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The Modulated Structure of the Layered Perovskite γ-Bis(*n*-propylammonium) Tetrachloromanganate(II): Refinement of the Average Structure, the Possible Superspace Group and a Model for the Modulated Structure

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Abstract

Between 344 K and 396 K, $(C_3H_7NH_3)_2MnCl_4$, M_r = 316·98, forms a modulated structure as indicated by satellite reflexions of two different kinds. The average structure, with space group *Abma*, a = 7·39(1), b = 7·25 (2), c = 26·72 (5) Å, V = 1432 (8) Å^3, Z = 4, D_c = 1·47 Mg m^{-3}, $F(000)$ = 652, has been determined with Mo $K\alpha$ radiation at T = 360 (10) K [λ(Mo $K\alpha$) = 0·7107 Å]. Refinement for 553 reflexions converged to R = 0·072 with anisotropic temperature factors. The perovskite-type layer is described with split Mn and Cl atoms. The modulation consists mainly of transverse distortion waves running along a with amplitudes parallel to c. Some weak extra satellites in the $hk0$ reciprocal plane have been interpreted as arising from a small additional longitudinal component of the modulation. The Janner–Janssen–de Wolff (3 + 1)-dimensional superspace-group symbol for the most important satellites is a subgroup of $N^{Abma}_{\bar{1}11}$ and a model of the

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modulated structure is given under the assumption that $N^{Abma}_{\bar{1}11}$ itself is the superspace group describing its symmetry. The model has been verified in a superstructure approximation by structure factor calculations for 55 first-order satellites measured on an *h*0*l* film. With an amplitude of 0·5 Å the *R* value for these satellites was 0·21.

Introduction

The title compound (whose various phases will be designated γ-C3Mn, δ-C3Mn *etc.*) belongs to a group of compounds with the general formula $(C_nH_{2n+1}NH_3)_2MCl_4$ (M = Mn, Cd, Fe, Cu, Pd) which have a structure of the K_2NiF_4 type. These compounds have been regarded as two-dimensional perovskites because an important feature of their structures is layers of corner-sharing MCl_6 octahedra. These layers may be thought of as slabs cut parallel to (100) from a three-dimensional perovskite. On both sides attached to these layers are positively charged alkylammonium ions, taking the positions of the *A* cations in the three-dimensional perovskites. These ions are fixed by N—H···Cl hydrogen bonds and their alkyl chains point away from the layers, thus forming neutral strata which stack on each other. Eight Cl atoms can act as possible acceptors for three hydrogen bonds from each cation. Depending on the temperature, different hydrogen-bonding schemes and orientation states of the alkyl chains are possible and these result in different structures. Phase transitions resulting from such reorientation mechanisms have been described for the methyl compounds of Mn (Heger, Mullen & Knorr, 1975, 1976) and Cd (Chapuis, Arend & Kind, 1975; Chapuis, Kind & Arend, 1976; Seliger, Blinc, Kind & Arend, 1976) and for the ethyl compounds of Mn (Depmeier, 1977) and Cd (Chapuis, 1977). Chapuis (1978) also reported the two phases of $(C_3H_7NH_3)_2CdCl_4$ above and below the 183 K transition.

The phase-transition behavior of C3Mn is quite different from that of the other compounds studied so far in that it exhibits more and more complex phase transitions. Its sequence of phase transitions is $\zeta \overset{110\,\mathrm{K}}{\leftrightarrow} \varepsilon \overset{165\,\mathrm{K}}{\leftrightarrow} \delta \overset{344\,\mathrm{K}}{\leftrightarrow} \gamma \overset{396\,\mathrm{K}}{\leftrightarrow} \beta \overset{446\,\mathrm{K}}{\leftrightarrow} \alpha$ (Depmeier, Felsche & Wildermuth, 1977). The δ → ε transition is marked by the formation of a commensurate superstructure with a tripling of the *b* axis, whereas the δ → γ transition leads to an incommensurate phase with $a_{\mathrm{super}}:a_{\mathrm{sub}} \simeq 5{\cdot}6$. This phase is the subject of this work. Details of the structure of δ-C3Mn have been reported from X-ray work at room temperature (Peterson & Willet, 1972) and from neutron work at 180 K (Depmeier & Mason, 1978). This phase is characterized by dynamical disorder of the hydrogen-bonding system and of C(1) and C(2) (counting from the N atom), each of which take two mirror-related positions with a probability of 0·5. The dynamic character of the disorder in compounds of this kind has been shown by spectroscopic methods by Kind & Roos (1976).

Some recent studies have revealed that C3Mn seems to represent a border-line case in the series $(C_nH_{2n+1}NH_3)_2MnCl_4$ (Depmeier, 1979; Depmeier & Chapuis, 1979).

Experimental

Crystals suitable for X-ray work were grown by slow evaporation of a solution of appropriate amounts of n-$C_3H_7NH_3Cl$ and $MnCl_2$ in a mixture of water and ethanol. The first evidence of a phase transition was obtained from a heating Guinier photograph on which a drastic effect on the *c* and *a* lattice parameters was recognizable by discontinuities in the 002 and 200 reflexion lines. The transition was confirmed and characterized by single-crystal photographs using a focusing monochromator and by differential scanning calorimetry (for the corresponding findings, see Depmeier, Felsche & Wildermuth, 1977). The incommensurate or, at least, superstructural character of γ-C3Mn became obvious from the photographs when in *h*0*l* reciprocal planes sharp satellites around the extinct main reflexions became visible.

For the intensity measurements a crystal of *ca* 0·4 × 0·4 × 0·2 mm, covered with silicon grease to prevent thermal decomposition, was mounted along its ⟨100⟩ direction on a two-circle diffractometer (Fa. Huber). The crystal was positioned in a *U*-shaped temperature-controlled heating device. The agreement between the temperature reading and the true temperature of the crystal was certainly not very reliable but the stability was within ±3 K. By measuring the satellites (they appear at the δ → γ transition and disappear at the γ → β transition) it was guaranteed that the crystal was in the γ phase. From the lattice parameters and by comparison with former powder results the temperature was estimated to be about 360 K. By centering 19 reflexions the lattice parameters (see *Abstract*) were obtained by least-squares refinement. For the main reflexions the extinction rules for *Abma*, *viz* *hkl*: $k + l = 2n + 1$, 0*kl*: $k = 2n + 1$, *hk*0: $h = 2n + 1$, were found to be valid. The non-standard setting for this space group was chosen in order to facilitate the comparison with the other phases of this compound. From the distribution of normalized structure factors the non-centrosymmetric space group *Ac*2*a* was ruled out. Main reflexions on layers *h*0*l*–*h*10*l* were measured up to $\Gamma = 60°$ using the $\omega/2\theta$ scan technique with a scan width of 2·3° using Mo $K\alpha$ radiation from a flat quartz monochromator. A total of 1069 reflexions with $+h$, $+k$, $+l$ were measured, 553 of which with $F_o > 3\sigma(F_o)$ were used in the subsequent refinement.

The intensities were reduced to F's by the usual technique, but no absorption correction was applied. The structure determination started with the Mn and Cl positions of δ-C3Mn (Depmeier & Mason, 1978). Soon it became evident that this assumption resulted in poor agreement with the measured values and that some disorder had to be taken into account. Therefore, the Mn and Cl positions were split in the z direction, which allowed the separation of two half atoms in this direction. In addition, the Cl(21) and Cl(22) atoms were split in the y direction. This latter splitting is attributed to dynamical disorder and has been discussed elsewhere (*e.g.* Depmeier & Mason, 1978). It should be emphasized that the splitting of the second type is probably not related to the distortion waves discussed below and it will not be used for the discussion of these waves.

This model refined immediately and in a difference Fourier synthesis positions for N and C were revealed. Various cycles of isotropic and finally anisotropic refinement converged to $R = 0{\cdot}072$ ($R = \sum\Delta/\sum|F_o|$) for 553 reflexions with $F_o > 3\sigma(F_o)$ and 64 parameters, ten of which were layer scale factors. Split Cl atoms of the same kind have been refined in different cycles and the same is true for y and U_{22} of Cl(22) and N. Unit weights were used and complex scattering factors for C, N, Cl^- and Mn^{2+} were employed (*International Tables for X-ray Crystallography*, 1974). For the same reason as for Cl(21) and Cl(22), *i.e.* dynamical disorder, the C and N atoms were refined as split atoms with site-occupancy factors of 0·5 on positions away from the mirror planes at $y = 0{\cdot}5$. Any further splitting of C and N (*i.e.* in the z direction) gave no improvement. No attempt was made to locate the H atoms. The refined positional parameters are listed in Table 1 together with the values for δ-C3Mn.*

It was intended to measure the satellites after the main reflexions had been measured. During the centering procedure for the satellites, however, a technical accident (short circuit and subsequent uncontrolled heating) destroyed the crystal. Since the author changed his affiliation shortly after, he decided to tackle the problem in the first instance without diffractometrically measured satellites; he instead contented himself with a set of 55 satellite reflexions measured densitometrically on a precession photograph.

The values for the modulation vectors corresponding to the A and B satellites have been determined from a Weissenberg photograph, and it should be noted that the reported values are preliminary and need a more precise and also temperature-dependent determination. Such a measurement is planned.

Results and discussion

This part will be arranged in the following order: Firstly, we discuss the results and merits of the average

Table 1. *Final positional parameters for* γ-C3Mn *together with the* U_{eq} *values* [$= \frac{1}{3}(\text{trace } U_{ij}) \times 10^3$]

E.s.d.'s are given in parentheses. Corresponding values for δ-C3Mn at 182 K are in the second row.

	Wyckoff notation	Site symmetry	x	y	z	Site occupancy	U_{eq} (Å^2)
Mn	8(*f*)	*m*	0	0	0·0111 (1)	0·5	25 (1)
	4(*a*)	2/*m*	0	0	0	1·0	15 (2)
Cl(11)	8(*e*)	2	0·75	0·75	0·5201 (2)	0·5	37 (2)
	8(*e*)	2	0·75	0·75	0·5107 (0)	1·0	19 (1)
Cl(12)	8(*e*)	2	0·75	0·75	0·4974 (2)	0·5	33 (2)
	8(*e*)	2	0·75	0·75	0·5107 (0)	1·0	19 (1)
Cl(21)	16(*g*)	1	0·0323 (9)	0·0355 (7)*	0·0983 (3)	0·25	49 (4)
	8(*f*)	*m*	0·0485 (2)	0	0·0957 (1)	1·0	26 (1)
Cl(22)	16(*g*)	1	0·0498 (9)	0·018 (1)*	0·0823 (3)	0·25	61 (4)
	8(*f*)	*m*	0·0485 (2)	0	0·0957 (1)	1·0	26 (1)
N	16(*g*)	1	−0·023 (2)	0·012 (5)	0·4191 (5)	0·5	72 (6)
	16(*g*)	1	−0·0240 (2)	0·021 (5)	0·4147 (1)	0·5	19 (1)
C(1)	16(*g*)	1	0·052 (3)	−0·004 (9)	0·374 (1)	0·5	157 (9)
	16(*g*)	1	0·0721 (3)	−0·0324 (5)	0·3658 (1)	0·5	28 (2)
C(2)	16(*g*)	1	−0·011 (4)	−0·063 (5)	0·333 (1)	0·5	187 (9)
	16(*g*)	1	−0·0133 (5)	−0·0476 (6)	0·3191 (1)	0·5	52 (3)
C(3)	16(*g*)	1	0·068 (5)	−0·051 (6)	0·283 (1)	0·5	237 (9)
	16(*g*)	1	0·0918 (5)	−0·006 (3)	0·2700 (1)	0·5	50 (2)

* This deviation from $y = 0$ is connected with dynamical disorder and is probably not related to the transverse modulation wave.

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* Lists of structure factors and anisotropic temperature factor coefficients for the average structure, as well as the atom list for the superstructure model and the corresponding structure factor table for the satellite reflexions, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35706 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

structure (I). Then the observed satellite reflexions will be described (II). A symmetry description of the modulated structure will be given in terms of the Janner–Janssen–de Wolff notation for superspace groups (III) and from that the modulated structure can be deduced which will be tested by structure factor calculations for satellite reflexions and this also provides a possibility to determine the amplitude of an average modulation wave.

(I) *The average structure*

Diffraction patterns of modulated structures are characterized by the appearance of satellite reflexions which, in contrast to the main reflexions, cannot be indexed integrally with respect to the normal lattice parameters *a*, *b*, *c*.

The main reflexions carry the main information about the structure and, thus, they provide the main features of the structure. The satellites, carrying the more detailed information, can be used in a second step to find the modulation of the structure.

One peculiarity of C3Mn is the dynamical disorder of the propylammonium groups. Even at temperatures as low as 180 K this disorder leads to physically unreliable bond distances (Depmeier & Mason, 1978). Therefore, not surprisingly, the combination of modulation, higher temperature and inherent dynamical disorder leads to uncommon values of the calculated atom–atom distances and it is hardly worthwhile to discuss them as is the usual practice in structural work. This applies especially for distances within the propylammonium chain. However, distances within the octahedra correspond to those in δ-C3Mn; this is even true for the hydrogen bonds, as shown by the N$\cdots$Cl distances. The most significant differences between the γ and δ phase make sense and help to elucidate the real structure.

Fig. 1 illustrates the most striking differences between the δ phase and the average structure of the γ phase. A $MnCl_6$ octahedron of the δ phase is sketched with the Mn and Cl(2) atoms as open circles on a mirror plane at $y = 0{\cdot}5$. Filled circles are Cl(1) atoms at $y = 0{\cdot}25$ and $0{\cdot}75$. Crosses denote the refined positions of the split-atom model, but only insofar as splitting in the *x* and *z* directions is concerned (splitting in the *y* direction has been attributed to dynamical disorder). The splitting is easily explained by assuming a periodical distortion wave (*e.g.* sinusoidal) for each atom involved. The projection into the average unit cell produces the observed splitting.

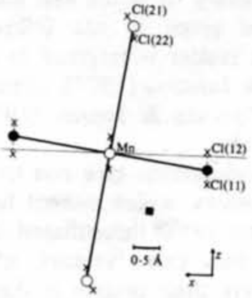

Fig. 1. Side view of a $MnCl_6$ octahedron of the δ phase. Open circles are Mn and Cl(2) atoms at $y = 0$, filled circles are Cl(1) atoms at $y = 0{\cdot}25$ and $0{\cdot}75$. This octahedron splits up in the average structure of the γ phase due to a transverse modulation wave. The refined split-atom positions are denoted by crosses.

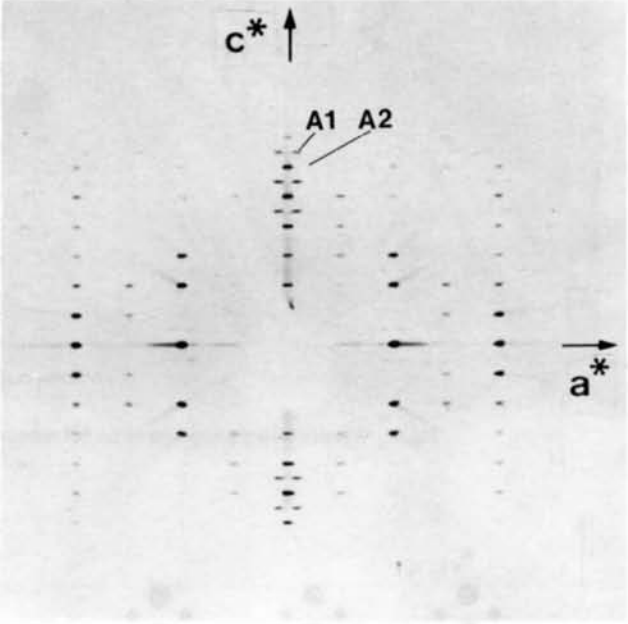

Fig. 2. Precession photograph of an *h*0*l* reciprocal layer showing *A*1 and weak *A*2 satellite reflexions.

It should be remembered that the N and C positions could not be split further than they had already been in the δ phase.

(II) *The satellite reflexions*

Besides the main reflexions, which all obey the extinction rules for space group *Abma*, three types of satellites are observable on diffractograms of γ-C3Mn. They are visible on Figs. 2 and 3 and are listed in Table 2. Fig. 4 is a schematic representation of the satellites.

Table 2. *Observed satellite reflexions in* γ-C3Mn

Type	Indices	Conditions for non-extinction
*A*1	$h \pm \delta_1, k, l,$	$k + l$ odd
*A*2	$h \pm 2\delta_1, k, l$	$k + l$ even
B	$h \pm \delta_2, k, l$	$k + l$ odd

$\delta_1 = 0{\cdot}178\ (2)$
$\delta_2 = 0{\cdot}05\ (1)$

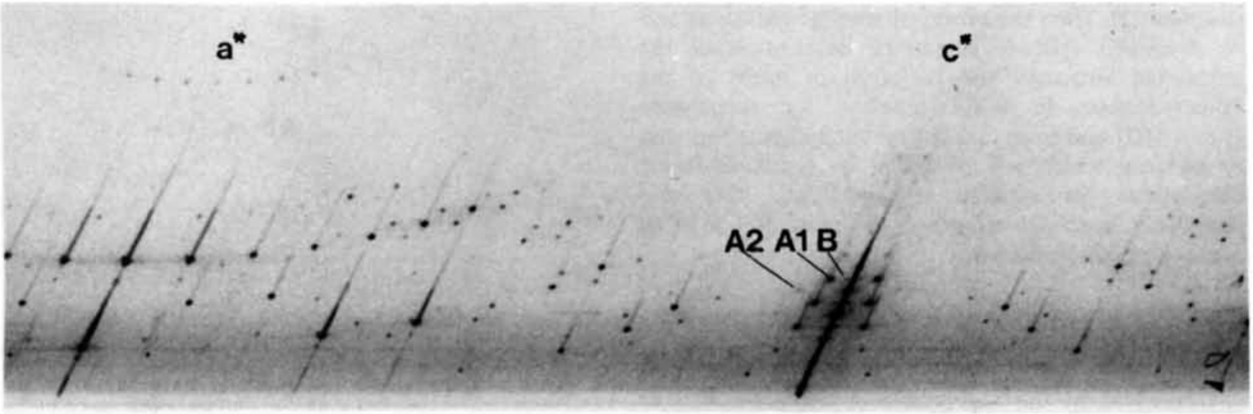

Fig. 3. Weissenberg photograph of an $h0l$ reciprocal layer showing $A1$, $A2$ and B satellite reflexions.

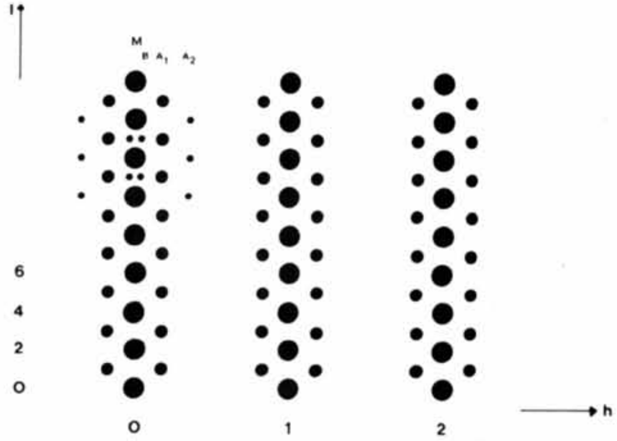

Fig. 4. Schematic representation of $A1$, $A2$ and B satellite reflexions around main reflexions M.

At temperatures well away from the phase transitions all satellites are sharp. Only on approaching or reaching the phase transitions, in particular the upper one, do they become diffuse.

Satellites of type $A1$ are the most prominent ones and appear throughout the reciprocal space around the extinct main reflexions. Chronologically, they were the first ones to be discovered. Their properties together with their, at that time, supposed non-existence in the $hk0$ reciprocal plane prompted the first ideas of transverse distortion waves, which run along the a axis, have their amplitudes parallel to the c axis and destroy the A centering (Depmeier, Felsche & Wildermuth, 1977).

There are only a few very weak satellites of type $A2$. They appear in the $h0l$ plane near to the strongest $A1$ satellites. Examples are $0 \pm 2\delta_1,0,10$ and $0 \pm 2\delta_1,0,12$. They are regarded as second order to the $A1$ satellites and both together obey an extinction rule which will be discussed in §III.

It was only on overexposed precession photographs that very weak $A1$ and $A2$ satellites could also be discovered in the $hk0$ planes. Their existence means that the originally assumed pure transverse distortion wave must have an additional longitudinal component. The model, discussed in §IV, will provide us with an explanation for the longitudinal component. The strongest satellites in the $hk0$ plane are $2 - \delta_1,1,0$; $4 \pm \delta_1,1,0$ and $2 \pm 2\delta_1,2,0$.

The B satellites appear together with the strongest A reflexions in the $h0l$ plane. Their nature is still unclear and more precise measurements have to be done to elucidate whether they really represent an independent modulation or not. This independence from the A satellites has recently been doubted (de Wolff, 1980).

The wave vectors for the distortion waves as determined from Fig. 3 are $0{\cdot}178a^*$ and about $0{\cdot}05a^*$. These correspond to wavelengths of 41·5 and about 150 Å, respectively. These values, of course, are only valid for the temperature at which the photograph has been taken and the temperature dependence of δ_1 and δ_2 is still an open question.

(III) *The symmetry in* (3 + 1) *dimensions*

A short summary of terms and ideas useful in this context will be given in the following. For more information the reader is referred to de Wolff (1974, 1977), Janner & Janssen (1977), Janner, Janssen & de Wolff (1979), Janssen & Janner (1979) and to references cited therein.

Structural modulations give rise to the extra reflexions, called satellites, which cannot be indexed rationally with reference to the three-dimensional basis $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$. Instead of this, extra vectors, $\mathbf{q}^*$, may be introduced which have their origins in the main reflexions. More than one modulation vector $\mathbf{q}^*$ may occur and the dimensionality n of the modulation is equal to the number of different $\mathbf{q}^*$'s. Satellites and main reflexions together may then be described with extended vectors in reciprocal space, *e.g.* $H = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}^*$ for a one-dimensional modulation, and the reflexions are indexed with the notation *hklm*. Main reflexions have $m = 0$ and satellites have $m \neq 0$ with m usually a small integer, called the order of the satellite. Since $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$ form a basis in three-dimensional space, $\mathbf{q}^*$ may be expressed in terms of these: $\mathbf{q}^* = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}^*$. If at least one of α, β, γ is an irrational number, the terms 'modulated' or 'incommensurate' (sometimes also 'incommensurable') have been adopted. On the other hand, if only rational numbers ($\neq 0$) occur, one should speak of commensurate superstructures. The difference is especially striking if the irrational number depends on experimental conditions, *e.g.* on the temperature (*cf.* de Wolff, 1974). It is even more striking in cases where the temperature-dependent incommensurate wave vector of the modulated phase becomes commensurate at a certain temperature (lock-in phase transition, *e.g.* K_2SeO_4, Iizumi, Axe, Shirane & Shimaoka, 1977).

Let us assume a one-dimensional modulation wave consisting of transverse distortions $\mathbf{u}_i(\mathbf{q}^*,\mathbf{r}_i)$ with modulation vector $\mathbf{q}^*$ and wavelength $1/|\mathbf{q}^*|$. This wave adds equal displacements $\mathbf{u}_i$ to atoms of the ith kind, which are $1/|\mathbf{q}^*|$ apart and whose position vectors in the undistorted structure are $\mathbf{r}_i = \mathbf{n} + \mathbf{r}_i^0$, where $\mathbf{r}_i^0$ is the position vector in the zero unit cell and $\mathbf{n} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$ is a lattice vector. The distortion is periodic, hence $\mathbf{u}_i(\varphi) = \mathbf{u}_i(\varphi + 1)$.

Atoms of different kinds need not have identical modulation functions, but have the same modulation vector provided that the structure is really one-dimensionally modulated, which means that only one $\mathbf{q}^*$ exists.

For simplicity we assume an orthorhombic structure with only one irrational coefficient for $\mathbf{q}^* = \alpha\mathbf{a}^* + 0.\mathbf{b}^* + 0.\mathbf{c}^*$. That means the modulation wave is running along a of the basic (undistorted) structure. Atoms which are translationally identical in the basic structure now have different distortions and are therefore no longer identical. The distortions of adjacent atoms are related by the phase shift α. Now, since α is irrational, the translational period a of the basic structure and the modulation wavelength are incommensurate. Consequently, the translational symmetry in this direction is lost and the crystal no longer has three-dimensional periodicity. Furthermore, symmetry operations, which do not leave this direction invariant, are destroyed. The description of one of the classical space groups must therefore be low-symmetrical, although the intrinsic symmetry may be much higher (pseudosymmetry). It was de Wolff (1974) who found the means to overcome this dilemma, by proposing that the one-dimensionally modulated crystal be regarded as a three-dimensional section through a four-dimensional, now again periodic, crystal. The fourth dimension could be regarded as an internal degree of freedom. The basic vector in the fourth dimension was assumed to be perpendicular to the other three basic vectors. With this approach it is possible to find a direct *basis* in four-dimensional space corresponding to the reciprocal basis which is observed on the diffractograms of the modulated crystal. Furthermore, taking the phase of the distortion wave into account, it proved possible to express *symmetry operations* of the modulated crystal by normal space-group operations, possibly combined with sign reversals of the modulation wave and/or shifts of the phase (de Wolff, 1977). A more general treatment in higher dimensions was given by Janner & Janssen (1977). Janner, Janssen & de Wolff (1979) determined the complete list of (3 + 1)-dimensional superspace groups and proposed a notation for them. It is based on the international space-group symbol combined with a bottom row which gives information on sign reversal or phase shifts of the modulation wave. A capital letter in front of the two rows denotes the Bravais class of that superspace group. In the following the satellites occurring in γ-C3Mn will be analyzed with the help of the above-mentioned symmetry description.

The modulated structure of γ-C3Mn can be described starting from the basic structure, which is assumed to be essentially the structure of δ-C3Mn below 344 K. This assumption seems to be justified by the following facts: (i) the refined average structure of γ-C3Mn can be explained as a distorted version of the structure of δ-C3Mn and (ii) the major structural features of δ- and β-C3Mn are clearly the same and, therefore, γ-C3Mn is regarded as an intermediate between δ- and β-C3Mn.

The space group of the assumed basic structure is *Abma* which is generated by an *A*-centered orthorhombic Bravais group and by the following symmetry operators: $[m_x\colon (x,y,z) \to (\tfrac{1}{2} - x, \tfrac{1}{2} + y, z)]$; $[m_y\colon (x,y,z) \to (x,\bar{y},z)]$; $[m_z\colon (x,y,z) \to (\tfrac{1}{2} + x, y, \tfrac{1}{2} - z)]$. There are four formula units of $(C_3H_7NH_3)_2MnCl_4$ in the unit cell. On the time average all atoms occupy special positions: four Mn are on Wyckoff position 4(*a*) (0,0,0) with site symmetry $2/m$, eight Cl(1) atoms (which link the $MnCl_6$ octahedra) are on 8(*e*) $(\tfrac{1}{4},\tfrac{1}{4},z)$ with site symmetry 2 and, respectively, eight Cl(2), N, C(1), C(2) and C(3) atoms are on 8(*f*) $(x,0,z)$ with site symmetry m. The atoms on 8(*f*), as well as the H atoms attached to N and C, are dynamically disordered, so only their average is on 8(*f*). For further discussion it is not necessary to distinguish between the average and the (dynamical) split positions. For the present purpose a convenient description of the structure is that of alternating layers of Mn, Cl(2), N, C and of Cl(1), respectively, perpendicular to y. The former layer coincides with the mirror plane at $y = 0$, the latter with the c glide at $y = \tfrac{1}{4}$.

The diffraction pattern of the modulated phase is invariant under the following point-group operations:

$$m_x = \begin{pmatrix} \bar{1} & & & \\ & 1 & & \\ & & 1 & \\ & & & \bar{1} \end{pmatrix}, m_y = \begin{pmatrix} 1 & & & \\ & \bar{1} & & \\ & & 1 & \\ & & & 1 \end{pmatrix}, m_z = \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & \bar{1} & \\ & & & 1 \end{pmatrix}.$$

The diagonal matrices apply to indices *hklm* and are valid for all observed types of satellites. Hence, the Laue group for each of the *A* and *B* satellites is $\frac{2}{m'}\frac{2'}{m}\frac{2'}{m}$, where a prime denotes a sign reversal for the fourth index.

Let us now turn to the *A*1 satellites. These reflexions occur around extinct main reflexions and, according to Janner, Janssen & de Wolff (1979), the components of $\mathbf{q}^*$ are $\sigma = (\alpha_1,0,1)$ with $\alpha_1 \simeq 0{\cdot}178$. A basis in R_4^* is, therefore, $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*,\mathbf{q}^* + \mathbf{e}^*$ $(= \alpha_1\mathbf{a}^* + \mathbf{c}^* + \mathbf{e}^*)$. Reciprocal to that we find a basis in R_4 with $\mathbf{s}_1 = \mathbf{a} - \alpha_1\mathbf{e}$, $\mathbf{s}_2 = \mathbf{b}$, $\mathbf{s}_3 = \mathbf{c} - \mathbf{e}$, $\mathbf{s}_4 = \mathbf{e}$, where $\mathbf{e}$ is the basic vector in the fourth direction. This is, however, a nonprimitive basis. Corresponding to the *A* centering, a primitive basis is then $\mathbf{s}_1, \frac{1}{2}(\mathbf{s}_2 + \mathbf{s}_3), \frac{1}{2}(-\mathbf{s}_2 + \mathbf{s}_3), \mathbf{s}_4$ or, in full: $\mathbf{s}_1 = \mathbf{a} - \alpha_1\mathbf{e}$, $\mathbf{s}_2 = \frac{1}{2}(\mathbf{b} + \mathbf{c} - \mathbf{e})$, $\mathbf{s}_3 = \frac{1}{2}(-\mathbf{b} + \mathbf{c} - \mathbf{e})$, $\mathbf{s}_4 = \mathbf{e}$. The superspace-group translations are $(1,0,0,-\alpha_1)$, $(0,\frac{1}{2},\frac{1}{2},-\frac{1}{2})$, $(0,-\frac{1}{2},\frac{1}{2},-\frac{1}{2})$, $(0,0,0,1)$. The standard setting for $\sigma = (\alpha,0,1)$ is $\sigma_{\rm st} = (1,0,\gamma)$. This is compatible with an *L* lattice, whose superspace-group symmetry (holohedry) is $N^{Cmmm}_{1\,1\,\bar{1}}$. In the non-standard setting, as used above, the symmetry of the lattice is described as $N^{Ammm}_{\bar{1}\,1\,1}$ (Janssen, 1979). The combination of this lattice with the three-dimensional space group *Abma* allows two combinations as maximal superspace groups: $N^{Abma}_{\bar{1}\,1\,1}$ and $N^{Abma}_{\bar{1}\,s\,1}$. This means that the symmetry of the modulated structure is described either by one of these groups or by one of their subgroups, if parts of their symmetry elements are absent.

A rigorous determination would require an analysis of the phases of the modulation waves, which is not possible in this study. We assume, admittedly rather arbitrarily, that the maximum symmetry is fulfilled and, thus, we only have to decide between $N^{Abma}_{\bar{1}\,1\,1}$ and $N^{Abma}_{\bar{1}\,s\,1}$. The generating symmetry operations for the first group are $[m_x\colon (x,y,z,t) \rightarrow (\frac{1}{2} - x, \frac{1}{2} + y, z, -t)]$, $[m_y\colon (x,y,z,t) \rightarrow (x,\bar{y},z,t)]$, $[m_z\colon (x,y,z,t) \rightarrow (\frac{1}{2} + x, y, \frac{1}{2} - z, t)]$, and for the second $[m_x\colon (x,y,z,t) \rightarrow (\frac{1}{2} - x, \frac{1}{2} + y, z, -t)]$, $[m_y\colon (x,y,z,t) \rightarrow (x, \bar{y}, z, t + \frac{1}{2})]$, $[m_z\colon (x,y,z,t) \rightarrow (\frac{1}{2} + x, y, \frac{1}{2} - z, t)]$. A general point in superspace $x\mathbf{a} + y\mathbf{b} + z\mathbf{c} + t\mathbf{e}$ is thereby denoted as (x,y,z,t). Due to the translation $(0,\frac{1}{2},\frac{1}{2},\frac{1}{2})$, both groups require a general extinction rule for *hklm*: $k + l + m = 2n + 1$. In addition, however, $N^{Abma}_{\bar{1}\,s\,1}$ would require that all reflexions *h*0*lm* with *m* odd should be absent. Since this is clearly not the case we find that $N^{Abma}_{\bar{1}\,1\,1}$ (or one of its subgroups) is compatible with the *A*1 satellites.

For the explanation of the *A*2 satellites we again use the general extinction rule $k + l + m = 2n + 1$. This rule means that around extinct main reflexions with $k + l$ odd only odd-order satellites are allowed, whereas around nonextinct main reflexions with $k + l$ even, *m* must also be even. Actually, *A*2 satellites are found with $m = 2$ and we conclude that *A*1 and *A*2 satellites are first- and second-order satellites belonging to the same modulation wave.

The *B* satellites accompany the *A*1 satellites around extinct main reflexions. They are much less intense and neither second-order reflexions nor reflexions in the *hk*0 reciprocal plane could be observed. This is not, of course, a proof against their existence. At the present stage it is not possible to make definite statements about their real quality and it has already been mentioned that their independence has been doubted (de Wolff, 1980). If these satellites are finally established as independent from the *A* satellites, then an appropriate description for the two modulation waves would require (3 + 2) dimensions. For the Bravais class $N^{Ammm}_{p\,2\,1\,1}$ ($L^{Cmmm}_{p\,1\,1\,2}$ in the original tables of Janner & Janssen, 1979) which would then apply to γ-C3Mn, the possible (3 + 2)-dimensional superspace groups have been determined (Janssen, 1979).

(IV) *A model for the one-dimensionally modulated structure and the determination of an approximate average amplitude*

Having determined the (3 + 1)-dimensional space group as being at least a subgroup of $N^{Abma}_{\bar{1}\,1\,1}$ and assuming that it is this group itself, we can apply its symmetry elements to the basic structure which provides us with a model of the modulated structure. Fig. 5 is an attempt to visualize schematically the modulated structure, but only insofar as the Mn and Cl atoms are concerned. For simplicity the modulation waves are assumed to be sinusoidal; they have a wavelength of about 41 Å and their amplitudes are parallel to *c*.

At $y = 0$ and $0{\cdot}5$ we find the planes containing Mn and Cl(2). Curved strata at $z = 0$, $0{\cdot}5$ and $1{\cdot}0$ are shown. The upper and lower curves in each stratum represent the modulation waves of the Cl(2) atoms and the intermediate ones those of Mn. Straight lines signify the connexions between Mn and the apexes of the octahedra, *i.e.* the Cl(2) atoms. The respective obliqueness denotes the tilt system of the octahedra in the basic structure and is bound up with hydrogen bonding (*cf.* Depmeier, 1979). The distance between two parallel lines corresponds to the *a* lattice constant in the basic structure.

Planes at $y = 0{\cdot}25$ and $0{\cdot}75$ contain the Cl(1) atoms. Arrows pointing up and down designate atoms above and below the planes of Mn in the basic structure. This puckering is due to the tilting of the octahedra. It can be seen that mutually inclined lines Cl(2)–Mn–Cl(2) at $y = 0$ or $0{\cdot}5$ are connected to a Cl(1) atom at $y = 0{\cdot}25$ pointing down. This is a consequence of the arrangement of the $\mathrm{MnCl_6}$ octahedra in the structure: the Cl(1)

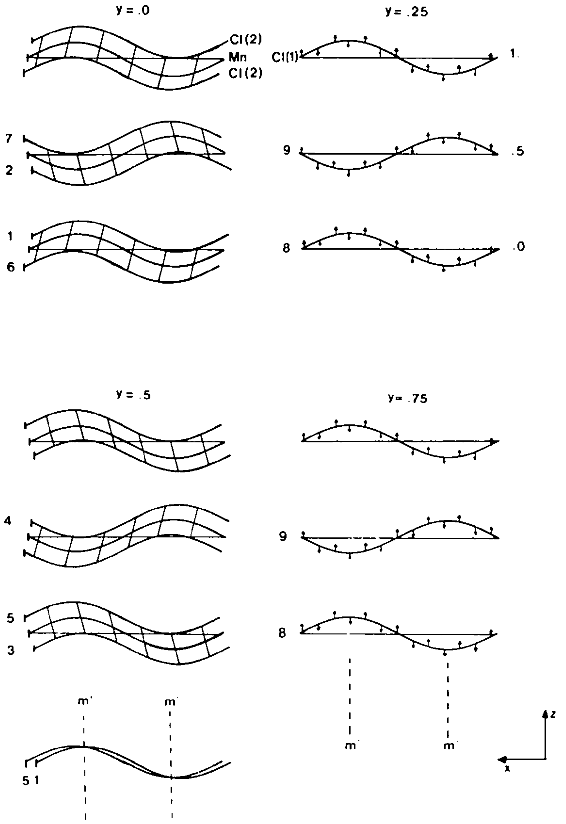

Fig. 5. Schematic representation of the proposed modulated structure of γ-C3Mn, demonstrating the symmetry elements of superspace group $N^{Abma}_{\bar{1}11}$ (in conjunction with Table 3). Four sections through the structure at $y = 0{\cdot}0$, $0{\cdot}25$, $0{\cdot}5$ and $0{\cdot}75$ are shown, each of which contains three curved strata (left side) or three curves (right side) at heights $z = 0{\cdot}0$, $0{\cdot}5$ and $1{\cdot}0$. The curved strata consist again of three curves, the outward ones representing the modulation functions of Cl(2) atoms, the inner ones representing that of Mn. Straight lines denote the connexion Cl(2)–Mn–Cl(2) (this is the height of the octahedron) and the distance between these lines corresponds to the *a* lattice parameter in the undistorted structure. The curves on the right side represent the modulation function for Cl(1) atoms. Arrows pointing up and down denote Cl(1) atoms above or below the plane of Mn in the undistorted structure. The numbering 1–9 is used in Table 3 to demonstrate the symmetry elements of N^{Abma}_{111}. Mirror planes m' are formed due to the $\begin{pmatrix} b \\ \bar{1} \end{pmatrix}_x$ symmetry operation.

atoms serve as hinges for the otherwise nearly rigid octahedra. Table 3 lists the superspace-group elements (mirror and glide planes only) of $N^{Abma}_{\bar{1}11}$ ($\equiv N^{Accn}_{\bar{s}ss}$). To exemplify the effect of their action on the modulated structure some symmetry-related pairs of curves are included in the table. To this end several curves in Fig. 5 have been numbered in the margin.

Note that the functions for Cl(1) atoms must be symmetrical (m') because, in the basic structure, these atoms lie on the *b* glide (*cf.* de Wolff, 1977). It may be further noted that no symmetry elements exist which transform atoms from planes at $y = 0$ into those at $y = \frac{1}{4}$. This might provide a starting point for an explanation of different wavelengths concerning the *A* and *B* satellites, if that difference exists.

No information is available so far on the behavior of the propylammonium chains enclosed between the perovskite-like layers. However, it is highly probable that they follow the bending of the layers.

The model also provides an explanation for the longitudinal component of the modulation: the bending of the perovskite-like layer as a whole entails that Cl(2) atoms which belong to a crest of a transverse wave have elongated distances from each other in the *x* direction, whereas Cl(2) atoms which are in troughs have shortened distances. These shorter and longer distances are periodic with the transverse wave. This argument also applies to the Cl(1) atoms but not to Mn, N and C; hence, it seems that the latter atoms do not take part in the longitudinal component of the modulation waves.

An attempt was made to confirm the proposed model and to determine the amplitude of an 'average' modulation wave. For this purpose the modulated structure was approximated as a sixfold superstructure and only Mn and Cl atoms were taken into account. As deduced above, the Bravais group $N^{Ammm}_{\bar{1}11}$ contains among its translations $(0,\frac{1}{2},\frac{1}{2},\frac{1}{2})$. This corresponds to a body-centering in the y,z,t space and, consequently, space group $I1m1$ was chosen for the superstructure.

Corresponding to a sine curve, appropriate deviations from the *z* coordinates of the basic structure (δ-C3Mn) were attached to the atoms. Amplitudes were between $0{\cdot}2$ and $1{\cdot}2$ Å. For each value a structure factor calculation was performed for the 55 first-order satellite reflexions measured. Indices $h,0,l \pm$

Table 3. *Symmetry elements of superspace group* $N^{Abma}_{\bar{1}11}$ ($\equiv N^{Accn}_{\bar{s}ss}$) *and their action on the modulation functions of atoms* Cl(2) *and* Cl(1), *given in terms of pairs of symmetry-related curves as numbered in Fig.* 5

$(0,\frac{1}{2},\frac{1}{2},\frac{1}{2})$	1 → 4	2 → 3	$8_{0\cdot25}$ $9_{0\cdot75}$
$\begin{pmatrix} b \\ \bar{1} \end{pmatrix}_x$	1 → 5	3 → 6	$9_{\uparrow 0\cdot25} \rightarrow 8_{\uparrow 0\cdot75}$
$\begin{pmatrix} c \\ \bar{s} \end{pmatrix}_x$	1 → 7	4 → 5	$8_{\uparrow} \rightarrow 9_{\uparrow}$
$\begin{pmatrix} m \\ 1 \end{pmatrix}_y$	1 → 1	6 → 6	$8_{0\cdot25} \rightarrow 8_{0\cdot75}$
$\begin{pmatrix} c \\ s \end{pmatrix}_y$	1 → 4	2 → 3	$8_{\uparrow} \rightarrow 9_{\uparrow}$
$\begin{pmatrix} a \\ 1 \end{pmatrix}_z$	1 → 2	3 → 4	$8_{\downarrow} \rightarrow 9_{\uparrow}$
$\begin{pmatrix} n \\ s \end{pmatrix}_z$	1 → 3	2 → 4	$8_{\uparrow 0\cdot25} \rightarrow 8_{\downarrow 0\cdot75}$

1 had thereby to be transformed into $6h \pm 1,0,l$ to be compatible with the program (XRAY system, 1976). Fig. 6 is a plot of the conventional R value *vs* amplitude. The best R value was 0·21 for an amplitude of 0·5 Å. This value gives at least an overall estimation of the magnitude of the amplitudes. It must be kept in mind, however, that the amplitudes for independent atoms may have quite different values. The small number of observations used, did not, however, allow for a more precise determination of the individual amplitudes.

To get a still better confirmation for the model all 108 second-order satellites around the main reflexions $h0l$ with $h = 0,1,2,3,4$ and $l = 2,4, \ldots, 24$ were now introduced into the 0·5 Å model. Only three of them could be observed on precession films and their intensities were estimated by comparison: reflexions 0,0,10,2 and 0,0,12,2 were thereby taken to be equal to 3,0,15,1 and 0,0,22,2 equal to 1,0,15,$\bar{1}$. All other second-order satellites were arbitrarily given an intensity equal to one third of that of 0,0,22,2. The result of the structure factor calculation yielded an R of 0·34 and the three observed second-order satellites came out with the highest values in the F_c calculation.

The results seem to be sufficiently convincing to assume that the proposed model is basically correct. Of course, a more precise determination is necessary.

The value for the amplitude as obtained from the intensities of the satellites may be compared with the result of another method to estimate the amplitudes of transverse distortion waves. This was given by Korekawa (1967) and is based on the fact that such distortion waves exhibit a marked dependence of the intensities of main and satellite reflexions on the index which runs in the direction of the amplitude, *e.g.* on l if the amplitude is parallel to c, as it is in our case. The intensities of the main and satellite reflexions follow squared Bessel functions of zero and first order, respectively. The squared Bessel function of zero order takes the value of zero for the first time for the argument being about 2·4: $I(00l) = J_0^2(2\pi lA) = 0$ if $2\pi lA = 2\cdot4$, A is the amplitude. From precession photographs it can be established by inspection that the 0,0,20 main reflexion of the modulated phase is very weak compared with the unmodulated phase. We assume that its intensity has become zero at the phase transition and the above equation gives an amplitude of about 0·51 Å.

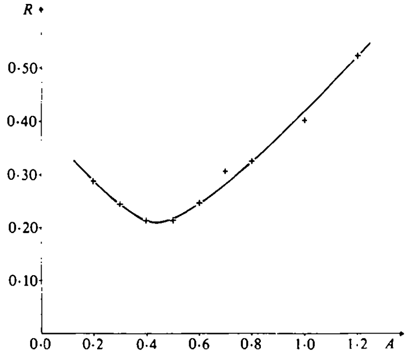

Fig. 6. The R value as a function of the 'average' modulation amplitude A. 55 $h0l$ first-order satellite reflexions were used for the structure factor calculations.

Experiment has shown that a drastic increase of the unit-cell volume occurs at the $\delta \rightarrow \gamma$ phase transition (*cf.* Fig. 7 of Depmeier, Felsche & Wildermuth, 1977). An increased pressure is expected to counteract the volume increase. A high-pressure experiment would therefore be worthwhile, where one can expect the $\delta \rightarrow \gamma$ transition point to shift to higher temperatures with increasing pressure. Using the Clausius–Clapeyron equation with $\Delta V = 10$ Å^3, the transition temperature 344 K and the latent heat $\Delta H = 796$ J mol^{-1} (Depmeier, Felsche & Wildermuth, 1977), one obtains an estimation of $6\cdot6 \times 10^3$ K Pa^{-1}.

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Organometallic Structures. IV.* 1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3-μ-dimethyliminiocarbene-2,3-μ-hydrido-*triangulo*-triiron

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Abstract

(μ-H) [μ-C=N(CH$_3$)$_2$]Fe$_3$(CO)$_{10}$, M_r = 504·74, m.p. 435–437 K (dec.), crystallizes (red prisms or needles elongated along [001]) in space group $P2_12_12_1$, with Z = 4, a = 16·255 (6), b = 12·148 (4), c = 9·428 (3) Å, V = 1861·7 (11) Å^3, D_c = 1·801 Mg m^{-3}, F(000) = 1000. The structure was refined to R = 4·84% for the correct enantiomorph (1423 diffractometer intensities, Mo $K\alpha$ radiation, μ = 2·253 mm^{-1}). The molecular structure is similar to that of the Ru analogue, thus confirming conclusions drawn from mass spectrometric and Mössbauer measurements. The shortening of the doubly bridged Fe–Fe bond compared to the unbridged Fe—Fe bonds is accounted for in terms of the different coordination numbers of the Fe atoms involved. The molecules in their crystal environment show appreciable deviations from the mirror symmetry anticipated from the chemical formula, and this is in accordance with the chiral space group of the crystals.

1. Introduction

The title compound was first prepared by Rhee, Ryang & Tsutsumi (1968); the correct formula and structure, inferred from a combination of mass spectrometric and Mössbauer measurements, were proposed by Greatrex, Greenwood, Rhee, Ryang & Tsutsumi (1970). The present analysis confirms their conclusions and provides geometrical information for comparison with analogous molecules; in particular, there is considerable current interest in transition-metal complexes with bridging hydride ligands (Bau & Koetzle, 1978; Churchill, 1978; Bau, Teller, Kirtley & Koetzle, 1979). The structure of the Ru analogue has been reported (Churchill, DeBoer, Rotella, Abel & Rowley, 1975) as well as those of many related Fe, Ru and Os compounds.

2. Experimental

The compound was prepared by Altman & Welcman (1979) from the reaction of Fe$_3$(CO)$_{12}$ and chlorodimethylformiminium chloride. A cubic crystal (edge ~0·2 mm) was sealed in a capillary (the crystals appear to decompose slowly in air). Crystal data (Philips PW 1100 four-circle diffractometer) are given in the *Abstract*. The intensities of 1659 reflections were measured [Mo $K\alpha$ radiation; $\omega/2\theta$ technique, scan width 1·4° in ω, scan speed 0·05° (ω) s^{-1}, background measured for 28s at each of the scan extremities]; 219 reflections had $I < 3\sigma(I)$ and were omitted. In the final stage of the refinement another 17 reflections were found to have been affected by spurious counts and were also omitted. Thus 244 parameters were determined with 1423 measured intensities. Intensities were not corrected for absorption ($\mu R \sim 0{\cdot}2$).

The positions of the three Fe and fourteen other

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* Part III: Cais, Dani, Herbstein & Kapon (1978).

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