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Refinement of the crystal structure of NiCl₂ and of unit-cell parameters of some anhydrous chlorides of divalent metals. By ADOLFO FERRARI, ANTONIO BRAIBANTI and GINO BIGLIARDI, *Istituto di Chimica generale and Istituto di Mineralogia, Università di Parma, Italy*

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After the chemical researches of Sandonnini (1914) on solid solutions between LiCl and MgCl₂, Bruni & Ferrari (1925, 1926, 1927), Ferrari (1927), Ferrari, Celeri & Giorgi (1929) studied the same problem on a structural basis and found that complete solubility is connected with the presence in MgCl₂ of a multiple rhombohedral cell with $\alpha = 90^\circ$ (i.e. the cell is a cube) of the same size as the doubled cubic cell of LiCl. In the cube half of the lithium positions are occupied by magnesium atoms, leaving chlorine atoms unaffected. They found also that MnCl₂, FeCl₂, CoCl₂, NiCl₂ and CdCl₂ have the same structure as MgCl₂. Pauling (1929), and Pauling & Hoard (1930), were able to find the rhombohedral unit cell and space group of CdCl₂ and to determine more precisely the positions occupied by the atoms in the unit cell. The structure was defined as *C19* in *Strukturbericht* (vol. I, p. 742).

We have measured new photographs of the same compounds and applied new methods of extrapolation to the data obtained. Moreover, the general coordinates of the chlorine atoms in NiCl₂ have been refined by the use of intensity data obtained from a single crystal.

Compounds were prepared by dehydrating the hexahydrated chlorides in gaseous HCl at high temperature (500–800 °C). Magnesium chloride was obtained by heating NH₄Cl.MgCl₂.6H₂O in flowing gaseous HCl.

The powder photographs were obtained in a 57.3 mm diameter camera; Cu *K*α radiation was used ($\lambda = 1.5418 \text{ \AA}$).

Refinement of unit-cell constants

Lattice constants were determined by the Myers & Davies (1961) graphical method and the least-squares refinement was applied to the data obtained by the graphical method.

The least-squares normal equations were derived as follows. The usual expression for the hexagonal system:

$$\frac{4 \sin^2 \theta}{\lambda^2} = \frac{4}{3} \frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2} \quad (1)$$

was rewritten in the form

$$\frac{4 \sin^2 \theta}{\lambda^2 l^2} = \frac{1}{a^2} \left[\frac{a^2}{c^2} + \frac{4}{3} \frac{(h^2 + hk + k^2)}{l^2} \right]. \quad (2)$$

Hence

$$\frac{4 \sin^2 \theta_c}{\lambda^2 l^2} = \frac{r^2 + K}{a_0^2 + Bx}, \quad (3)$$

when one puts

$$\frac{a_0}{c} = r, \quad \frac{4}{3} \frac{(h^2 + hk + k^2)}{l^2} = K, \quad a^2 = a_0^2 + Bx,$$

with

$$x = \frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right),$$

the Nelson & Riley (1945) and Taylor & Sinclair (1945) extrapolation function.

These authors extrapolated to $x=0$ the function $a = a_0 + Bx$, but Myers & Davies (1961) found satisfactory the extrapolation of the function $a^2 = a_0^2 + Bx$ as well, because it is applied to a narrow range of a .

$\sin \theta_c$ in (3) indicates the value resulting from the introduction in (2) of the values of a_0^2/c^2 , a_0^2 and B obtained by graphical extrapolation according to Myers & Davies (1961), or of further values of a_0^2/c^2 , a_0^2 and B obtained in successive cycles of the least-squares procedure.

If one indicates $C_c = 4 \sin^2 \theta_c / \lambda^2 l^2$ and $C_o = 4 \sin^2 \theta_o / \lambda^2 l^2$ (θ_c is defined as above and θ_o is the Bragg angle observed), the following least-squares normal equations can be obtained (partially diagonalized matrix):

$$\left. \begin{aligned} \Sigma(C_o - C_c) \frac{\partial C_c}{\partial(r^2)} &= \Sigma \left[\frac{1}{a_0^2 + Bx} \right]^2 \Delta(r^2) \\ &\quad - \Sigma \left[\frac{1}{a_0^2 + Bx} \frac{r^2 + K}{Q_0^2 + Bx} \right] \Delta(a_0^2) \\ \Sigma(C_o - C_c) \frac{\partial C_c}{\partial(a_0^2)} &= - \Sigma \left[\frac{1}{a_0^2 + Bx} \frac{r^2 + K}{(a_0^2 + Bx)^2} \right] \Delta(r^2) \\ &\quad + \Sigma \left[\frac{r^2 + K}{(Q_0^2 + Bx)^2} \right] \Delta(Q_0^2) \\ \Sigma(C_o - C_c) \frac{\partial C_c}{\partial B} &= \Sigma \left[\frac{(r^2 + K)x}{(a_0^2 + Bx)^2} \right] \Delta B. \end{aligned} \right\} \quad (4)$$

Iterative application of all the equations (4) gives the best values of r^2 and a_0^2 in a few cycles. The correctness of the procedure can be judged by the reasonable agreement of the final results with single-crystal data obtained for NiCl₂ (Table 1).

From (4) the e.s.d.'s can also be calculated (*International Tables for X-ray Crystallography*, 1959).

The photograph of MgCl₂ was indexed in terms of a pseudo-cubic cell, and the data then transformed to the hexagonal cell. The pseudo-cubic cell of MgCl₂ has $a = 10.274 \text{ \AA}$, which can be compared to the cube in LiCl having $2a = 10.2796 \text{ \AA}$ (Jevinš, Straumanis & Karlsons, 1938).

The unit-cell constants are quoted in Table 1.

Refinement of the structure of NiCl₂

The crystal used for the photographs was obtained from a solidified mass. One fragment was sealed in a Lindemann glass capillary tube. Rotation and Weissenberg photographs (Cu *K*α radiation) were taken. The rotation axis was [10·0] of the hexagonal cell.

Table 1. *Unit-cell constants of divalent metal chlorides (Å)*
Hexagonal cell, space group $R\bar{3}m (D_{3d}^5)$

Compound	Ferrari <i>et al.</i> *		Grime & Santos, 1934 (CoCl ₂) Pauling & Hoard, 1930 (CdCl ₂)		Present work			
	a	c	a	c	Graphical method		Least-squares method	
					a	c	a	c
MgCl ₂	3.603	17.627			3.632	17.78	3.632 ± 0.004	17.795 ± 0.016
MnCl ₂	3.682	17.480			3.709	17.59	3.711 ± 0.002	17.59 ± 0.07
FeCl ₂	3.585	17.555			3.593	17.60	3.593 ± 0.003	17.58 ± 0.09
CoCl ₂	3.547	17.385	3.551	17.46	3.553	17.41	3.553 ± 0.001	17.39 ± 0.05
NiCl ₂	3.542	17.355			3.481	17.30	3.478 ± 0.001†	17.41 ± 0.12†
CdCl ₂			3.862	17.495	3.845	17.49	3.8457 ± 0.0003	17.48 ± 0.02

* Bruni & Ferrari (1925, 1926, 1927), Ferrari (1927), Ferrari, Celeri & Giorgi (1929).

† From a single crystal, $a = 3.483 \pm 0.006$ Å, $c = 17.40 \pm 0.03$ Å.

Unit-cell data have been found to be $a = 3.483 \pm 0.006$, $c = 17.40 \pm 0.03$ Å. Calculated and observed density were $\rho_c = 3.537$ g.cm⁻³ and $\rho_o = 3.51$ g.cm⁻³. The ($h0l$) integrated reflexions were recorded by an integrating Weissenberg camera and measured by a microdensitometer. Polarization and Lorentz corrections were introduced. Absorption corrections were calculated by Ferrari, Braibanti & Tiripicchio's (1961) method; a contribution, due to the Lindemann tube, deduced from a curve for cylindrical specimens was added to the transmission factors calculated. Atomic form factors were evaluated graphically from the Thomas & Umeda (1957) data. During refinement, anomalous dispersion (*International Tables for X-ray Crystallography*, 1961) and secondary extinction (Pinnock, Taylor & Lipson, 1956) were taken into account.

Ni is in position (a) and Cl in position (c) of the space group $R\bar{3}m$. Only the positional parameter z_{Cl} and the thermal parameters were refined by the least-squares method.

The resulting chlorine coordinate is $z_{Cl} = 0.2551 \pm 0.0008$. The variations of the thermal parameters from the isotropic value ($B = 2.0 \pm 0.2$ Å²) are within the e.s.d.'s.

The structure (*Strukturbericht*, vol. I, p. 742) is formed by octahedra [NiCl_{6/3}] grouped in layers. The metal-halogen distance is Ni-Cl = 2.426 ± 0.008 Å, which is somewhat shorter than the sum of the ionic radii. The distances between two chlorine atoms are Cl...Cl = 3.385 ± 0.016 Å and 3.483 ± 0.006 Å within each octahedron and Cl...Cl = 3.674 ± 0.016 Å between different octahedra. The latter distance is in good agreement with twice the van der Waals radius of chlorine. The angles Cl-Ni-Cl are $89 \pm 3^\circ$ and $92 \pm 3^\circ$.

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A demonstration of a moiré pattern and a pure twist boundary model. By H. OCKEN and E. N. AQUA, *Hammond Metallurgical Laboratory, Yale University, New Haven, Connecticut, U.S.A.*

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This communication describes interference phenomena resulting from two-dimensional point networks which can be interpreted either in terms of moiré patterns or dislocation models of pure twist boundaries.

Moiré patterns may be described as coarse arrange-

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ments produced by the superposition and, in this case, rotation of identical fine networks. The coarse patterns are enlarged versions of the fine ones. Using Gevers's (1962) notation, the size of the magnified moiré image, A , is related to the separation distance of the fine net-