gested for finding the replaceable atom position, namely, the one which uses the coefficients

$$(|F^{(1)}|-|F^{(2)}|)^2$$

for a Fourier synthesis.

This synthesis, which we may call the $(MD)^2$ synthesis [$(MD)^2$ stands for modulus difference squared], can be shown to give approximately the Patterson of the replaceable atoms both in centrosymmetric and non-centrosymmetric crystals, although it should be more effective for the former.* Rossmann (1960) has used the method to determine the position of the replaceable atoms in protein crystals. However, the method is reported to have been a failure when applied to the case of caffeine and theophylline (Sutor, 1956), where the replaceable 'atom' is just a methyl group. The synthesis was actually tried in the present case also and is shown in Fig. 3. Although there is a broad peak at the required position of the (PP) vector (marked by a cross in Fig. 3), there are also other strong peaks in the map. A similar feature was also observed by Sutor (1956). Thus, the $(MD)^2$ synthesis is not likely to prove useful in such cases, where the replaceable atom is of the same strength as the other atoms in the structure, although, it might work when the replaceable atom itself is heavy (Perutz, 1956).

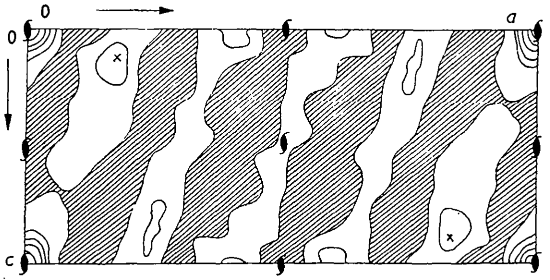

Fig. 3. The $(MD)^2$ synthesis of tyrosine and tyrosine+O, projected down the b axis. Contours are at arbitrary intervals. Shaded areas correspond to troughs.

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* The details will be published in a later paper from the aboratory.

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The Crystal Structure of Chromium(II) Iodide

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CrI_2 crystallizes with a monoclinic (pseudo hexagonal) unit cell, $C2/m$, with

$$a_0=7\cdot545,\ b_0=3\cdot929,\ c_0=7\cdot505\ \text{Å};\ \beta=115°\ 31'.$$

The structure consists of infinite parallel planar ribbons formed by chromium atoms bridged by pairs of iodine atoms. The ribbons stack together so as to form a 'sandwich' layer structure in which the iodine atoms are approximately in a close-packed array and each chromium atom is at the center of a distorted octahedron of iodine atoms.

The crystal structures of chromium(II) fluoride (Jack & Maitland, 1957) and chromium(II) chloride (Tracy *et al.*, 1961) have been reported previously. These two substances are not isostructural; the fluoride is monoclinic and the chloride orthorhombic, and both are also structurally different from chromium(II) bromide and chromium(II) iodide (Handy & Gregory, 1951). Continuing a study of this series of compounds, we now wish to report the structure of chromium(II) iodide.

Experimental

CrI_2 was prepared by reaction of iodine (Mallinckrodt, AR) with chromium metal (Fischer Scientific, 98%

pure). CrI_3 was formed initially by heating the elements in a sealed pyrex tube (Gregory & Handy, 1957); the tri-iodide was decomposed into CrI_2 and iodine in an evacuated system at 500–600 °C. CrI_2 was then purified by sublimation in high vacuum in a quartz tube at 700 °C. Crystals suitable for X-ray examination were grown by sublimation in a quartz tube under a pressure of ca. 25 cm. Hg of argon. The main sample was held near 835 °C.; after a twenty-four hour period small lath-shaped purple prisms were found attached to the wall of the tube near the mouth of the furnace. To protect the highly deliquescent crystals from the atmosphere during exposure to X-rays, specimens were mounted in thin-walled pyrex capillary tubes, diameter 0·4–0·6 mm. with wall thickness 0·02–0·03 mm. Crystals were selected and inserted in the capillaries in a dry box; the crystal ends were anchored in Apiezon wax W and the capillary closed and finally sealed off with a flame. No interaction of the crystals with the wax was noted over a period of several months. However, crystals which had been mounted for periods approaching a year were observed to have blackened through apparent interaction with the wax and no longer gave usable diffraction patterns. The crystal from which final intensity data were collected was a rectangular needle, 0·06 mm. × 0·125 mm., elongated along *b*.

The monoclinic cell dimensions,

$$a_0=7\cdot545\pm0\cdot004,\ b_0=3\cdot929\pm0\cdot004,$$
$$c_0=7\cdot505\pm0\cdot004\ \text{Å};\ \beta=115^\circ\ 31',$$

and space group were determined from rotation, Weissenberg and precession photographs, using Cu$K\alpha$ radiation ($\lambda=1\cdot5418$ Å). Diffraction lines from sodium chloride (a_0 taken as 5·640 Å) were superimposed on rotation and Weissenberg photographs used to determine cell dimensions. Systematic absence of reflections with $h+k$ odd indicated space group $C2$, Cm or $C2/m$. Corresponding $h0l$ and $h2l$ reflections were observed to have similar intensities, after allowance for angular factors. This observation, together with packing considerations, led to the conclusion that the space group must be $C2/m$ with all atoms at either $y=0$ or $y=\frac{1}{2}$. The cell contains the equivalent of two CrI_2 units. The density reported by Biltz & Birk (1924) is 5·196 g.cm.$^{-3}$ (calc. 5·033).

Determination of structure

$h0l$ intensity data were obtained using a Nonius Weissenberg instrument with multiple films, inte-

Table 1. *Observed and calculated structure factors*

CrI_2. $F(h0l)\times10$ observed and calculated. $R=0\cdot094$

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
2	0	0	1314	−1402	4	0	−2	1173	−1111	4	0	−4	1368	1547	6	0	−6	1152	1059
4	0	0	1569	1530	6	0	2	795	792	6	0	4	430	−378	8	0	−6	608	−579
6	0	0	715	−676	6	0	−2	1227	1168	6	0	−4	901	−822	0	0	7	< 251	−173
8	0	0	587	621	8	0	−2	446	−508	8	0	−4	813	824	2	0	7	646	500
0	0	1	565	523	0	0	3	< 167	78	0	0	5	674	506	2	0	−7	< 264	289
2	0	1	< 154	−87	2	0	3	675	714	2	0	5	< 264	−285	4	0	−7	< 264	212
2	0	−1	709	676	2	0	−3	200	236	2	0	−5	< 224	175	6	0	−7	< 251	−98
4	0	1	838	809	4	0	3	274	−389	4	0	5	680	612	8	0	−7	404	445
4	0	−1	285	−239	4	0	−3	633	640	4	0	−5	< 237	16	0	0	8	1004	797
6	0	1	435	−432	6	0	3	652	657	6	0	−5	560	541	2	0	−8	828	−698
6	0	−1	834	767	6	0	−3	325	−314	8	0	−5	< 235	−331	4	0	−8	1059	979
8	0	−1	321	−447	8	0	−3	584	662	0	0	6	1048	−817	6	0	−8	766	−665
0	0	2	1118	−1429	0	0	4	1657	1615	2	0	6	1040	893	8	0	−8	693	724
2	0	2	1517	1735	2	0	4	878	−869	2	0	−6	1282	1303	2	0	−9	< 161	−74
2	0	−2	1248	2141	2	0	−4	907	−1180	4	0	6	430	−425	4	0	−9	< 180	131
4	0	2	761	−815	4	0	4	954	885	4	0	−6	761	−906	6	0	−9	< 154	212

CrI_2. $F(h1l)\times10$ observed and calculated. $R=0\cdot19$

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
1	1	0	285	194	5	1	2	800	710	3	1	−4	544	392	3	1	−6	< 298	171
3	1	0	993	743	5	1	−2	858	712	5	1	4	316	−400	5	1	−6	693	372
5	1	0	648	−371	7	1	2	204	−429	5	1	−4	< 281	−160	7	1	−6	< 282	−225
7	1	0	741	698	7	1	−2	307	−394	7	1	−4	792	606	9	1	−6	502	498
1	1	1	945	2052	9	1	−2	539	609	9	1	−4	511	−378	1	1	7	657	−600
1	1	−1	737	−1431	1	1	3	940	−1090	1	1	5	1243	1177	1	1	−7	950	1013
3	1	1	1110	−1047	1	1	−3	936	1844	1	1	−5	880	−979	3	1	−7	973	−782
3	1	−1	1115	1798	3	1	3	1194	1212	3	1	5	756	−614	5	1	−7	1099	1031
5	1	1	1110	1079	3	1	−3	1037	−1161	3	1	−5	1330	1423	7	1	−7	812	−629
5	1	−1	876	−868	5	1	3	656	−561	5	1	5	528	582	1	1	−8	544	341
7	1	1	257	−457	5	1	−3	1121	1349	5	1	−5	950	−874	3	1	−8	< 267	43
7	1	−1	779	848	7	1	−3	796	−638	7	1	−5	953	946	5	1	−8	< 258	25
1	1	2	685	623	9	1	−3	610	607	9	1	−5	595	−454	7	1	−8	263	329
1	1	−2	197	347	1	1	4	< 267	−148	1	1	6	680	499	3	1	−9	763	800
3	1	2	< 257	−277	1	1	−4	237	392	1	1	−6	< 302	−39	5	1	−9	671	−606
3	1	−2	< 194	−15	3	1	4	800	645	3	1	6	298	−325					

grating circumferentially only. Intensities were determined with a recording microphotometer, scanning parallel to the axis of rotation, and intensities assumed proportional to the areas under the peaks. Results were checked by visual estimation. Lorentz and polarization factors were then applied and the square root of the adjusted intensities taken as the relative observed structure factors. Scattering factors for Cr^{++} (Berghuis *et al.*, 1955) were used; since values for I^- were not available, factors for iodine atoms (Thomas & Umeda, 1957) were used. Although the crystal was somewhat larger than the optimum size, no correction for absorption was included. For the least-squares calculation data were weighted according to Hughes (1941).

CrI_2 crystals show a pronounced tendency to delaminate, which, together with consideration of space group and ionic radii, suggested a 'sandwich' type trial structure, i.e. 1*m*2, 3*m*4, etc. where the numbers represent layers of halogen atoms (approximately close-packed) and *m*, layers of interspersed metal atoms. Chromium atoms were assumed to be at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0) and *h*0*l* Fourier projections used to fix trial values of x and z for the iodine atoms. The coordinates determined from Fourier methods were refined by full matrix least-squares on an IBM 709 (simulating an IBM 704 program by Busing & Levy (1959)). The only positional parameters permitted to refine were the x and z coordinates of the iodine atom (final values: $x=0\cdot2336$, $z=0\cdot2420$). The isotropic temperature factors of both iodine and chromium were allowed to refine, resulting in the final values $B_{\text{Cr}}=1\cdot54$ Å^2 and $B_{\text{I}}=0\cdot98$ Å^2. The final $R(\Sigma||F_o|-|F_c||/|F_o|)$ for the *h*0*l* set, Table 1, is 0·094 (002 and $20\bar{2}$ considered extinguished).

Unfortunately, only a preliminary unintegrated Weissenberg single film for *hll* was available (the crystal was accidentally lost before further data could be collected). Eye estimated intensities were assigned by comparison with a gray scale. It became evident that several of the most intense spots were so black that their intensities could not be quantitatively distinguished. It will be observed in the comparison of F_c and F_o that the intensities assigned to some of these reflections were too small. However, even without allowance for this difficulty the agreement of calculated and observed values was considered an adequate confirmation of the structure (1st level $R=0\cdot19$, excluding 111 and $11\bar{1}$ as extinguished, see Table 1).

Discussion

As in CrF_2 and $CrCl_2$, it may be said that the chromium atoms in CrI_2 are surrounded by halogens in a distorted octahedral arrangement (see Fig. 1 and Table 2). The CrI_6 octahedra share their shortest edge (I(2)–I(3), 3·821 Å) giving rise to a densely packed linear 'ribbon', extending parallel to *b*, with chromium atoms bridged by iodine atoms (Cr–I distance 2·74 Å). In the *a* direction adjacent octahedra within each sandwich layer also share the longer edge I(2)–I(5), 4·229 Å, with the longer (inter-ribbon Cr–I distance 3·237 Å. The I–I distance in the *b* direction is fixed by the cell dimension, 3·929 Å. The I(2)–I(4) distance 4·253 Å, the longest in the octahedral set, is the same as the distance I(5)–I(6) between two adjacent 'sandwich' layers and somewhat longer than I(5)–I(7), 4·215, the shortest distance between iodine atoms in two adjacent layers. The dominant feature of the structure is the linear 'ribbon' arrangement with a co-planar rectangular set of iodine atoms around each chromium. As one would expect, the strongest interaction of these planar ribbons occurs when the iodine atoms of alternate ribbons lie above and below the chromium atoms of an interspersed neighbor. However the appreciably greater Cr–I distance between ribbons indicates a weaker interaction than within the ribbon itself. In CrI_2 the ribbons pack together to form an infinite two-dimensional sandwich layer structure, whereas in $CrCl_2$, which does not cleave easily, similar ribbons interact in a three dimensional pattern. The iodine atoms in CrI_2 are not greatly displaced from an ideal close-packed arrangement. The interatomic distances within the ribbons are slightly less than expected on an ionic basis (radii; I^-, 2·16 Å (Pauling, 1960); Cr^{++}, 0·64 Å in CrF_2 and $CrCl_2$ (loc.cit.)). The I–I interlayer distances are generally consistent

Table 2. *Interatomic distances in* CrI_2

(Ångström, ±0·01)

	Cr(1)–I(2) and Cr(1)–I(3)	2·740 Å
	Cr(1)–I(4) and Cr(1)–I(5)	3·237
	I(2)–I(3)	3·821
	I(2)–I(4)	4·253
	I(2)–I(5)	4·229
	I(5)–I(7)	4·215
	I(5)–I(6)	4·253
Bond angle	I(2)–Cr(1)–I(4)	90·3°

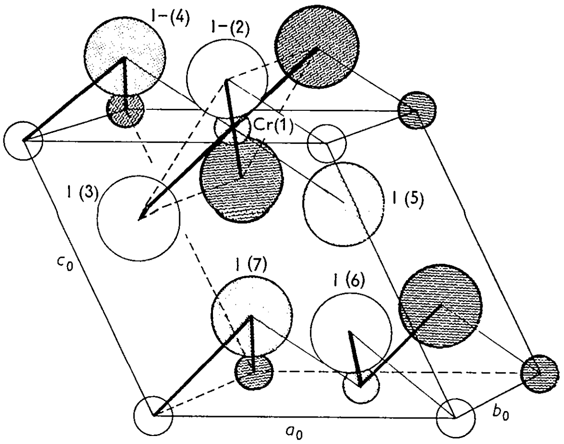

Fig. 1. Crystal structure of CrI_2. Large circles, iodine; small circles, chromium. Open, $y=0$; half-shaded, $y=\frac{1}{2}$; shaded, $y=1$.

with the expected value; however b_0 is significantly less than the normal diameter of I^-.

During the preliminary search for suitable crystals, it was observed more frequently than not that specimens displayed extra spots along the festoons of constant h and k, although the irregularity was not observed on the $00l$ line. Such behavior suggests some kind of modified layer stacking arrangement with a longer than normal c_0; at no time was a tendency toward a change in a_0 or b_0 observed. It was, in fact, only after a considerable search that a crystal which gave a simple orderly pattern was found. We have found numerous crystals with the 'perfected' structure elucidated in this manuscript, however, and believe it to be the correct one to ascribe to CrI_2. Specimens which showed irregular spots gave poor quality photographs and the irregularities were not reproducible in the various imperfect crystals examined; hence no attempt was made to determine the structure of anyone of them. In extreme cases, the festoons appeared as a nearly continuous line. These irregularities may be a consequence of the non-equilibrium conditions under which crystals were grown.

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Lattice Vibrations of Molecular Chains

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The lattice vibrations of linear chains consisting of one and of two different types of ring-shaped molecules are derived assuming central and non-central harmonic restoring forces between next neighbours. Restricting the problem to two degrees of freedom at a time it is shown that the general normal modes of the chain consist of mixed vibrations containing both translational and rotational components. The contribution of the translational and rotational components changes continuously along each branch of the dispersion curve; their phase relationships however remain constant through the entire fundamental range. Dispersion curves and amplitude ratios are calculated for different sets of parameters. The extension of the results to centrosymmetrical molecules of other shapes is discussed.

Introduction

Since Born & Kármán's pioneer paper (1912) on the lattice vibrations of monatomic chains the vibrational modes of atomic lattices have been the subject of many theoretical investigations (Brillouin, 1946; Blackman, 1955; de Launay, 1956). The study of the lattice vibrations of molecular structures has been given much less attention, most of the investigations having been concerned with the internal vibrations of the molecules. These internal vibrations lie in the visible and ultraviolet range ($1/\lambda \sim 300$–3000 cm.$^{-1}$) while the lattice vibrations lie in the far infrared ($1/\lambda \sim 50$–150 cm.$^{-1}$). Apart from the far infrared emission and absorption spectra, lattice vibrations are observable also in the low-frequency Raman spectra and they are mainly responsible for the diffuse scattering of X-rays and the inelastic scattering of

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