability factor R converged at 0.068. The structure is isomorphous with that of $CsNiCl_3$.

Many complex halides of composition $CsMCl_3$ where M represents a metal ion in the first transition series, have the same structure as $CsNiCl_3$, (Tishchenko 1955, Goodyear *et al.* 1977), which consists of hexagonally close-packed $CsCl_3$ layers with Ni octahedrally coordinated by Cl ions such that the Ni-Cl octahedra share opposite faces to form infinite chains of composition ($NiCl_3$) ... parallel to c, the space group being $P6_3/mmc$ with a = 7.2 Å, c/a ~ 0.82 and Z = 2.

$CsMgCl_3$ is a linear-chain diamagnetic compound. It is easily deformed to accommodate impurity atoms (Chen 1992). Single crystals of $CsMgCl_3$ doped with V^{2+} (Chen 1992, Takeuchi and Tanaka 1992, Chen *et al.* 1992), Ni^{2+} (Chen 1992, Chen *et al.* 1992), Mn^{2+} (Chen 1992), Cr^{3+} and Cr^{2+} (Chen *et al.* 1992, Takeuchi *et al.* 1993) Tm^{3+} (Gharavi and McPherson 1992) and Er^{3+} (Garava and McPherson 1993) were prepared by the Bridgman and the Czochralski methods, and subjected to EPR studies at 77K to find the EPR parameters for the corresponding ions.

Luminescence, absorption and excitation spectra of Pd^{2+} doped into $CsMgCl_3$ were reported (Oetliker and Gudel 1994). Luminescence due to octahedral and square plannar Pd^{2+} sites in $CsMgCl_3$ and $CsCdCl_3$ are identified by comparison with K_2PdCl_4.

The unit-cell dimentions of the material examined in this work suggested that its structure is of the $CsNiCl_3$ type. Subsequent refinement of the structure confirmed this result.

Experimental

Single crystals of $CsMgCl_3$ were prepared by heating an equimolar mixture of $MgCl_2$ and CsCl in a sealed evacuated silica tube, using the setup given by Aql *et al.* 1996), to a temperature above the melting point and then cooling the specimen to room temperature at a rate of about 5° C per hour. Because of the extremely hegroscopic nature of the material, single crystals suitable for X-ray examination were selected and examined in a stream of dry nitrogen and were then mounted in Lindemann - glass capillary tubes containing P_2O_5.

Crystals were chosen from a crushed bulk sample using a low power (X35) polarizing microscope. A suitable crystal fulfills the criterion that when placed on the microscope stage, rotated between the crossed polarizers and illuminated with parallel white light, it shows complete extinction over the whole crystal at a certain position, repeated every 90° of rotation. The crystals must also be small and approximately cylinderical in shape in order to reduce and correct for absorption of the incident X-ray beam. In practice rectangular crystals of the appropriate size were selected typically 0.27 mm in length and 0.135 mm in width and thickness.

Oscillation and Weissenberg photographs were taken about the a-axis with Cuk_α radiation. The unit cell dimensions were determined from $\alpha_1 - \alpha_2$ doublet separations on a zero layer Weissenberg photograph taken with Cuk_α radiation, using the method of Main and Woolfson (Main and Woolfson 1963).

The macroscopic density of the material was determined by weighing the sample in air and in toluene and agreement between the observed D_o and calculated D_c densities was obtained by assigning 2 molecules of $CsMgCl_3$ per unit cell. The complete crystal data are shown in Table 1.

Intensity data were collected from equi-inclination Weissenberg photographs taken about the a-axis with MoK_α radiation. The intensities of symmetrically independent reflections were measured visually against a calibrated scale, on layer lines 0-6 from accurately timed film exposures. The systematically absent reflections

Table 1. Crystal data.

Formula	F.W.	Crystal Structure	a(Å)	c(Å)	Z	D_o(gcm^{-3})	D_c(gcm^{-3})
$CsMgCl_3$	263.576	Hexagonal cell	7.26(2)	6.18(1)	2	3.08	3.09

were of the type hhl with l = 2n + 1; hence the space group must be either $P6_3mc$ or $P6_3/mmc$. The latter, which is centro-symmetric was chosen since it is the space group of $CsNiCl_3$. The observed data were corrected for the Lorentz - polarization factor and for absorption using the factors given by Bond (1959) for a cylindrical specimen. A computer program was used to apply these corrections. The linear absorption coefficient μ (= 82.84 cm^{-1} (λ = 0.717Å)) used in the absorption correction program was calculated from the mass absorption coefficients of the consitituent elements, taken from the 'International Tables for X-ray Crystallography' (International Tables for X-ray Crystallography 1962).

Determination and description of the structure

The initial structure was determined by considering a stacking arrangement of $CsCl_3$ layers which would explain a c-parameter of the order of 6Å. In the $CsNiCl_3$ structure, the c-parameter accommodates two close-packed layers, indicating a layer separation of about 3Å. This suggested that $CsMgCl_3$ is isostructural with $CsNiCl_3$.

Since each Cs atom must be in contact with 12 Cl atoms, there are three possible positions of a layer in relation to the outline of the unit cell; these correspond to the types A,B and C of Fig. 1. The stacking sequence of $CsMgCl_3$ would then be BABA ... which is shown in Fig. 2. In the close-packed array of $CsCl_3$ layers, only one quarter of the octahedral sites are bounded exclusively by Cl atoms and each of these must be occupied by a Mg atom in order to obtain the correct compositional formula. The triangles in Fig. 1 indicate these sites in the unit cell between different pairs of layers; for example, that labelled ab in such a site between A and B type layers. Fig. 3 is a c-axis projection of the $CsMgCl_3$ structure where Cs and Cl atoms form an approximate hexagonal close-packed array such that each Cs atom has 12 nearest Cl atoms.

The atoms were assigned to the following positions in the space group $P6_3/mmc$: Cs at (1/3, 2/3, 3/4), Mg at (0,0,0) and Cl at (x, 2x, 1/4). The least square refinement was carried out using an initial positional parameter for the chlorine atom equal to that of the chlorine atom in the $CsNiCl_3$ structure (namely x = 0.156, 2x = 0.312).

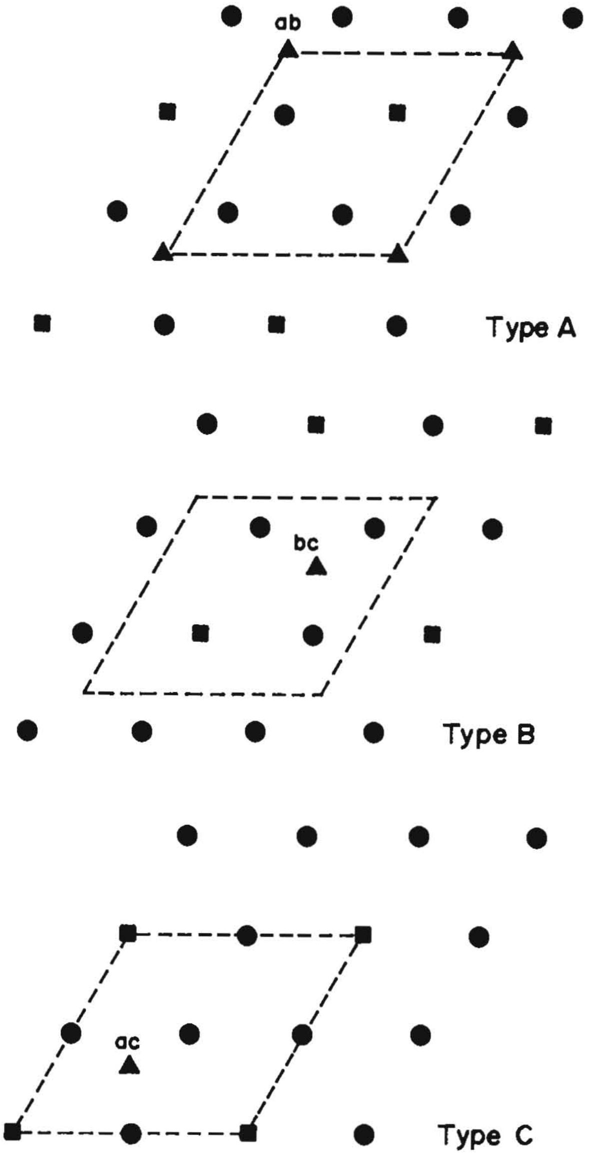


Fig. 1. Close-packed $CsCl_3$ layers classified according to the position of the unit cell (broken line). The circles and squares represent Cl and Cs respectively. The triangles show possible sites for Mg atoms between different pairs of layers; ab, bc and ac are sites between types A and B, B and C, A and C, respectively.

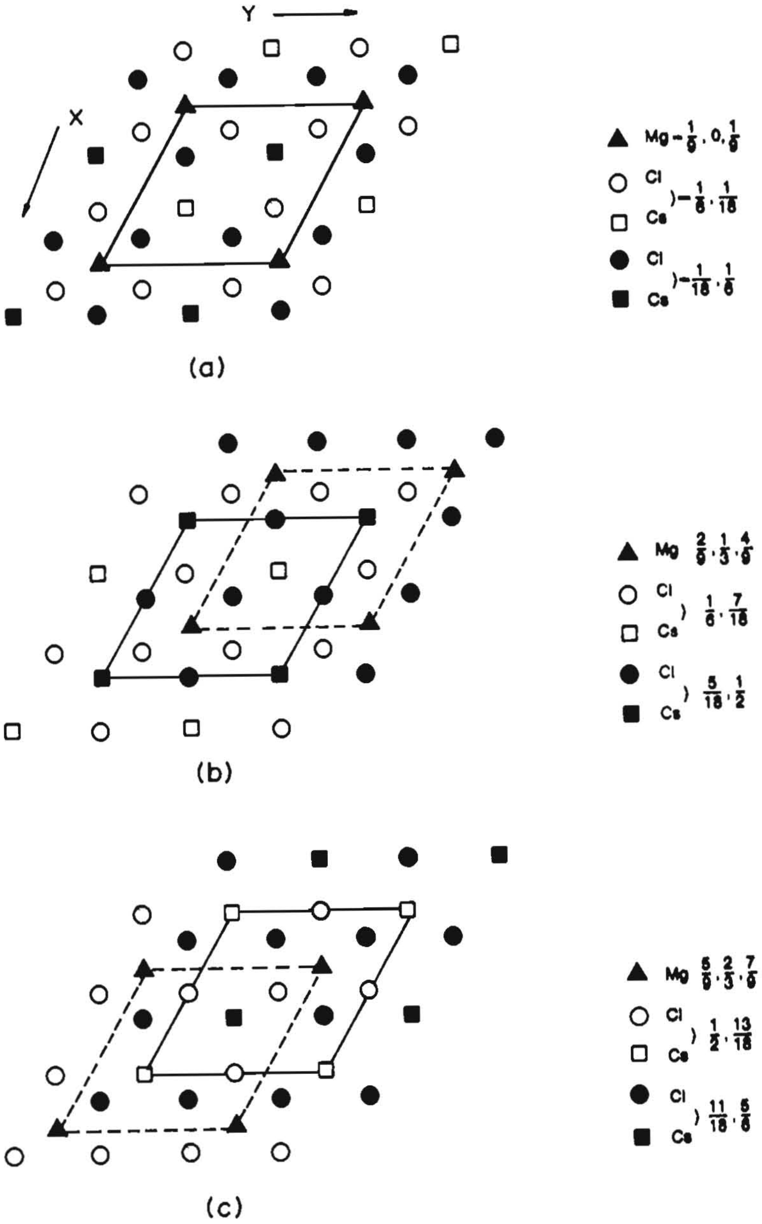
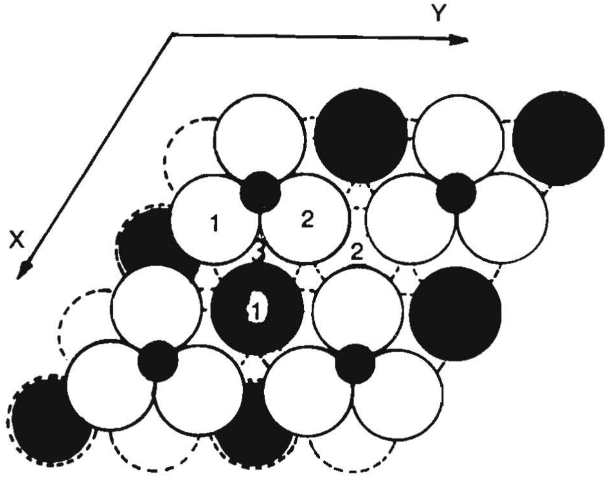


Fig. 2. A c-axis projection of $CsMgCl_3$ structure showing its relation to the $CsNiCl_3$ stucture. The full line represents the base of the cell and the broken line indicates the base of a sub-cell of $CsNiCl_3$ -tupe structure; in (a) the unit cell and sub-cell coincide.



○ Cl, z = 1/4 (dotted, z = −1/4).

● Cs, z = 1/4 (dotted, z = −1/4).

● Mg, z = 1/2 and 0.

Fig. 3. The crystal structure of $CsMgCl_3$. Projection on the x-y plane.

An isotropic temperature factor of $1.5Å^2$ was assigned to each atom.

Several cycles of least-square refinement of the hkl data reduced the reliability factor $R = \Sigma||F_0|-|F_c||/\Sigma|F_0|$ from 0.186 to 0.068, at which stage the shifts in the atomic parameters were all less than 1/50 of the estimated standard deviations. In these calculations the atomic scattering factors given in "International Tables for X-ray Crystallography" (1962) for Cs^+, Cl^- and Mg^{2+} were used.

The calcualted structure factors of 55 symmetrically independent unobserved reflections were all less than the minimum observable value. The final atomic parameters are given in Table 2 and the observed and calcualted structure factors compared in Table 3.

The Mg-Cl octahedra share opposite faces to form chains of composition $[MgCl_3]_n^{n-}$, parallel to the c-axis. The trigonal distortion of the octahedra is

Table 2. Final atomic parameters.

Atom	Position	X	Y	Z	B(Å²)
Mg	2(a)	0	0	0	1.78(32)
Cs	2(d)	1/3	2/3	3/4	2.34(17)
Cl	6(h)	0.156	0.312	1/4	1.72(11)

Standard deviation is given in parentheses.

presumably due to the repulsion of successive Mg^{2+} ions in the chains so that the Cl atoms in the shared faces are brought closer together, thereby making the Cl (1)-Mg-Cl(1) and Cl(2)-Mg-Cl(2) angles less than 90° and the Cl(1)-Mg-Cl(2) angle correspondingly greater. Bond lengths are given in Table 4, and shown in Fig. 4.

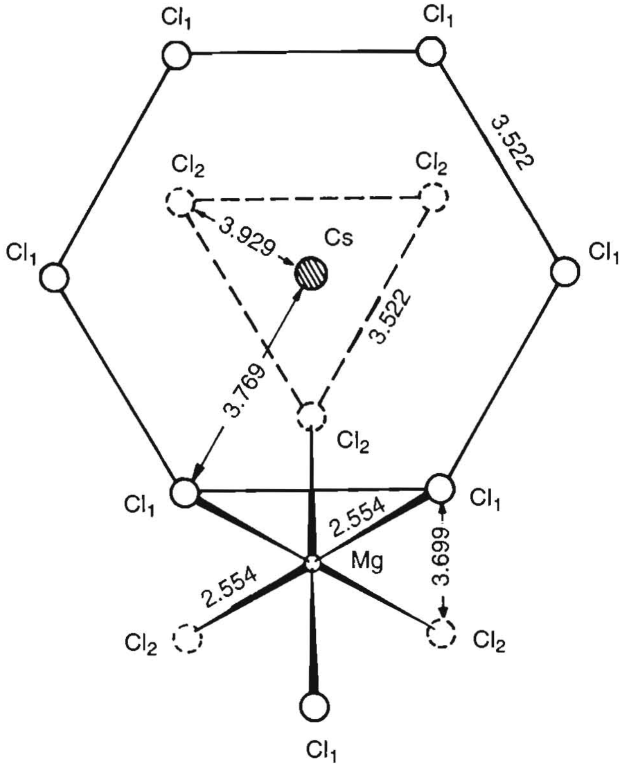


Fig. 4. A projection down the c-axis showing the near-hexagonal close packing about cesium ion (shaded circle). Chloride represented by full circles are at z = 3/4. Those represented by dotted circles are at z = 1/4.

Table 3. Observed and calculated structure factors

H	K	F_o	F_c		H	K	F_o	F_c
L = 0					**L = 1**			
2	0	96	–92		2	0	188	–219
3	0	69	60		3	0	15	–18
4	0	70	–64		4	0	149	153
6	0	132	134		7	0	21	15
7	0	27	26		3	0	60	–59
8	0	26	–24		10	0	32	31
1	1	81	75		2	1	17	19
2	1	7	10		3	1	17	–24
3	1	26	22		4	1	17	13
4	1	48	43		3	2	32	25
6	1	18	19		4	2	126	–117
7	1	19	21		5	2	19	–19
2	2	202	231		6	2	82	73
3	2	32	31		6	4	55	–48
4	2	53	–4		8	4	30	26
5	2	30	26					
6	2	29	–30					
8	2	50	56					
3	3	39	38					
5	3	12	10					
6	3	18	17					
4	4	109	106					
5	4	17	21					
6	4	22	–19					
6	6	35	38					

H	K	F_o	F_c		H	K	F_o	F_c
L = 2					L = 3			
2	0	145	147		2	0	175	170
4	0	106	106		3	0	17	14
5	0	43	43		4	0	129	–128
6	0	89	–93		8	0	45	51
8	0	39	42		10	0	23	–28
2	1	55	53		2	1	11	–14
3	1	34	33		3	1	14	19
5	1	29	30		4	1	13	–11
2	2	151	–154		3	2	20	–20
3	2	19	16		4	2	105	100
4	2	86	82		5	2	17	16
6	2	52	52		6	2	66	–63
7	2	27	24		6	4	40	41
8	2	41	–38		8	4	24	–23
4	3	35	34					
4	4	75	–74					
6	4	35	34					

H	K	F_o	F_c		H	K	F_o	F_c
L = 4					L = 5			
2	0	58	58		2	0	114	–116
3	0	37	37		4	0	94	93
4	0	43	–45		8	0	37	–39
6	0	97	99		2	4	80	74
7	0	13	20		2	6	50	–48
1	1	42	44		4	6	30	32
2	1	11	6					
3	1	20	15					
4	1	26	29					
6	1	16	15					
2	2	173	156					
3	2	26	23					
4	2	35	–36					
5	2	22	18					
6	2	20	–23					
6	2	39	43					
3	3	20	26					
4	4	83	80					

Table 4. Bond lengths.

Bond	Multiplicity	Bond lengths (Å)
Mg-Cl octahedron:		
Mg - Cl(1)	3	2.554(6)
Mg - Cl(2)	3	2.554(6)
Cl(1) - Cl(1)	3	3.522(12)
Cl(2) - Cl(2)	3	3.522(12)
Cl(1) - Cl(2)	6	3.699(5)
Cs-Cl distances:		
Cs - Cl(1)	6	3.769(8)
Cs - Cl(2)	3	3.929(4)
Location of atoms:		
Mg at (000)		
Cs at (2/3, 1/3, 1/4)		
Cl(1) at height z = 3/4		
Cl(2) at height z = 1/4		

Standard deviations are given in parentheses.

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التركيب البلوري للمركب $CsMgCl_3$

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و خضر محمد الشيباني و عبد الله صالح الجفالي

قسم الفيزياء - كلية العلوم - جامعة الملك سعود
ص .ب (٢٤٥٥) - الرياض ١١٤٥١
المملكة العربية السعودية

تمت دراسة التركيب البلوري للمركب $CsMgCl_3$ باستخدام طريقة ويزنبرج (Weissenberg) وقد تبين أن البلورات ذات تركيب سداسي وتحتوي خلية الوحدة على جزئين من المركب . أما أبعاد هذه الخلايا فهي :

$$a = 7.26\ (2)\ \text{Å}\ ,\ c = 6.18\ (1)\ \text{Å}$$

وتتواجد الذرات Cl, Mg, Cs في المواضع الخاصة 6(h), 2(a), 2(d) على الترتيب من مجموعة الفراغ $P6_3/mmc$. وبعد عدة دورات من التشذيب باستخدام طريقة تخفيض فرق المربعات ، فإن معامل التراخي R أصبح مساوياً 0.068 ، وهذا التركيب مشابه لتركيب المركب $CsNiCl_3$.