Acta Cryst. (1985). B41, 330–336

Modulated Crystal Structure of $[N(CH_3)_4]_2[CoCl_4]$

By E. Fjaer†

Department of Physics, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, Scotland

(*Received* 26 *November* 1984; *accepted* 18 *March* 1985)

Abstract

The crystal structure of tetramethylammonium tetrachlorocobaltate(II) (TMATC-Co) in a commensurate phase between 279·5 and 281·2 K was investigated by X-ray diffraction. The phase occurs as an incommensurate modulation temporarily locks in at $\mathbf{q} = \frac{2}{5}\mathbf{c}^*$. The basic structure was found to be close to the structure others have reported for the normal phase (above 293·8 K). The modulation was found to involve, for the $CoCl_4$ group, a translation along the $\hat{x}$ axis with amplitude 0·21 Å, a rotation around the $\hat{y}$ axis with amplitude 3·2° and a rotation around the $\hat{z}$ axis with amplitude 9·9°. The agreement with previously reported ESR results is limited. The $N(CH_3)_4$ groups are seen to follow the movements of neighbouring $CoCl_4$ groups. A reasonable agreement between the calculated and measured values for the structure factors of the second-order satellites supports the assumption that the modulation is very nearly a plane wave.

1. Introduction

TMATC-Co has attracted interest because of the sequence of incommensurate and commensurate phases at and below room temperature. Starting from the high-temperature normal phase (I), an incommensurate modulation appears on cooling below 293·8 K with wavenumber $0{\cdot}42 \gtrsim \zeta \geq 0{\cdot}4$ (phase II). At 281·2 K the modulation locks in at $\zeta = \frac{2}{5}$ (phase III); ζ decreases again from 279·5 to 277·7 K (phase IV) when it discontinuously jumps to $\zeta = \frac{1}{3}$ (phase V) (Hasebe, Mashiyama & Tanisaki, 1980).

The crystal structure of the normal phase was investigated by Wiesner, Srivastava, Kennard, DiVaira & Lingafelter (1967). The space group was found to be *Pnma* (D_{2h}^{16}) with $Z = 4$. In the following we prefer to use the orientation of the unit cell that is most commonly used for this material, and accordingly denote the space group as *Pmcn*. The space group of phase III is found to be $P2_1cn$ (C_{2v}^9) with $Z = 20$, and that of phase V $P112_1/n$ (C_{2h}^5) with $Z = 12$ (Hasebe, Mashiyama & Tanisaki, 1982). ESR studies indicate that the different structures involve a rotation of the $CoCl_4$ groups along an axis parallel to the modulation wavevector (Tsuchida, Imaizumi, Abe & Suzuki, 1982; Fukui, Abe & Tsuchida, 1983).

The aim of this work is to determine the structure of phase III by means of X-ray diffraction. We describe the structure as a (commensurate) modulation superimposed on a basic structure. The modulation is initially assumed to be a plane wave. The validity of this assumption is tested by comparing the measured and calculated intensities of a set of second-order reflections.

The space group of phase III is polar, and dielectric measurements (Sawada, Shiroishi, Yamamoto, Takashige & Matsuo, 1978) showed that the phase is indeed ferroelectric, with a spontaneous polarization $P_s \lesssim 5 \times 10^{-3}\mu C\ cm^{-2}$. This implies that the modulation wave couples to a zone-centre polarization mode (Mashiyama, 1980). However, this low value of P_s corresponds to a displacement of the $CoCl_4^{2-}$ groups relative to the $N(CH_3)_4^+$ groups of only 0·0007 Å, which we cannot hope to detect with any accuracy. Hence we shall ignore the zone-centre mode in this work.

The structure is analysed in a formalism similar to that used by Iizumi, Axe, Shirane & Shimaoka (1977) in the study of incommensurate K_2SeO_4. Both materials are members of the A_2BX_4 family and have the same space group in the high-temperature phase (I). The two structures are also very similar; the main difference is that the K atoms in K_2SeO_4 are replaced with the complex groups, $N(CH_3)_4$, in TMATC-Co. The orientations of these groups are probably disordered in the high-temperature phase (Blinc, Burgar, Slak, Rutar & Milia, 1979), but they may be at least partially ordered in phase III.

The two works we shall mainly refer to in this work, Wiesner *et al.* (1967) and Iizumi *et al.* (1977), both use an orientation of the unit cell different from ours. Corresponding axes are: this work: (**a**, **b**, **c**); Wiesner *et al.*: (**b**, **c**, **a**); Iizumi *et al.*: (**c**, **b**, **a**).

2. Symmetry of the modulated structure

The structure of phase III is described as a modulation superimposed on a basic structure. The basic structure is obtained by taking into account only those reflections that are also present in phase I. Thus the

† Permanent address: Department of Physics, The Norwegian Institute of Technology, N-7034 Trondheim-NTH, Norway.

0108-7681/85/050330-07$01.50 © 1985 International Union of Crystallography

unit cell of the basic structure corresponds to the unit cell of phase I, and the space group of phase I was also assumed for the basic structure. The unit cell of the basic structure is shown schematically in Fig. 1. It contains three independent molecular groups, one $CoCl_4$ and two $N(CH_3)_4$, denoted (I), (II*a*) and (II*b*) respectively. The four equivalents of each group are mapped out by the symmetry elements $(E|000)$, $(C_2^z|\frac{1}{2}\frac{1}{2}\frac{1}{2})$, $(C_2^y|0\frac{1}{2}\frac{1}{2})$, and $(C_2^x|\frac{1}{2}00)$, respectively.

Denoting by $\mathbf{x}_\mu^0$ the position of an atom μ in the basic structure, and by $\mathbf{u}_\mu$ its displacement due to the modulation, the actual position of the atom is $\mathbf{x}_\mu = \mathbf{x}_\mu^0 + \mathbf{u}_\mu$. For a plane wave modulation with wavevector $\mathbf{q}$ and phase φ.

$$\mathbf{u}_\mu = \tfrac{1}{2}\mathbf{U}_\mu \exp(i\psi_\mu) + \text{c.c.}, \tag{1}$$

where $\psi_\mu = 2\pi\mathbf{q}\,.\,\mathbf{x}_\mu^0 + \varphi$.

If the atom belongs to a rigid molecular group, then $\psi_\mu \to 2\pi\mathbf{q}\,.\,(\mathbf{x}_\mu^0 - \mathbf{X}_\mu^0) + \varphi$, where $\mathbf{X}_\mu^0$ is the position of the atom relative to the centre of mass of the molecular group.

The eigenvectors $\mathbf{U}_\mu$ are subject to symmetry restrictions which we shall introduce, following Iizumi *et al.* (1977), by expressing $\mathbf{U}_\mu$ as a linear combination of symmetry-adopted modes $\mathbf{s}_\lambda$:

$$\mathbf{U}_\mu = \sum_\lambda A_\lambda \boldsymbol{\varepsilon}_\lambda^\mu, \tag{2}$$

$$\text{where } \boldsymbol{\varepsilon}_\lambda^\mu = \begin{cases} \mathbf{s}_\lambda & \text{for translational modes} \\ \mathbf{s}_\lambda \times \mathbf{X}_\mu^0 & \text{for rotational modes.} \end{cases}$$

The coefficients A_λ represent the contribution from each symmetry-adopted mode in $\mathbf{U}_\mu$. In §5(*b*) we shall obtain these coefficients from the experimental data.

The modulation wavevector $\mathbf{q} = \frac{2}{5}\mathbf{c}^*$ lies on the Σ line in the Brillouin zone [*i.e.* on the same line as the modulation in K_2SeO_4; see Iizumi *et al.* (1977) and § 1]. The space group of the whole structure is C_{2v}^9

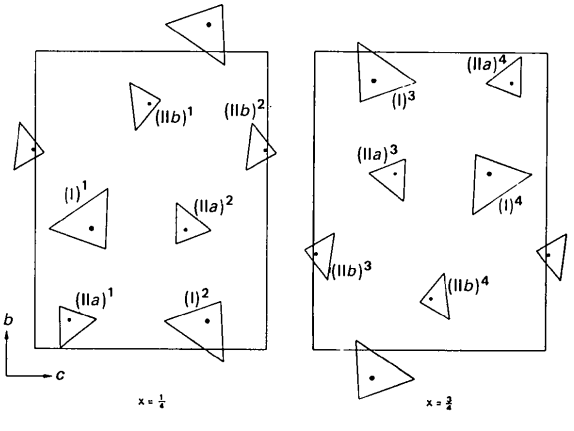

Fig. 1. Schematic picture of the basic structure of TMATC-Co. The molecules are situated in the two mirror planes at $x = \frac{1}{4}$ and $x = \frac{3}{4}$. Data are from Wiesner *et al.* (1967).

if the modulation belongs to the irreducible representation Σ_3 (different from K_2SeO_4), with phase $\varphi = 0$. In the notation of de Wolff, Janssen & Janner (1981) the superspace group of the modulated structure is then P_{S11}^{mcn}.

Assuming that deformations of the molecular groups can be ignored, there are 18 symmetry-adopted modes transforming as Σ_3. These are:

$$\begin{aligned}
&\mathbf{s}_1 = (\mathbf{T}_a, 0, 0, 0, 0, 0) && \mathbf{s}_2 = (\mathbf{T}_s, 0, 0, 0, 0, 0)\\
&\mathbf{s}_3 = (0, \mathbf{T}_a, 0, 0, 0, 0) && \mathbf{s}_4 = (0, \mathbf{T}_s, 0, 0, 0, 0)\\
&\mathbf{s}_5 = (0, 0, \mathbf{T}_a, 0, 0, 0) && \mathbf{s}_6 = (0, 0, \mathbf{T}_s, 0, 0, 0)\\
&\mathbf{s}_7 = (0, 0, 0, \mathbf{R}_a^y, 0, 0) && \mathbf{s}_8 = (0, 0, 0, \mathbf{R}_s^y, 0, 0)\\
&\mathbf{s}_9 = (0, 0, 0, \mathbf{R}_a^z, 0, 0) && \mathbf{s}_{10} = (0, 0, 0, \mathbf{R}_s^z, 0, 0)\\
&\mathbf{s}_{11} = (0, 0, 0, 0, \mathbf{R}_a^y, 0) && \mathbf{s}_{12} = (0, 0, 0, 0, \mathbf{R}_s^y, 0)\\
&\mathbf{s}_{13} = (0, 0, 0, 0, \mathbf{R}_a^z, 0) && \mathbf{s}_{14} = (0, 0, 0, 0, \mathbf{R}_s^z, 0)\\
&\mathbf{s}_{15} = (0, 0, 0, 0, 0, \mathbf{R}_a^y) && \mathbf{s}_{16} = (0, 0, 0, 0, 0, \mathbf{R}_s^y)\\
&\mathbf{s}_{17} = (0, 0, 0, 0, 0, \mathbf{R}_a^z) && \mathbf{s}_{18} = (0, 0, 0, 0, 0, \mathbf{R}_s^z).
\end{aligned} \tag{3}$$

The six components of each $\mathbf{s}_\lambda$ represent translation of the groups (I), (II*a*) and (II*b*), and rotation of (I), (II*a*) and (II*b*), respectively. The translational components are:

$$\begin{aligned}
\mathbf{T}_a &= \tfrac{1}{2}(100, 100, 100, 100)\\
\mathbf{T}_s &= \tfrac{1}{2}(100, 100, -100, -100),
\end{aligned} \tag{4}$$

where the four subvectors describe the displacements of the four corresponding symmetry equivalents in the basic structure. For example, the mode $\mathbf{s}_4$ represents a translation of the groups $(\text{II}a)^1$ and $(\text{II}a)^2$ in positive x direction, and $(\text{II}a)^3$ and $(\text{II}a)^4$ in negative x direction. The rotational modes, describing angles of rotation, are:

$$\begin{aligned}
\mathbf{R}_a^y &= \tfrac{1}{2}(010, 010, 0{-}10, 0{-}10)\\
\mathbf{R}_s^y &= \tfrac{1}{2}(010, 010, 010, 010)\\
\mathbf{R}_a^z &= \tfrac{1}{2}(001, 00{-}1, 001, 00{-}1)\\
\mathbf{R}_s^z &= \tfrac{1}{2}(001, 00{-}1, 00{-}1, 001).
\end{aligned} \tag{5}$$

The suffixes *s* and *a* indicate whether the modes are symmetric or antisymmetric with respect to inversion. As shown by Iizumi *et al.* (1977) this property has the consequence that

$$\begin{aligned}
&A_\lambda \text{ must be real for } a\text{-type modes}\\
&A_\lambda \text{ must be imaginary for } s\text{-type modes.}
\end{aligned} \tag{6}$$

3. Principles of data analysis

The expression for the structure formula was derived by de Wolff (1974) and Yamamoto (1982). After a slight modification needed to include rigid molecular

groups, the result is

$$F_{\mathbf{G},m} = \sum_{\mu} f^{\mu}_{\mathbf{G},m} \exp[-W_{\mu}(\mathbf{G}, m)] \times \exp[2\pi i(\mathbf{G}.\mathbf{x}^0_{\mu} + m\mathbf{q}\mathbf{X}^0_{\mu})] \times \frac{1}{M}\sum_{v=1}^{M} \exp\{2\pi i(\mathbf{G}+m\mathbf{q}).\mathbf{u}_{\mu}[\psi_{\mu}(v)] + im\psi_{\mu}(v)\} \quad (7)$$

with $\psi_{\mu}(v) = 2\pi[\mathbf{q}.(\mathbf{x}^0_{\mu} - \mathbf{X}^0_{\mu}) + v/m]$.

Here $\mathbf{G}+m\mathbf{q}$ represents the location in reciprocal space of the actual reflection, m is the satellite order, $f^{\mu}_{\mathbf{G},m}$ is the atomic form factor, $\exp[-W_{\mu}(\mathbf{G},m)]$ is the Debye–Waller factor, M is the number of basic unit cells in the unit cell of the modulated structure (here $M=5$), and the sum over μ includes all atoms in the basic unit cell.

To obtain the basic structure, we put $\mathbf{u}_{\mu}=0$ and restrict our attention to the main reflections ($m=0$). Formula (7) then reduces to the standard expression for the structure factor used in X-ray diffraction. Starting from the structure determined by Wiesner *et al.* (1967), a simple least-squares refinement rapidly converged to give the basic structure.

In some cases the modulated structure may be solved by equally simple means. As pointed out by Yamamoto (1982), the structure factor (7) is nearly linear in $\mathbf{u}_{\mu}$ if the displacements are small, so that the solution of the modulated structure might be established simply through a least-squares refinement procedure, starting from the basic structure. In our case, this technique was tried but did not converge, however.

One way of actively solving the structure is to analyse the so-called 'partial Patterson function', *i.e.* a Patterson function $P_s(\mathbf{x})$ calculated only from the first-order ($m=\pm 1$) satellite intensities. Interpretation of $P_s(\mathbf{x})$ is generally complicated, but it can be shown (Cochran, 1968) that at a point $\mathbf{x}^0_{\mu\nu} \equiv \mathbf{x}^0_{\mu} - \mathbf{x}^0_{\nu}$ the contribution to $P_s(\mathbf{x}^0_{\mu\nu})$ from the two atoms μ and ν can be approximated by

$$\frac{1}{M}\sum_{v=1}^{M} \mathbf{u}_{\mu}[\psi_{\mu}(v)].\mathbf{u}_{\nu}[\psi_{\nu}(v)]. \quad (8)$$

If contributions from other pairs of atoms can be ignored, equation (8) connects the displacements of the two atoms. In our case it was only possible to establish a sufficient number of equations to identify the displacements of the heaviest atoms in the structure. Furthermore, these equations only give the relations between the displacements. The absolute values were estimated from the temperature factors β^{Co}_{ij} of the Co atoms, by assuming

$$\langle u^x_{\mathrm{Co}}.u^x_{\mathrm{Co}}\rangle = \beta^{\mathrm{Co}}_{xx} - \tfrac{1}{2}[\beta^{\mathrm{Co}}_{yy} + \beta^{\mathrm{Co}}_{zz}]. \quad (9)$$

Finally, we tried to solve the structure by the 'direct method', *i.e.* the method in which the phases $\varphi_{\mathbf{G},m}$ of the structure factors are estimated, so that the complete values $F_{\mathbf{G},m} = |F_{\mathbf{G},m}|\exp(i\varphi_{\mathbf{G},m})$ can be obtained. A simple estimate $\langle\varphi_{\mathbf{G},m}\rangle$ for the phase of a satellite is found by combining the phases of another satellite and an appropriate main reflection (Fan, Yao, Main & Woolfson, 1983):

$$\langle\varphi_{\mathbf{G},m}\rangle = \varphi_{\mathbf{G}',0} + \varphi_{\mathbf{G}-\mathbf{G}',m}. \quad (10)$$

The process of mapping out estimates $\langle\varphi_{\mathbf{G},m}\rangle$ is simplified since the phases $\varphi_{\mathbf{G}',0}$ of the main reflections are known from the study of the basic structure. In our case the work is further simplified by the fact that the basic structure is centrosymmetric. This restricts the structure factors of the main reflections to be real, and those of the first-order satellites to be imaginary. [Notice that the formula derived by Iizumi *et al.* (1977) – which allows the structure factor of the satellites to have real and imaginary parts – is not correct.]

Now, returning to the structure factor formula (7), it is clear that a linearization in $\mathbf{u}_{\mu}$ is valid for sufficiently small values of $|\mathbf{G}+m\mathbf{q}|$. Introducing expressions (1) and (2), the linearized formula is:

$$F_{\mathbf{G},m} = i\sum_{\lambda}[Q^{+}_{\lambda}(\mathbf{G},m)A_{\lambda} + Q^{-}_{\lambda}(\mathbf{G},m)A^{*}_{\lambda}], \quad (11)$$

where

$$Q^{\pm}_{\lambda}(\mathbf{G},m) = \pi\sum_{\mu} Q^{\mu}_{\lambda}(\mathbf{G},m).\frac{1}{M}\sum_{v=1}^{M}\exp[i\psi_{\mu}(v) \times (m\pm 1)] \quad (12)$$

and

$$Q^{\mu}_{\lambda}(\mathbf{G}, m) = f^{\mu}_{\mathbf{G},m}.\exp[-W_{\mu}(\mathbf{G}, m)] \times \exp[2\pi i(\mathbf{G}.\mathbf{x}^0_{\mu} + m\mathbf{q}.\mathbf{X}^0_{\mu})] \times (\mathbf{G}+m\mathbf{q}).\boldsymbol{\varepsilon}^{\mu}_{\lambda}.$$

Using plausible values for the temperature factors, it is straightforward to calculate the coefficients $Q^{\pm}_{\lambda}$. (A scale factor, needed to match the experimental observations, is determined in the analysis of the basic structure.) Thus, when a sufficient number of structure factors $F_{\mathbf{G},m} = |F_{\mathbf{G},m}|\exp(i\varphi_{\mathbf{G},m})$ have been obtained for small $|\mathbf{G}+m\mathbf{q}|$, the components A_{λ} can be found directly by a set of linear equations of type (11).

A set of temperature factors β^{μ}_{ij} is already available from the solution of the basic structure. These factors do, however, contain the atomic displacements due to the structure modulation. Once a set of $\mathbf{u}_{\mu}$ has been obtained, we estimate the corrected temperature factors ${}^{c}\beta^{\mu}_{ij}$ as

$${}^{c}\beta^{\mu}_{ij} = \beta^{\mu}_{ij} - \langle u^{\mu}_{i}.u^{\mu}_{j}\rangle. \quad (13)$$

4. Experimental

Single crystals of TMATC-Co were grown by slow evaporation at 307 K from an aqueous solution con-

taining a stoichiometric proportion of $[N(CH_3)_4]Cl$ and $CoCl_2 . 6H_2O$. The X-ray diffraction data were collected with an Enraf–Nonius CAD-4 four-circle X-ray diffractometer using Mo $K\alpha$ radiation.

Intensity data for 2262 main reflections, 583 first-order satellites and 223 second-order satellites were collected and corrections made for the background, Lorentz and absorption factors. Those reflections which, after subtraction of background, gave negative intensities were ignored in the further analysis. 64 of the first-order satellites were furthermore excluded because they were not well centred in the scans and therefore suspected of being recorded when the temperature deviated, or of being scattering from a nearby main reflection.

The temperature was controlled by a (nitrogen) gas-flow cooling apparatus. The data were collected at $281{\cdot}0 \pm 1{\cdot}5$ K. The large deviation indicates the experimental problems in keeping the temperature stable. Thus many of the intensities were probably measured outside the small phase III we wish to study. This problem is not considered to have any significant influence on the main reflections, but it will add an additional random error to the intensities of the first-order satellites, since their intensities change by *ca* 6% per degree at these temperatures (Hasebe *et al.*, 1980). For the second-order satellites the effect is much larger, since the higher-order components of the modulation wave may well change abruptly at the phase transitions enclosing phase III.

5. Results

5(*a*) *The basic structure*

The cell parameters of the basic structure were found to be: $a = 8{\cdot}974 \pm 0{\cdot}014$, $b = 15{\cdot}485 \pm 0{\cdot}013$, $c = 12{\cdot}253 \pm 0{\cdot}010$ Å. The positional and thermal parameters were found by a least-squares refinement of the parameters obtained by Wiesner *et al.* (1967). One cycle refining the scale factor and the temperature factors, followed by three cycles refining the scale factor, positional and temperature factors brought the final R factor to 0·113. Attempts to correct for secondary extinction failed to reduce the R factor further. Wiesner *et al.* also obtained a similarly high R factor (0·111), having dismissed secondary extinction as a probable cause for the unsatisfactory fit.

Positional and thermal parameters are listed in Tables 1 and 2, while bond lengths and bond angles calculated for the molecular groups are listed in Table 3.

Table 1. *Positional parameters* ($\times 10^4$) *for the basic structure*

Estimated standard deviations are given in parentheses.

	Co	N(*a*)	N(*b*)
x	2500*	2500*	2500*
y	4065 (1)	945 (6)	8246 (6)
z	2454 (1)	1483 (7)	4928 (8)
	Cl(1)	C(1*a*)	C(1*b*)
x	2500*	2500*	2500*
y	4064 (3)	996 (13)	7365 (11)
z	622 (3)	2690 (11)	4496 (20)
	Cl(2)	C(2*a*)	C(2*b*)
x	2500*	2500*	2500*
y	5411 (2)	51 (9)	8904 (17)
z	3148 (4)	1090 (15)	4087 (19)
	Cl(3)	C(3*a*)	C(3*b*)
x	447 (3)	1200 (21)	1185 (20)
y	3374 (2)	1402 (14)	8430 (11)
z	3051 (2)	1053 (13)	5500 (18)

* Value required by symmetry.

Table 2. *Thermal parameters* ($\times 10^4$) *for the basic structure*

The temperature factor is defined by $\exp(-2\pi^2 \sum_{i,j} \beta_{ij} h_i a_i^* h_j a_j^*)$. Estimated standard deviations are given in parentheses.

	Co	N(*a*)	N(*b*)
β_{11}	649 (9)	691 (60)	602 (54)
β_{22}	419 (7)	660 (56)	500 (49)
β_{33}	440 (8)	489 (51)	614 (56)
β_{12}	†	†	†
β_{13}	†	†	†
β_{23}	2 (5)	3 (43)	−118 (45)
	Cl(1)	C(1*a*)	C(1*b*)
β_{11}	1303 (34)	2236 (238)	1883 (207)
β_{22}	1126 (30)	1501 (168)	723 (109)
β_{33}	442 (30)	445 (77)	2238 (241)
β_{12}	†	†	†
β_{13}	†	†	†
β_{23}	62 (18)	−59 (97)	−835 (139)
	Cl(2)	C(2*a*)	C(2*b*)
β_{11}	3211 (85)	2729 (271)	5104 (608)
β_{22}	479 (18)	567 (81)	1468 (213)
β_{33}	1053 (32)	1151 (141)	1037 (165)
β_{12}	†	†	†
β_{13}	†	†	†
β_{23}	−225 (21)	−344 (91)	23 (163)
	Cl(3)	C(3*a*)	C(3*b*)
β_{11}	787 (17)	2453 (198)	2039 (171)
β_{22}	1521 (27)	3473 (257)	1737 (151)
β_{33}	998 (19)	1549 (140)	3641 (274)
β_{12}	−325 (18)	2169 (194)	−810 (136)
β_{13}	272 (16)	−840 (140)	2031 (188)
β_{23}	43 (19)	−413 (158)	−1162 (172)

† Required to be zero by symmetry.

5(*b*) *The modulation*

Initial attempts to determine the coefficients A_λ with a least-squares fitting procedure were unsuccessful. In fact, at all stages of this work only marginal improvements, if any, were obtained through least-squares fitting.

Some information about the modulation was obtained through analysis of the partial Patterson function. First, it confirmed that the displacements

Table 3. *Bond lengths* (Å) *and angles* (°)

Primed atoms are related to unprimed ones by reflection in the mirror plane at $x=\frac{1}{4}$. Estimated standard deviations are given in parentheses.

Co–Cl(1)	2·245 (0·003)	C(1*a*)–N(*a*)–C(2*a*)	112 (2)
Co–Cl(2)	2·251 (0·004)	C(1*a*)–N(*a*)–C(3*a*)	110 (2)
Co–Cl(3)	2·253 (0·003)	C(2*a*)–N(*a*)–C(3*a*)	110 (2)
		C(3*a*)–N(*a*)–C(3*a*′)	106 (2)
Cl(1)–Co–Cl(2)	112·2 (0·3)		
Cl(1)–Co–Cl(3)	108·9 (0·2)	N(*b*)–C(1*b*) 1·46 (0·02)	
Cl(2)–Co–Cl(3)	108·5 (0·3)	N(*b*)–C(2*b*) 1·45 (0·03)	
Cl(3)–Co–Cl(3′)	109·7 (0·2)	N(*b*)–C(3*b*) 1·40 (0·02)	
N(*a*)–C(1*a*)	1·48 (0·02)	C(1*b*)–N(*b*)–C(2*b*)	113 (3)
N(*a*)–C(2*a*)	1.47 (0·02)	C(1*b*)–N(*b*)–C(3*b*)	112 (2)
N(*a*)–C(3*a*)	1·46 (0·02)	C(2*b*)–N(*b*)–C(3*b*)	102 (2)
		C(3*b*)–N(*b*)–C(3*b*′)	115 (3)

were mainly in the $\hat{x}$ direction, as expected from the symmetry considerations. We also obtained estimates for the modes affecting the $CoCl_4$ group. These results are given in Table 4, column 1. After correcting the temperature factors as in (13), the resulting R factor was 0·432 when this solution was tested on the 486 first-order satellites. Estimates for the remaining 12 modes could not be obtained. The validity of this analysis was somewhat reduced by the fact that we did not have intensity data for the complete set of first-order reflections, as a Patterson analysis formally requires. (Only satellites with $|\mathbf{G}+m\mathbf{q}|<1$ Å^{-1} were measured.)

Our best results were obtained by using direct methods. Starting with a set of symbols associated with the phases of the 8 strongest satellites, we were able to obtain a self-consistent set of phases for the 14 strongest satellites by application of equation (10). Combining these 14 with the 68 strongest main reflections, we obtained estimates for most of the other satellites. We then picked 33 reflections with $|\mathbf{G}+m\mathbf{q}|<0{\cdot}41$ Å^{-1} whose phases were reasonably well established (several consistent estimates for each reflection). Using the corrected temperature factors from the Patterson analysis, we could now calculate the coefficients [equation (12)] and establish 33 equations of type (11). After a least-squares reduction to 18 equations, these could be solved for the 18 variables A_λ. [Despite the fact that they are generally complex numbers, there are still only 18 free variables because of the conditions given by equation (6).]

After a trial-and-error procedure where poorly fitted reflections were omitted or had their phases changed, a best fit was found when the phases of 6 reflections were changed. Another 7 reflections with unknown phases were added to the list and had their phases determined. The solution obtained from these 40 reflections is given in Table 4, column 2.

After correcting the temperature factors as suggested by this solution, new coefficients [equation (12)] were calculated. This time the set was extended to 54 reflections. The best fit was obtained when all phases were in accordance with the previous solution. The results are given in Table 4, column 3. The solution resembes the previous one, but the resulting R factor is slightly higher. We therefore concluded that the solution could not be improved by further recycling of the process.

Starting from the previous solution (Table 4, column 2), a minor improvement was obtained by a least-squares refinement of the modes affecting the $CoCl_4$ group. Attempts to refine the remaining modes failed. This final solution is given in Table 4, column 4. The resulting R factor is seen to be 0·208. Observed and calculated structure factors have been deposited.*

In order to check whether the orientations of the $N(CH_3)_4$ groups really were affected by the modulation, the process was repeated assuming $A_\lambda=0$ for $\lambda=11, 12, \ldots, 18$. The resulting solution is given in Table 4, column 5. The final R factor was found to be 0·294 in this case.

The plane-wave assumption for the modulation was tested by calculating the structure factors for 100 second-order reflections in accordance with the best-fitted solution (Table 4, column 4). To do this consistently, we had to take into account also the radial displacements resulting from the molecule rotations, since these displacements have twice the periodicity of the modulation wave. The resulting R factor was 0·44, which implies that the disagreement $||F_{obs}|-|F_{calc}||$ is on average practically the same as for the main reflections.

6. Discussion

Our results for the basic structure are quite close to the results of Wiesner *et al.* (1967). The thermal parameters are generally higher in our case, which is to be expected since the structural modulation is contained in these parameters (13). We also notice that from our results equivalent bond lengths and angles (Table 3) are closer to each other, so that the molecules are less misshapen. This could be ascribed to the larger numbers of reflections involved in our solution, but it is worth noting that the shapes of the deformations are very similar in the two cases.

As for the displacements in the modulation, there may be room for some doubt about the results, since the least-squares fitting procedure failed to converge towards any unique solution, and the R factors for all trial solutions were rather high. However, the qualitative agreement between the various solutions (Table 4) does suggest that the solutions are generally correct. The agreement is particularly good for those

* Lists of observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42124 (34 pp.) Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Amplitudes A_λ of the symmetry-adopted modes*

	1	2	3	4	5
		Direct method		Best-fitted solutions	
	Partial Patterson function	40 reflections	54 reflections	All modes	No rotations of (II*a*) and (II*b*)
Group (I)					
A_1	−0·420	−0·362	−0·345	−0·368	−0·368
A_2	−0·005*i*	0·196*i*	0·207*i*	0·197*i*	0·197*i*
A_7	0·024	0·028	0·035	0·043	0·039
A_8	0·172*i*	0·081*i*	0·087*i*	0·105*i*	0·093*i*
A_9	0·376	0·325	0·315	0·347	0·344
A_{10}	0·144*i*	0·028*i*	0·023*i*	0·011*i*	0·002*i*
Group (II*a*)					
A_3		−0·40	−0·23	−0·40	−0·21
A_4		−0·14*i*	−0·22*i*	−0·14*i*	−0·23*i*
A_{11}		0·32	0·19	0·32	
A_{12}		0·29*i*	0·10*i*	0·29*i*	
A_{13}		0·90	0·68	0·90	
A_{14}		0·20*i*	0·11*i*	0·20*i*	
Group (II*b*)					
A_5		−0·31	−0·29	−0·31	−0·27
A_6		0·10*i*	0·04*i*	0·10*i*	0·05*i*
A_{15}		−0·57	−0·24	−0·57	
A_{16}		0·79*i*	0·45*i*	0·79*i*	
A_{17}		−0·08	0·01	−0·08	
A_{18}		0·57*i*	0·42*i*	0·57*i*	
R factor	0·432	0·229	0·235	0·208	0·294

modes which affect the $CoCl_4$ group, where even the results from the analysis of the partial Patterson function show a pattern similar to those of the other solutions. The fact that the *R* factor even for our best solution was as high as 0·208 may seem disturbing, but compared with $R = 0{\cdot}113$ for the basic structure it is probably as good as could be expected. The errors introduced by the temperature instabilities during the measurements (see §4) are also likely to increase the *R* factor.

Examining the best-fitted solution (Table 4 column 4), we find that the $CoCl_4$ group (I) is affected by the modulation by a displacement along the $\hat{x}$ axis with amplitude 0·21 Å, a rotation around the $\hat{y}$ axis with amplitude 3·2° and a rotation around the $\hat{z}$ axis with amplitude 9·9° (Fig. 2). These results show a limited agreement with the previously reported ESR results (Tsuchida *et al.*, 1982; Fukui *et al.*, 1983). Clearly, the rotation around the $\hat{z}$ axis is dominating, as shown by the ESR results, but we have also found a significant rotation around the $\hat{y}$ axis. Furthermore,

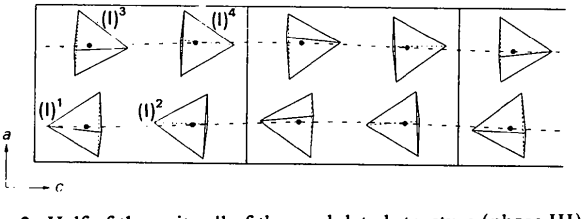

Fig. 2. Half of the unit cell of the modulated structure (phase III) of TMATC-Co, projected into the *xz* plane. Only the $CoCl_4$ groups are shown here.

the amplitude of the rotation was found to be considerably higher in the ESR studies (*ca* 27° at 281 K, Tsuchida *et al.*, 1982).

Comparing columns 2 and 3 in Table 4 confirms that the displacements and especially the rotations of the $N(CH_3)_4$ groups (II*a* and II*b*) have less impact on the observations than the modes affecting the $CoCl_4$ group. Hence the results obtained for the modes $\lambda = 3$ to 6 and 11 to 18 are less reliable than those of the remaining modes. The considerably higher *R* factor of column 5 does, however, indicate that there is a genuine contribution from all 18 modes to the modulation. Examining the solution (column 4) we find that the $N(CH_3)_4$ groups seem to follow the movements of the $CoCl_4$ groups in the neighbouring mirror planes, as if the $N(CH_3)_4$ groups are being pushed and pulled by the Cl atoms. For instance, the displacement along the $\hat{x}$ axis of group $(\mathrm{II}a)^3$ is very nearly in phase with the displacement of the Cl(2) atom of group $(\mathrm{I})^1$, while group $(\mathrm{II}b)^3$ is nearly in phase with Cl(1) of $(\mathrm{I})^1$. Furthermore, the rotations of the (II*a*) and (II*b*) groups are clearly related to the same pushing and pulling from the Cl atoms.

The measured intensities of the second-order satellites are all low, and so are consequently their relative accuracies. Thus the result obtained by comparing them to the calculated structure factors is indicative rather than conclusive. However, bearing in mind that in these calculations no parameters (including the scale factor) were varied to improve the fit, we accept that the agreement supports the assumption that the structure modulation in phase III is very nearly a plane wave.

The author greatly thanks Professor R. A. Cowley for valuable suggestions, discussions and assistance at all stages of this work. I also wish to thank T. W. Ryan for all technical and practical assistance, and R. J. Nelmes for practical advice.

This work was supported by the Science and Engineering Research Council and by the Royal Norwegian Council for Scientific and Industrial Research.

References

BLINC, R., BURGAR, M., SLAK, J., RUTAR, V. & MILIA, F. (1979). *Phys. Status Solidi A*, **56**, K65-K69.

COCHRAN, W. (1968). *Neutron Inelastic Scattering*, Vol. 1. Symp. Proc., Copenhagen, 1968. Vienna: International Atomic Energy Agency.

FAN, H.-F., YAO, J.-X., MAIN, P. & WOOLFSON, M. M. (1983). *Acta Cryst.* A**39**, 566-569.

FUKUI, M., ABE, R. & TSUCHIDA, K. (1983). *J. Phys. Soc. Jpn*, **52**, 4369-4376.

HASEBE, K., MASHIYAMA, H. & TANISAKI, S. (1980). *J. Phys. Soc. Jpn Lett.* **49**, 1633-1634.

HASEBE, K., MASHIYAMA, H. & TANISAKI, S. (1982). *J. Phys. Soc. Jpn Lett.* **51**, 2049-2050.

IIZUMI, M., AXE, J. D., SHIRANE, G. & SHIMAOKA, K. (1977). *Phys. Rev. B*, **15**, 4392-4411.

MASHIYAMA, H. (1980). *J. Phys. Soc. Jpn*, **49**, 2270-2277.

SAWADA, S., SHIROISHI, Y., YAMAMOTO, A., TAKASHIGE, M. & MATSUO, M. (1978). *Phys. Lett. A*, **67**, 56-58.

TSUCHIDA, K., IMAIZUMI, S., ABE, R. & SUZUKI, I. (1982). *J. Phys. Soc. Jpn*, **51**, 2199-2204.

WIESNER, J. R., SRIVASTAVA, R. C., KENNARD, C. H. L., DIVAIRA, M. & LINGAFELTER, E. C. (1967). *Acta Cryst.* **23**, 565-574.

WOLFF, P. M. DE (1974). *Acta Cryst.* A**30**, 777-785.

WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). *Acta Cryst.* A**37**, 625-636.

YAMAMOTO, A. (1982). *Acta Cryst.* A**38**, 87-92.

Acta Cryst. (1985). B**41**, 336-341

The Location of Manganese and Calcium Ion Cofactors in Pea Lectin Crystals by Use of Anomalous Dispersion and Tuneable Synchrotron X-Radiation

BY H. EINSPAHR,* K. SUGUNA† AND F. L. SUDDATH‡

Department of Biochemistry, Institute of Dental Research and Comprehensive Cancer Center, University of Alabama at Birmingham, Birmingham, Alabama 35294, *USA*

AND G. ELLIS, J. R. HELLIWELL AND M. Z. PAPIZ

Department of Physics, University of Keele, Keele, Staffordshire ST5 5BG and SERC, Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, England

(*Received* 26 *July* 1984; *accepted* 17 *April* 1985)

Abstract

The location of the Mn^{2+} and Ca^{2+} sites in single crystals of pea lectin by enhancement of the anomalous dispersion of the Mn^{2+} ions with a wavelength near the Mn *K* absorption edge on the tuneable, focused X-ray spectrometer for protein crystallography at the Daresbury Synchrotron Radiation Source is reported. Anomalous difference Fourier maps [Kraut (1968). *J. Mol. Biol.* **35**, 511-512] calculated with film data at wavelengths of 1·860 and 1·488 Å and with diffractometer data at 1·5418 Å are compared with one another and with the native electron density map. Accurate identification and location of the Mn^{2+} and Ca^{2+} ions is possible, based on the large relative difference in f'' anomalous components of the ions in the anomalous difference Fourier maps; such is not the case, based on the relative difference in atomic numbers of the ions, in the native electron density map.

Intense, tuneable synchrotron X-radiation is being increasingly used in data collection for protein crystal structure analysis. In particular, anomalous-dispersion effects at specific absorption edges of bound metal ions can be optimized or changed in a controlled way by finely varying the synchrotron X-ray wavelength. In the case of proteins with more than one kind of metal cofactor, differences in f'' can be used to distinguish among anomalous-scattering cofactors of otherwise similar atomic number. In the present study the difference in the anomalous-dispersion coefficients of calcium ions (18 electrons) and

* Present address: The Upjohn Company, Physical and Analytical Chemistry, 7255-209-1 Kalamazoo, Michigan 49001, USA.

† Present address: Laboratory of Molecular Biology, National Institute of Arthritis, Diabetes & Kidney Diseases, NIH, Bethesda, Maryland 20205, USA.

‡ Present address: School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, USA.

0108-7681/85/050336-06$01.50 © 1985 International Union of Crystallography