NEUTRON PROFILE REFINEMENT OF THE STRUCTURE OF FeOCl and $FeOCl(TTF)_{1/8.5}$*

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Abstract

Neutron diffraction studies on powder samples of FeOCl and $FeOCl(TTF)_{1/8.5}$ establish that TTF intercalated into FeOCl contributes to the diffraction pattern and exhibits long range order. Room-temperature time-of-flight diffraction results are reported. The structure of FeOCl was refined in space group Pmnm with $\underline{a}$=3.7730(1)Å, $\underline{b}$=7.9096(1)Å, and $\underline{c}$=3.3010(1)Å. Least squares Rietveld refinement (21 parameters, 3296 degrees of freedom) yielded R=0.0169, R_w=0.0248 ($R_{expected}$=0.0115). The structure of $FeOCl(TTF)_{1/8.5}$ was refined in space group Immm with $\underline{a}$=3.784(2)Å, $\underline{b}$=3.341(2)Å, and $\underline{c}$=25.97(2)Å, using a model in which the TTF molecules lie in the $\underline{bc}$ plane, with equal occupancy of the four possible sites.

Introduction

Intercalation compounds are of interest not only as catalytic materials[1] but also as low-dimensional conductors.[2] Neutron diffraction studies on TaS_2- and NbS_2-pyridine intercalates[3] showed that the aromatic ring is perpendicular to the host layers and that the C-N axis of the pyridine ring is oriented parallel to the sulfide layers. This result was contrary to initial ideas that the nitrogen lone pair was directed at metal atoms within the host or that the pyridine rings were parallel to the host layers.[4] A structure similar to that of $NbS_2(py)_{0.5}$ (py=pyridine) has been proposed for $FeOCl(py)_{1/3}$.[5] Structural models have been proposed for amine intercalates of FeOCl and other metal oxychlorides based on lattice expansions and Mössbauer,[5,6] NMR,[7] and pseudo single-crystal[8] studies. The currently accepted model is one in which the three-fold axis of the amine is not parallel to the b-axis of the host, and the amines are "nested" in the chloride layers.[7a]

A new class of intercalates currently under investigation in our laboratory employs tetrathiafulvalene (TTF) and related compounds as guest species.[29] A layered material such as FeOCl has the potential to enforce a self-stacked structure upon the intercalated electron donor molecules, a requirement for low-dimensional conductors.[10] In addition, charge transfer occurs between the tetrathiolene guest and the host lattice, resulting in stacks of radical cations between the layers.[9] Iron K-edge EXAFS (Extended X-ray Absorption Fine Structure) spectra show little perturbation of the local Fe environment in the intercalates,[11] indicating that the structure of the host layers has not changed significantly. Powder X-ray diffraction data confirm the existence of long range order and the crystallinity of the solid,[11] but are dominated by the FeOCl layers. Unfortunately, neither EXAFS nor

X-ray powder diffraction provides direct information on the position and orientation of the TTF guest.

The independence of neutron scattering power upon atomic number makes neutron powder diffraction a promising technique for elucidating the structure of FeOCl(TTF)$_{1/8.5}$. Neutron diffraction data are complementary to the X-ray data, and have provided the first evidence for long-range ordering of the TTF radical cations within FeOCl. The study required high neutron flux, a large data collection range (10–0.5Å) and resolution comparable to that of an X-ray powder experiment.

Experimental

FeOCl was prepared[6c] by reaction of α-Fe_2O_3 with excess $FeCl_3$ at 370° C for one week in a sealed, evacuated tube (quartz or Pyrex). Excess $FeCl_3$ was removed by washing with acetone that had been dried over $CaSO_4$ and degassed. The intercalate was prepared by reaction of FeOCl with TTF in dimethoxyethane for 10 days at 60°C.[9] The dimethoxyethane was distilled from CaH_2. Both FeOCl and FeOCl(TTF)$_{1/8.5}$ are water-sensitive, and all manipulations were carried out under a nitrogen atmosphere. The samples were characterized by X-ray powder diffraction and elemental analyses.

Neutron powder diffraction data were collected on the General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS) and analyzed at Argonne National Laboratory. IPNS uses a proton accelerator and synchrotron to produce high energy neutrons by bombardment of a spallation target (uranium). These neutrons are then moderated to lower energies before they are used for diffraction. The GPPD is equipped with time-of-flight (tof) detectors, of which there are two sets each at 30°, 45°, 60°, 75°, 90°, and 150°, Highest resolution data are obtained from the 150°

detector bank.[12] The samples (FeOCl and $FeOCl(TTF)_{1/8.5}$) were run at room temperature in a vanadium cell.

The neutron diffraction data obtained on the $2\theta=150°$ and $90°$ detector banks for FeOCl and $FeOCl(TTF)_{1/8.5}$, respectively, were used in the refinement. The neutron wavelength, $\lambda(\text{Å})$, is related to tof(sec) and to the distance L(m) between the sample and the detector by equation 1,

$$(1) \qquad \lambda = \frac{h}{mL}(\mathrm{tof}) = 3956\frac{\mathrm{tof}}{L} = 2d\sin\theta$$

in which m = mass of the neutron, h=Planck's constant.

The Rietveld refinement of the tof data was performed using a modified version of the original program written by Rietveld.[13] Two programs (TOFPRP, TOFLS) fit the background, peak shape, and scaling factors, accounting for frame overlap reflections (tof zero point), and perform a full-matrix least-squares refinement of the crystal structure.[15,16] (A frame overlap occurs when reflections generated by slow neutrons from one pulse have a sufficiently long tof to appear in the diffraction pattern from the next pulse.) The refinement is achieved by minimizing the sum of the squares of the weighted differences between the observed and calculated intensities for every point in the profile under the Bragg reflections by adjusting the structural and profile parameters.

The initial atomic positions for the unit cell of FeOCl were taken from the single crystal X-ray study.[14] The FeOCl structure was refined satisfactorily ($R=0.016899$, $R_w=0.024855$, $R_{expected}=0.011541$), varying 21 parameters in the final refinement (3296 degrees of freedom). The refined parameters were 2θ zero, background, half-width parameter, lattice parameters, an asymmetry parameter, a scale factor, an anisotropic parameter, and atomic positional and anisotropic thermal parameters.

The structure of $FeOCl(TTF)_{1/8.5}$ was initially refined using Fe,O, and Cl atomic positions calculated from an idealized model[11] and a limited range of data (1.359-5.0Å, 1428 degrees of freedom). A difference Fourier synthesis showed significant nuclear density between the host layers. Subsequent refinements were carried out using a model that includes a TTF molecule intercalated into the FeOCl host. Since one molecule of TTF spans four unit cells of the host lattice along c, atomic positions for C, S, and H were obtained by the superposition (at 1/4 occupancy) of C, S, and H positions in the four unit cells. The final refinement used a larger data range (0.766-3.515Å, 1984 degrees of freedom). The programs used for final refinement were TPRNEW and TLSMOD, recent modifications[15b] of the programs used in earlier refinements, which allow refinement of a 5-parameter background function and a 3-parameter linewidth function.

Results and Discussion

FeOCl. The FeOCl structure consists of stacked neutral layers of distorted cis-$(FeCl_2O_4)^{7-}$ octahedra, which share half their edges to produce a central sheet of $(FeO)_n$ with Cl^- layers outermost on either side of the sheet.[14] The iron atoms share a single oxygen atom along the a axis and both an oxygen and a chlorine atom along the c axis (Figure 1). FeOCl crystallizes in an orthorhombic space group, Pmnm. The refined cell parameters and atomic positional and thermal parameters are given in Table I. Figure 2 compares one section of the experimentally determined neutron diffraction pattern and the pattern calculated using the parameters given in Table I. The cell parameters obtained in the refinement are in good agreement with those reported by Rouxel and Palvadeau,[7a] but are more precise. The chlorine atoms exhibit relatively large thermal parameters along both the a and c axes, consistent with weak interlayer interactions and the ease of intercalation by Lewis bases. Selected interatomic distances and angles are given in Table II.

$FeOCl(TTF)_{1/8.5}$. For FeOCl intercalated with TTF, a number of constraints must be considered before a Rietveld profile analysis can be undertaken. The Rietveld method is a technique for structure refinement, not structure determination. The basic structure must be known (or guessed at) before the data can be fit.

To begin the analysis it was necessary to identify and index all the Bragg reflections in the powder pattern. The Bragg peaks were fit using TOFMANY,[18] a multiplet peak-fitting program. The program derives the d spacing from equation 2:

$$\mathrm{tof}(i)=(\mathrm{difc})*(D(i)) + (\mathrm{difa})*(D(i))^2 + \mathrm{zero}(i) \tag{2}$$

where tof(i) is the time of flight for each data point, difc, difa, and zero(i) are instrumental parameters for the GPPD at the time of the experiment, and D(i) is the d-spacing. The peak shape is computed from the profile parameters of the diffracted peaks by the convolution of a Gaussian peak with a hypothetical pulse shape composed of a rising exponential leading edge and a decaying exponential trailing edge.[16,18] Full widths at half-maximum height (FWHM) were compared to those of the instrument's calibration material, silicon (Figure 3). The diffracted peaks for $FeOCl(TTF)_{1/8.5}$ are broader than those of silicon, indicating that the intercalate may have small lattice strains resulting from intercalation, and that the mean particle size is smaller than for silicon. The smooth monotonic dependence of FWHM on d provides additional evidence that all Bragg reflections have been identified correctly.

The peaks were indexed by a computer-based method (TOFIDX).[15,19] Although there is usually not a unique solution, the program gives figures of merit that strongly discriminate between the solutions. A minimum of twenty Bragg reflections is necessary to obtain reliable results. Twenty experimental reflections whose peak positions had been determined from the peak fitting program were used. Three solutions were found by the indexing program for an orthorhombic cell (Table III). A large figure of merit indicates a good fit; solutions with figures of merit less than 4 were disregarded. In Table IV, the experimental d-spacings are compared to those calculated for the orthorhombic cell with the largest figure of merit.

The structural model used for the FeOCl layers of the intercalate results from translating alternate FeOCl layers by (1/2, 0, 1/2) and expanding the interlayer gap to accommodate the TTF molecules. The resulting symmetry necessitates a doubling of the b axis to form a centered unit cell (Figure 4). Such translations of the host layers and increases in interlayer distances have been observed upon intercalation of FeOCl and other layered hosts.[5,7a] A more standard unit cell description[20] (with c as the long axis) was employed in space group Immm for the remainder of the refinement. Initial atomic positions for Fe, O, and Cl were calculated based on the structure of FeOCl. A least squares refinement of 14 parameters over a limited data range (1310 degrees of freedom) using only Fe, O, and Cl atoms resulted in the following R factors: $R=0.060947$, $R_w=0.089157$, $R_{expected}=0.019004$; the fit to a portion of the experimental data is shown in Figure 5. A difference Fourier synthesis was performed on the observed and calculated structure factor amplitudes. The resulting Fourier difference map showed significant nuclear density between the FeOCl layers. This indicates that the TTF molecules contribute to the long-range order in $FeOCl(TTF)_{1/8.5}$.

The presence of TTF in the unit cell was modelled by superimposing, at 1/4 occupancy, the atomic positions of the C, S, and H atoms of TTF in each of the 4 unit cells spanned by a TTF molecule. Upon inclusion of the TTF in the model, the data range that could be fit in the least squares refinement expanded to 1894 degrees of freedom, and the R factors decreased substantially to $R=0.02025$, $R_w=0.028942$, $R_{expected}=0.011079$. One portion of the fit to the experimental data is shown in Figure 6, while Table V gives the final refined atomic and cell parameters.

The goodness of the final fit to the data leads to the conclusion that the TTF molecules must be aligned in the <u>bc</u> plane, perpendicular to the FeOCl layers as shown in Figure 7. This configuration locks the FeOCl layers into an eclipsed configuration, and places the sulfur atoms of TTF rather close to the chlorine atoms of the FeOCl host (3.32Å), well within the sum of the van der Waals radii (3.6Å). We postulate that the non-bonded electron density on the sulfur atoms of TTF occupies approximately sp^3 orbitals directed <u>between</u> the chlorine atoms of FeOCl, thus minimizing repulsive S---Cl interactions. Similar arrangments of electron density have been deduced for the Se atoms in TMTSF derivatives based on electron density maps [21] and theoretical calculations.[22] Short S---Cl distances have also been recently observed for $[TMTTF][FeCl_4]$.[23]

The model used here for TTF in $FeOCl(TTF)_{1/8.5}$ is a very general one, making no predictions about the specific stacking arrangement of the TTF molecules between the layers or in adjacent layers. The only restrictions on the TTF molecules are that they are perpendicular to the FeOCl layers and oriented along <u>b</u>. Disorder is used to take into account the four possible ways in which the TTF molecule may be arranged within a single orthorhombic unit cell of FeOCl (Figure 8). Obviously, the actual unit cell of the intercalate must include at least four of the unit cells defined in Figures 4 and 7. This structural model, in which the TTF molecule spans four unit cells along the b axis and one unit cell along the a axis, predicts a maximum stoichiometry of $FeOCl(TTF)_{1/8}$. This is in relatively good agreement with the experimentally determined stoichiometry of $FeOCl(TTF)_{1/8.5}$, allowing one unoccupied TTF site for every 16 occupied sites, and suggesting that the TTF molecules are approximately close packed within the layers. The random site model proposed here does not take this partial occupancy into account.

Conclusions

Analysis of neutron powder diffraction data has demonstrated that, upon intercalation of TTF, the b axis of FeOCl is expanded and doubled, resulting in a body-centered orthorhombic structure (space group Immm or I222). Both X-ray powder diffraction and EXAFS data[11] indicate that the intercalate is a well-defined solid with essentially undistorted FeOCl layers, thus supporting the hypothesis that the layers are locked by the intercalant. The neutron diffraction data indicate that the intercalated TTF molecules contribute to the long-range order of the solid, and that they are perpendicular to the FeOCl layers and oriented along the b axis. Further neutron diffraction studies are in progress to determine details of the long range order of the TTF, as are solid state NMR studies to probe the dynamics of the TTF-FeOCl interactions.

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References and Notes

1. Intercalation Chemistry, M. S. Whittingham, A. J. Jacobson, eds, Academic Press, New York, 1982.
2. Averill, B. A.; Kauzlarich, S. M. Mol. Cryst. Liq. Cryst. 1984, 107, 55-64.
3. (a) Riekel, C.; Hohlwein, D.; Schollhorn, R. J. Chem. Soc. Chem. Commun., 1976, 863-864; (b) Riekel, C.; Fischer, C. O. J. Solid State Chem., 1979, 29, 181-90.
4. (a) Gamble, F. R.; DiSalvo, F. J.; Klemm, R. A.; Geballe, T. H. Science, 1970, 168, 568-570; (b) Gamble, F. R.; Osieck, J. H.; DiSalvo, F. J. J. Chem. Phys., 1971, 55, 3525-3530.
5. Eckert, H.; Herber, R. H. J. Chem. Phys., 1984, 80, 4526-4540.
6. (a) Kanamaru, F.; Shimada, M.; Koizumi, M.; Takano, M.; Takada, T. J. Solid State Chem., 1973, 7, 297-299; (b) Kikkawa, S.; Kanamaru, F.; Koizumi, M. Physica, 1981, 105B, 249-252; (c) Kikkawa, S.; Kanamaru, F.; Koizumi, M. Bull. Chem. Soc. Japan, 1979, 52, 963-966; (d) Maeda, Y.; Yamashita, M.; Ohshio, H.; Tsutsumi, N.; Takashima, Y. Bull. Chem. Soc. Japan, 1982, 55, 3138-3143; (e) Herber, R. H. Acc. Chem. Res., 1982, 15, 216-224; (f) Herber, R. H.; Maeda, Y. Inorg. Chem., 1981, 20, 1409-1415; (g) Fatseas, G. A.; Palvadeau, P.; Venien, J. P. in Solid State Chemistry, 1982, Proc. 2nd Eur. Con., Veldhoven, the Netherlands, June 7-9, 1982, eds. Metselaar, R.; Heijligers, H. J. M.; Schoonman, J.; Studies in Inorganic Chemistry, vol. 3, Elsevier, Amsterdam, 1983, pp. 627-630.
7. (a) Rouxel, J.; Palvadeau, P. Rev. Chim. Min., 1982, 19, 317-332; (b) Clough, S.; Palvadeau, P.; Venien, J. P. J. Phys. C: Solid State Phys., 1982, 15, 641-655.
8. Fatseas, G. A.; Palvadeau, P.; Venien, J. P. J. Solid State Chem., 1984, 51, 17-37.

9. (a) Antonio, M. R.; Averill, B. A. *J. Chem. Soc. Chem. Commun.*, 1981, 382-383; (b) Averill, B. A.; Kauzlarich, S. M.; Antonio, M. R. *J. de Physique (Paris)*, 1983, *44* C3-1373-C3-1376; (c) Kauzlarich, S. M.; Averill, B. A.; Teo, B. K. *Mol. Cryst. Liq. Cryst.*, 1984, *107*, 65-74; (d) Averill, B. A.; Kauzlarich, S. M.; Teo, B. K.; Faber, J., Jr. *Mol. Cryst. Liq. Cryst.*, 1985, *120*, 259-262.

10. (a) Hoffman, B. M.; Ibers, J. A. *Acc. Chem. Res.*, 1983, *16*, 15-21; (b) Bryce, M. R.; Murphy, L. C. *Nature*, 1984, *309*, 119-126; (c) Lyubovskaya, R. N. *Russ. Chem. Rev.*, 1983, *52*, 736-750; (d) Williams, J. M.; Beno, M. A.; Wang, H. H.; Leung, P. C. W.; Enge, T. J.; Geiser, U.; Carlson, K. D. *Acc. Chem. Res.*, 1985, *18*, 261-267; (e) Wudl, F. *ibid.*, 1984, *17*, 227-232.

11. Kauzlarich, S. M.; Teo, B. K.; Averill, B. A. *Inorg. Chem.*, 1986, *25*, in press.

12. IPNS Progress Report, Argonne National Laboratory, Argonne, IL, 1981-1983; pp. 2-40.

13. Rietveld, H. M. *J. Appl. Crystallogr.*, 1969, *2*, 65-71.

14. Lind, M. D. *Acta Crystallogr.*, 1970, *B26*, 1058-1062.

15. (a) Rotella, F. J. "Users Manual for Rietveld Analysis of Time-of-Flight Neutron Diffraction Data at IPNS"; Argonne National Laboratory, Argonne, IL, 1983; (b) Rotella, F. J. "Notes on the Rietveld Analysis of Time-of-Flight Neutron Diffraction Powder Data using TLSMOD" Argonne National Laboratory, Argonne, IL, 1985.

16. Von Dreele, R. B.; Jorgensen, J. D.; Windsor, C. G. *J. Appl. Crystallogr.*, 1982, 15, 581-589.

17. Halbert, T. R., in Ref. 1, pp. 375-403.

18. Faber, J., Jr.; Hitterman, R. L. *Adv. in X-ray Analysis*, 1986, *29*, in press.

19. Visser, J. W. *J. Appl. Crystallogr.*, 1969, *2*, 89-95.

20. For $FeOCl(TTF)_{1/8.5}$:

    a=3.7841(2)Å, b=3.3407(2)Å, c=25.972(2)Å, V=328.32(2)$Å^3$, Z=4, space group Immm. Note that the b axis in this unit cell corresponds to the c axis of pristine FeOCl, while the interlayer distance is taken as c (rather than b in FeOCl).

21. Wudl, F.; Nalewajek, D.; Troup, J.M.; Extine, M. W. *Science*, 1983, 222, 415-417.

22. Grant, P. M. *Phys. Rev. B*, 1976, *26*, 6888-6895.

23. Batail, P.; Ouahab, L.; Torrance, J. B.; Pylman, M. L.; Parkin, S. S. P. *Solid State Commun.*, 1985, *55*, 597-600.

Table I. Cell parameters, and final positional and thermal parameters for FeOCl at 300K.

a(Å)	b(Å)	c(Å)
3.7730(1)	7.9096(1)	3.3010(1)

	x	y	z	$B_{xx}(10^3)$	$B_{yy}(10^3)$	$B_{zz}(10^3)$
Fe	0.25	0.11555(8)	0.75	13.8(4)	6.2(1)	14.6(5)
O	0.25	-0.04795(15)	0.25	10.7(6)	7.35(2)	17.6(8)
Cl	0.25	0.32961(7)	0.25	43.8(6)	5.6(5)	19.8(1)

$R=0.016899$ $R_w=0.024855$ $R_{expected}=0.011541$

Table II. Distances and angles obtained for FeOCl. There are 2 FeOCl formula units per unit cell.

	distance (Å)	number in unit cell
Fe-O	1.9608(4)	8
Fe-O	2.0968(8)	8
Fe-Cl	2.3645(7)	8
Fe...Fe	3.1023(7)	16
Fe...Fe	3.3010(1)	8
Fe...Fe	3.7730(1)	8
Fe...O	3.8395(2)	16
Fe...Cl	3.9946(8)	8

	angle(°)
O-Fe-O	103.84(6)
O-Fe-O	80.32(2)
O-Fe-Cl	83.81(3)
O-Fe-Cl	172.35(4)
Cl-Fe-Cl	88.35(4)
O-Fe-Cl	101.26(3)
O-Fe-O	148.35(8)

Table III. Cell constants and figures of merit obtained for twenty reflections from neutron powder diffraction data for $FeOCl(TTF)_{1/8.5}$

a(Å)	b(Å)	c(Å)	Figure of Merit	Unit Cell Volume(Å^3)
3.784	25.961	3.341	1614.9	328.17
10.016	12.986	3.854	14.2	501.31
6.688	25.959	4.585	11.5	796.02

Table IV. Observed and calculated d-spacings (Å) of the neutron powder diffraction data for FeOCl(TTF)$_{1/8.5}$ with the proposed indexing scheme: $\underline{a}$ = 3.7836(4) Å, $\underline{b}$ = 25.9629(3) Å, and $\underline{c}$ = 3.3410(4) Å

d_{obs}(Å)	h	k	l	d_{calc}(Å)
3.4676(1)	1	3	0	3.4667
3.3128(7)	0	1	1	3.3137
3.2452(5)	0	8	0	3.2452
2.8099(4)	0	5	1	2.8096
2.4827(1)	0	7	1	2.4823
2.3366(1)	1	4	1	2.3365
2.1834(1)	0	9	1	2.1834
2.0029(4)	1	11	0	2.0025
1.9828(4)	1	8	1	1.9826
1.9280(5)	0	11	1	1.9277
1.8918(1)	2	0	0	1.8918
1.8720(1)	2	2	0	1.8720
1.8551(2)	0	14	0	1.8544
1.8157(5)	2	4	0	1.8162
1.8026(1)	1	10	1	1.8024
1.6705(3)	0	0	2	1.6705
1.6566(3)	0	2	2	1.6568
1.6377(1)	1	12	1	1.6372
1.6220(1)	0	16	0	1.6226
1.5701(1)	2	5	1	1.5692
1.5049(1)	1	3	2	1.5049
1.4301(1)	2	9	1	1.4298
1.4164(1)	1	17	0	1.4161
1.4055(3)	0	10	2	1.4048
1.3893(2)	0	12	1	1.3889
1.3509(4)	1	9	2	1.3504
1.3241(1)	0	18	1	1.3242

Table V. Atomic Positions and Thermal Parameters for $FeOCl(TTF)_{1/8.5}$

Atom	x	y	z	B
Fe	0.0	0.0	0.2170(1)	1.35(6)
O	0.5	0.0	0.2345(2)	1.60(9)
Cl	0.0	0.5	0.1487(1)	1.82(7)
S	0.5	-0.064(15)	0.0599(2)	1.05[a]
C(1)	0.5	0.358(18)	0.0	1.04[a]
C(2)	0.5	0.539(8)	0.249(7)	1.36[a]
H	0.5	0.242(11)	0.678(18)	1.04[a]

[a] Isotropic thermal parameters for the atoms of TTF were held fixed at these values during the least squares refinement.

Figure Captions

Figure 1. Perspective view of two layers of the FeOCl structure. FeOCl is orthorhombic, Pmnm, a=3.780Å, b=7.917Å, c=3.303Å. Figure adapted from Ref. 17.

Figure 2. Profile refinement of a portion of the 150° bank data for FeOCl at 300K. The observed data are indicated by points and the calculated data by a solid line. Marks directly beneath the pattern indicate the positions of reflections. A difference curve appears at the bottom.

Figure 3. Plot of full width at half maximum (FWHM) of diffraction peaks of $FeOCl(TTF)_{1/8.5}$ compared with a standard silicon sample. Differences in particle size and residual strains are reflected in different slope and intercept values of the two samples. The monotonic rise in FWHM values for $FeOCl(TTF)_{1/8.5}$ indicates that all Bragg reflections in this d-spacing range have been detected.

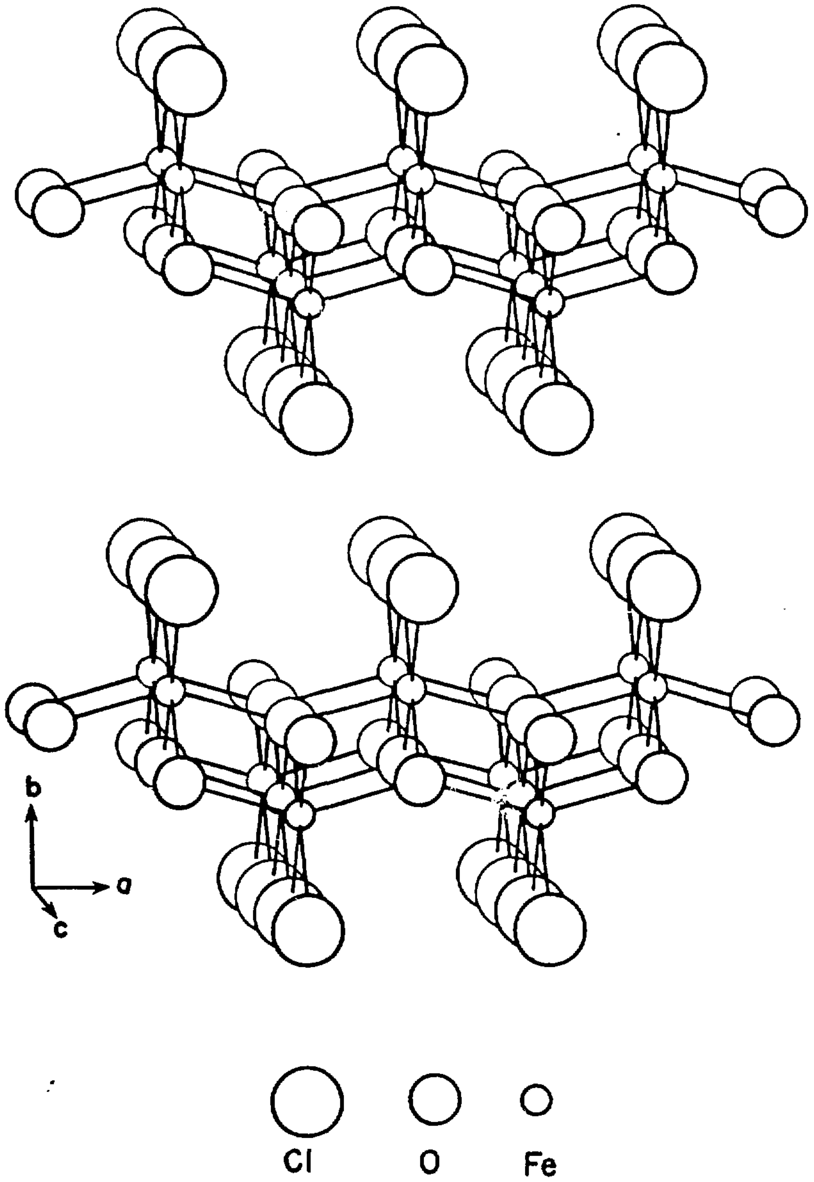
Figure 4. Projection of the unit cell of FeOCl showing the change in cell symmetry that accompanies cell expansion upon intercalation.

Figure 5. A portion of the profile refinement for $FeOCl(TTF)_{1/8.5}$, using a model that contains only Fe, O, and Cl atoms.

Figure 6. Portion of the profile refinement pattern obtained using a model that includes an entire TTF molecule.

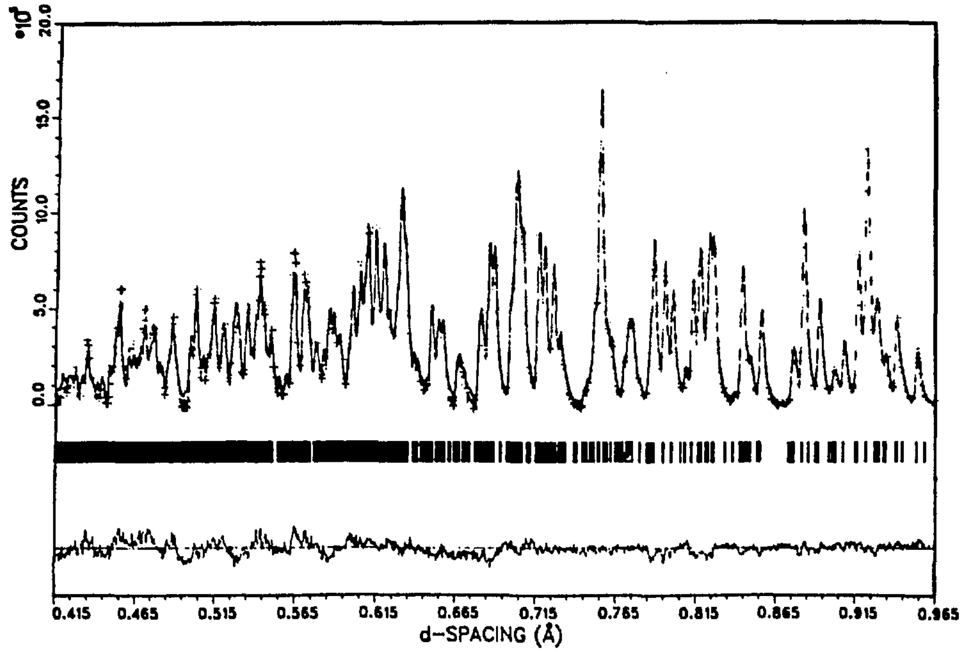
Figure 7. Orientation of one TTF molecule with respect to one unit cell (solid lines). A quadrupled unit cell along b (dashed lines) is required by the width of a TTF molecule.

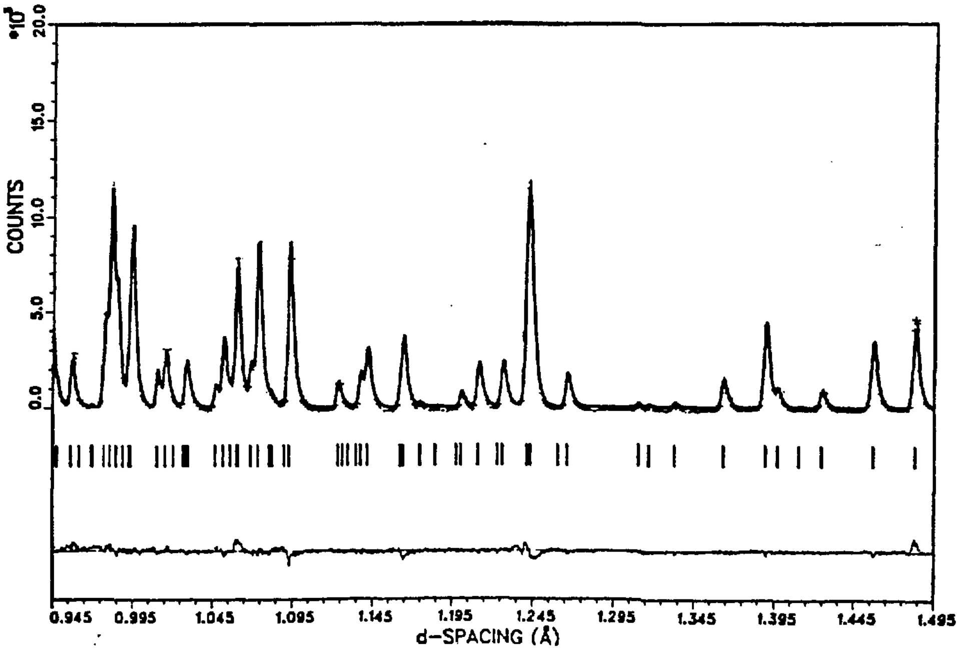
Figure 8. Four possible orientations of TTF within half of the defined unit cell (bold lines) and the quadrupled unit cell (dashed lines).



FeOCl
orthorhombic, Pmnm
$a = 3.780$ Å, $b = 7.917$ Å, $c = 3.303$ Å

Fig. 1


*10³
20.0
15.0
10.0
5.0
0.0
COUNTS
0.415
0.465
0.515
0.565
0.615
0.665
0.715
0.765
0.815
0.865
0.915
0.965
d-SPACING (Å)


*10³
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15.0
10.0
5.0
0.0
COUNTS
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0.995
1.045
1.095
1.145
1.195
1.245
1.295
1.345
1.395
1.445
1.495
d-SPACING (Å)

Fig. 2

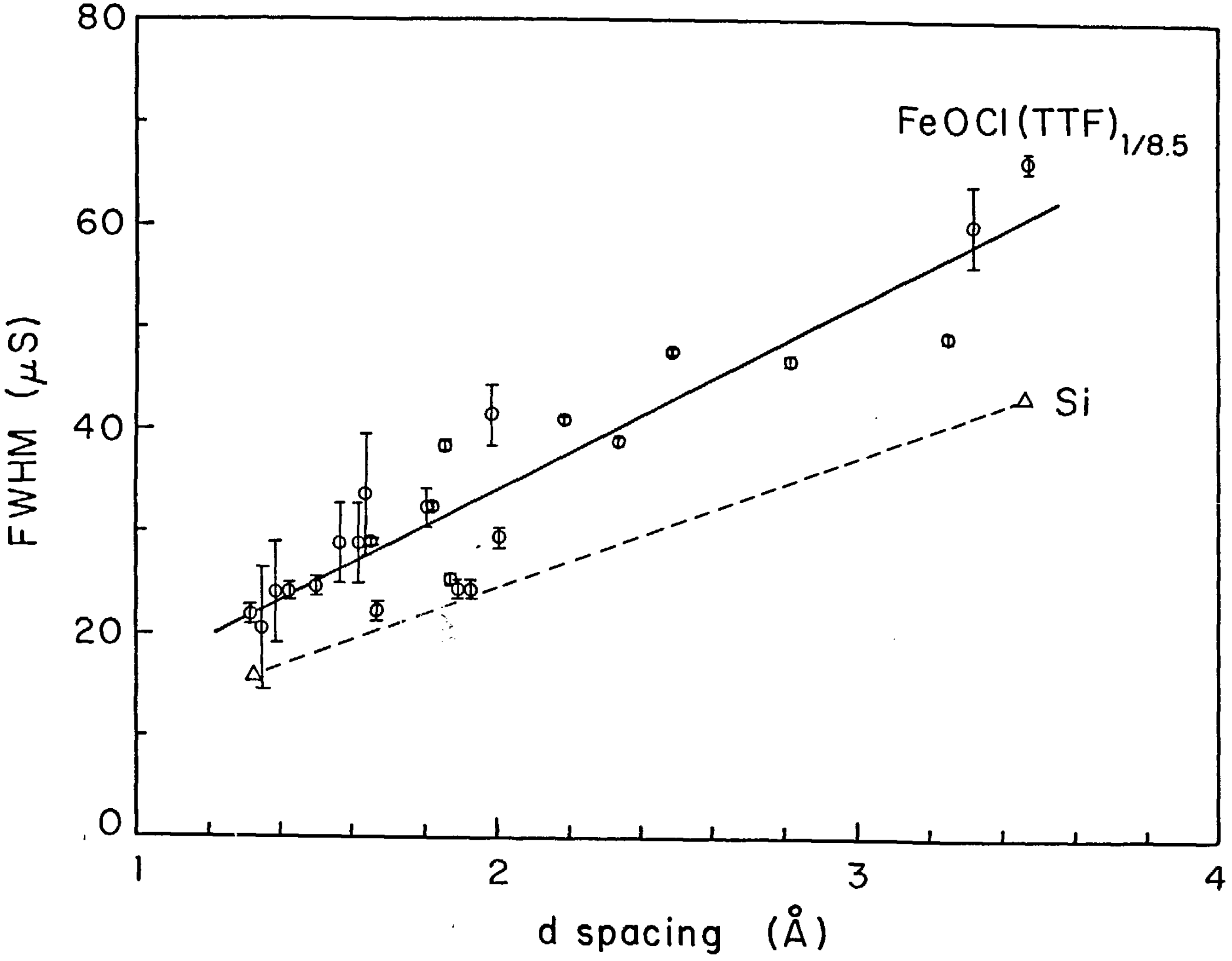


Fig. 3

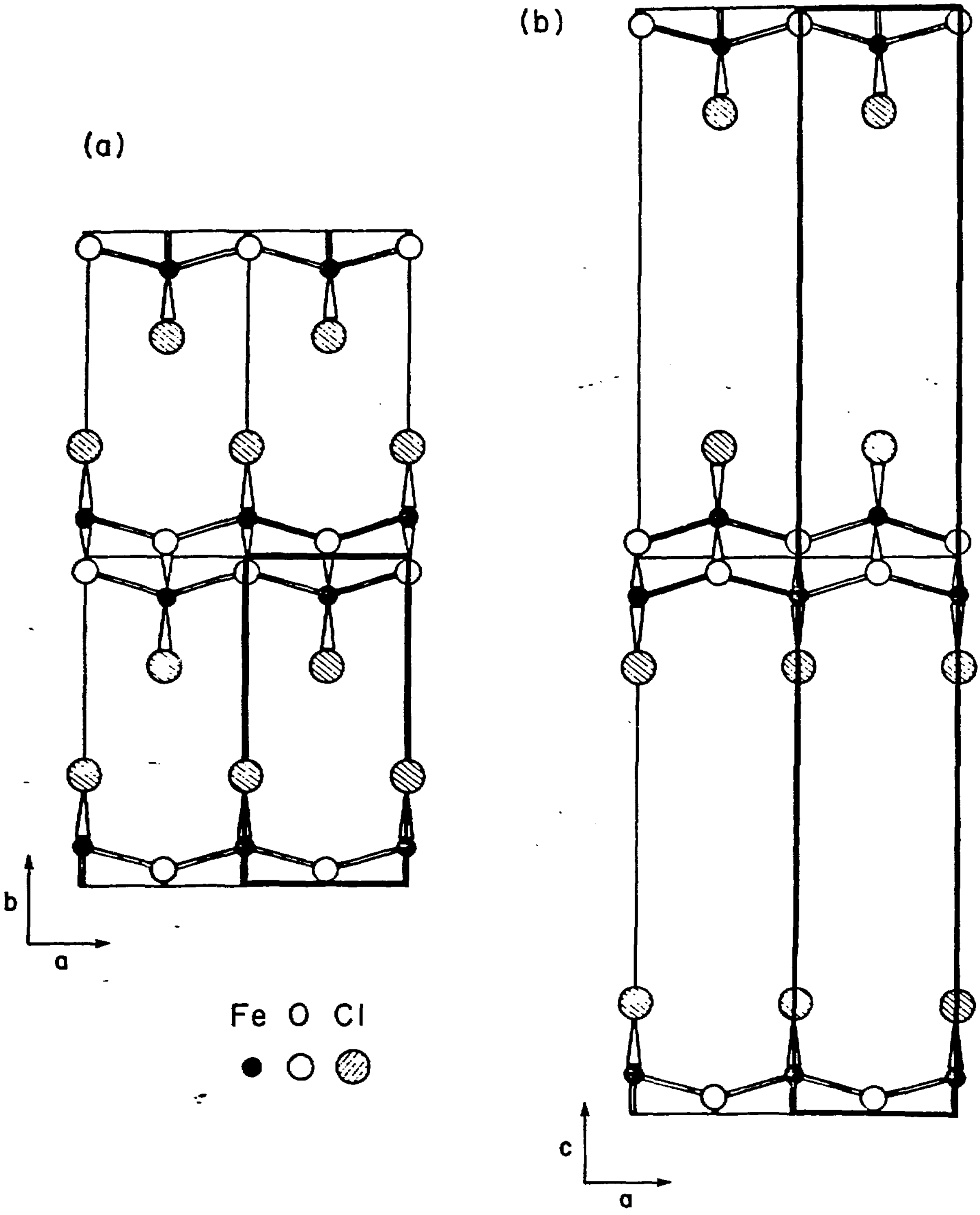
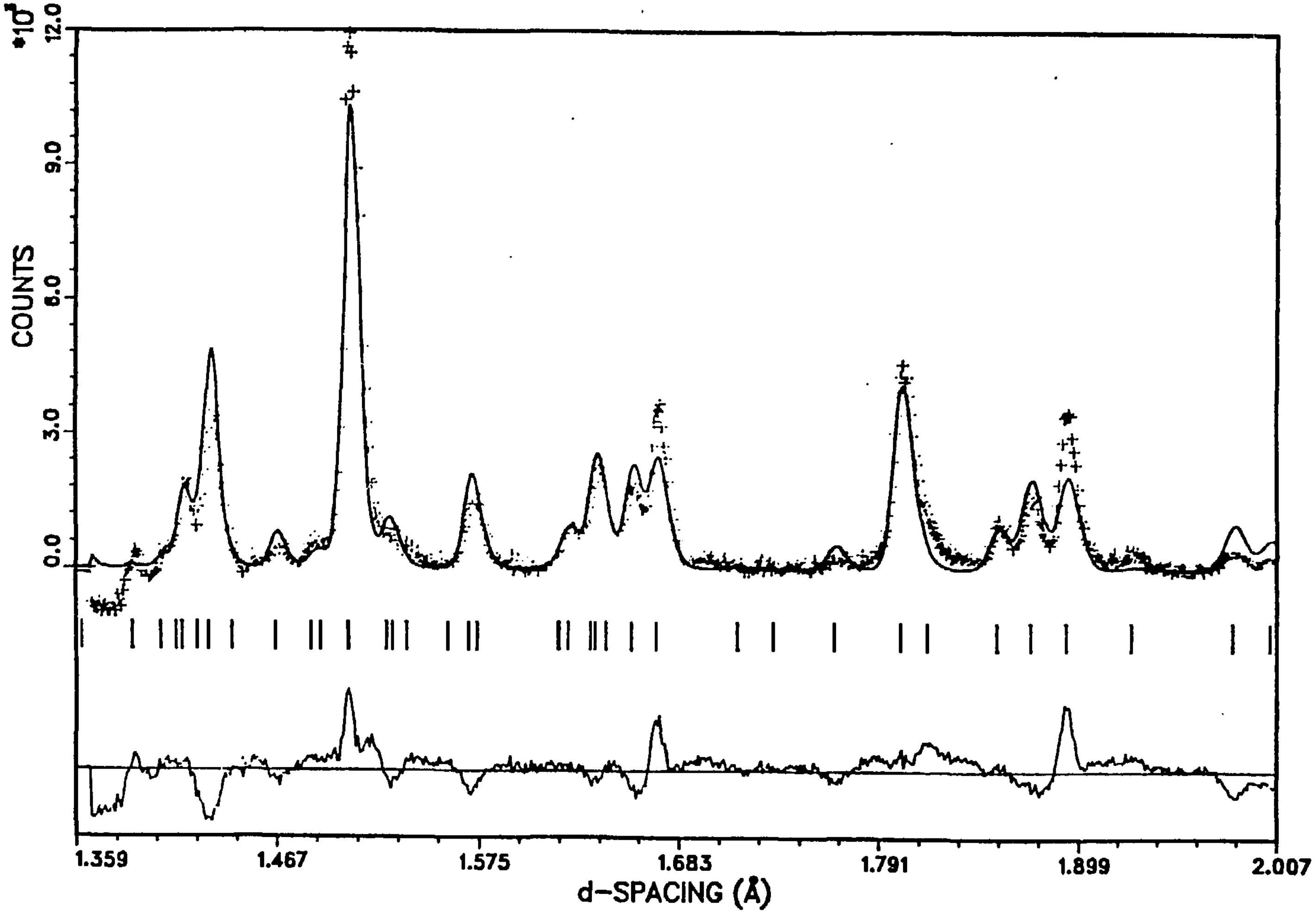


Fig. 4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9.0
6.0
3.0
0.0
COUNTS
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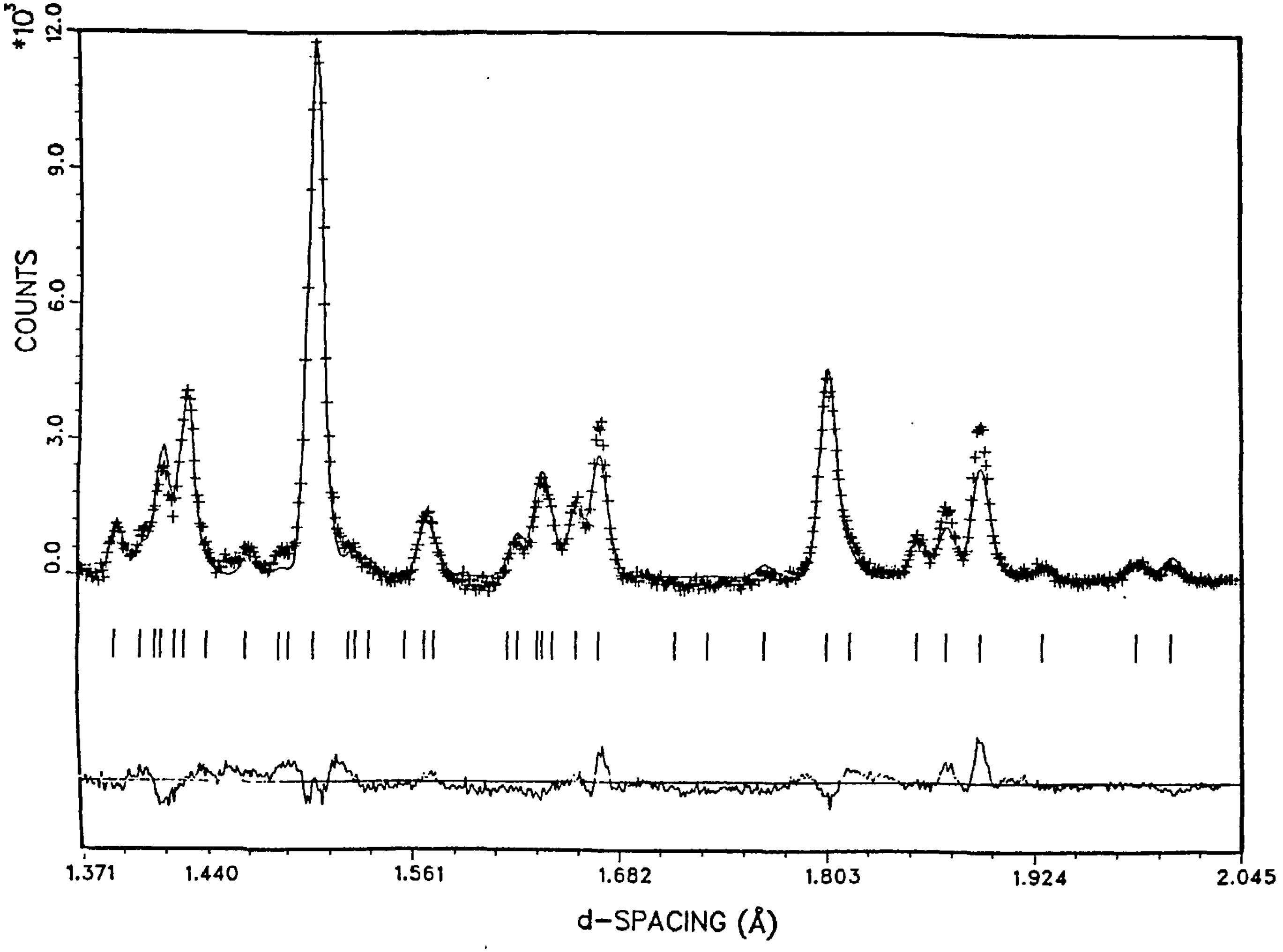
1.467
1.575
1.683
1.791
1.899
2.007
d-SPACING (Å)

Fig. 5


*10^3
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9.0
6.0
3.0
0.0
COUNTS
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1.561
1.682
1.803
1.924
2.045
d-SPACING (Å)

Fig. 6

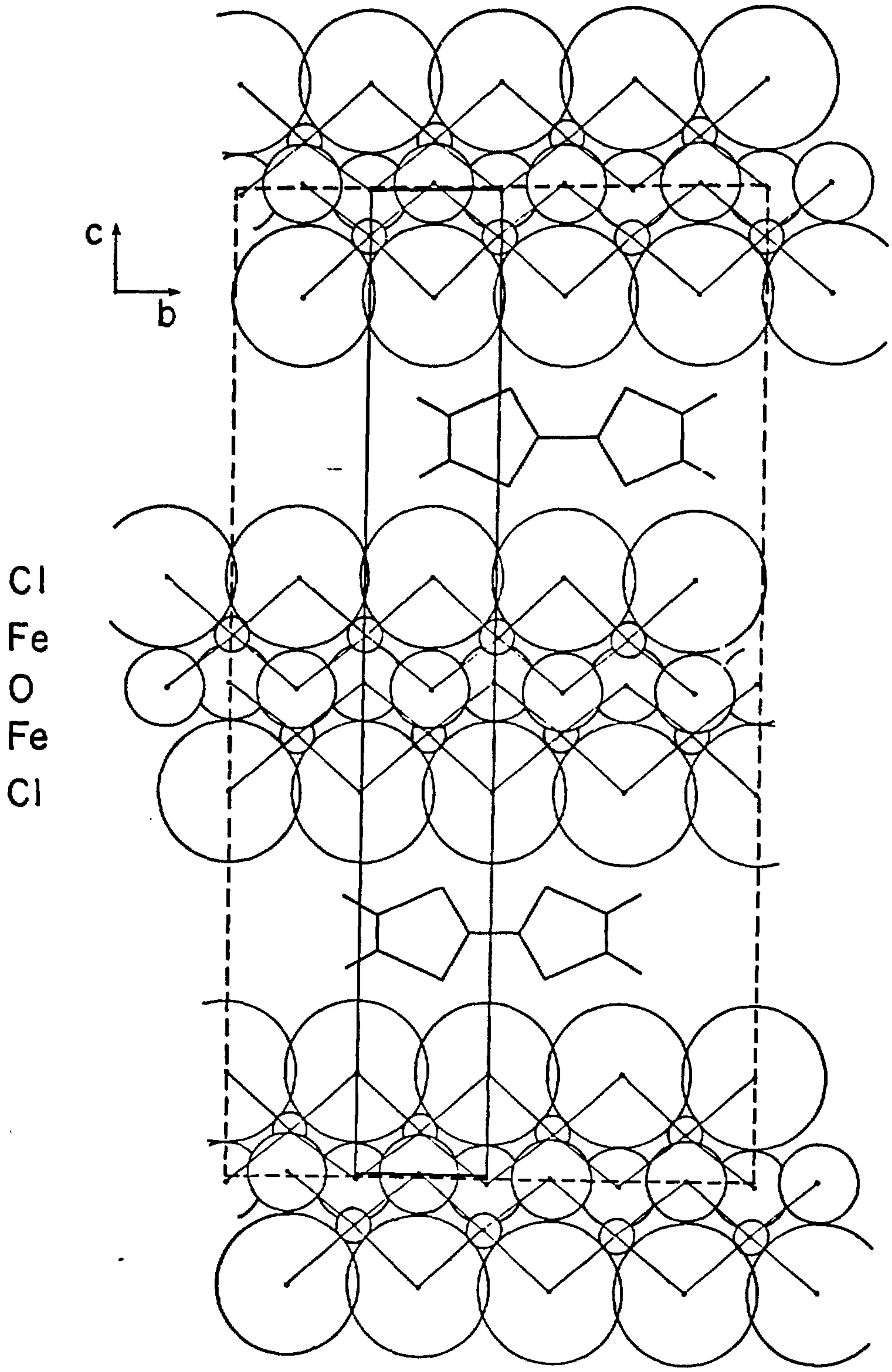

Fig. 7

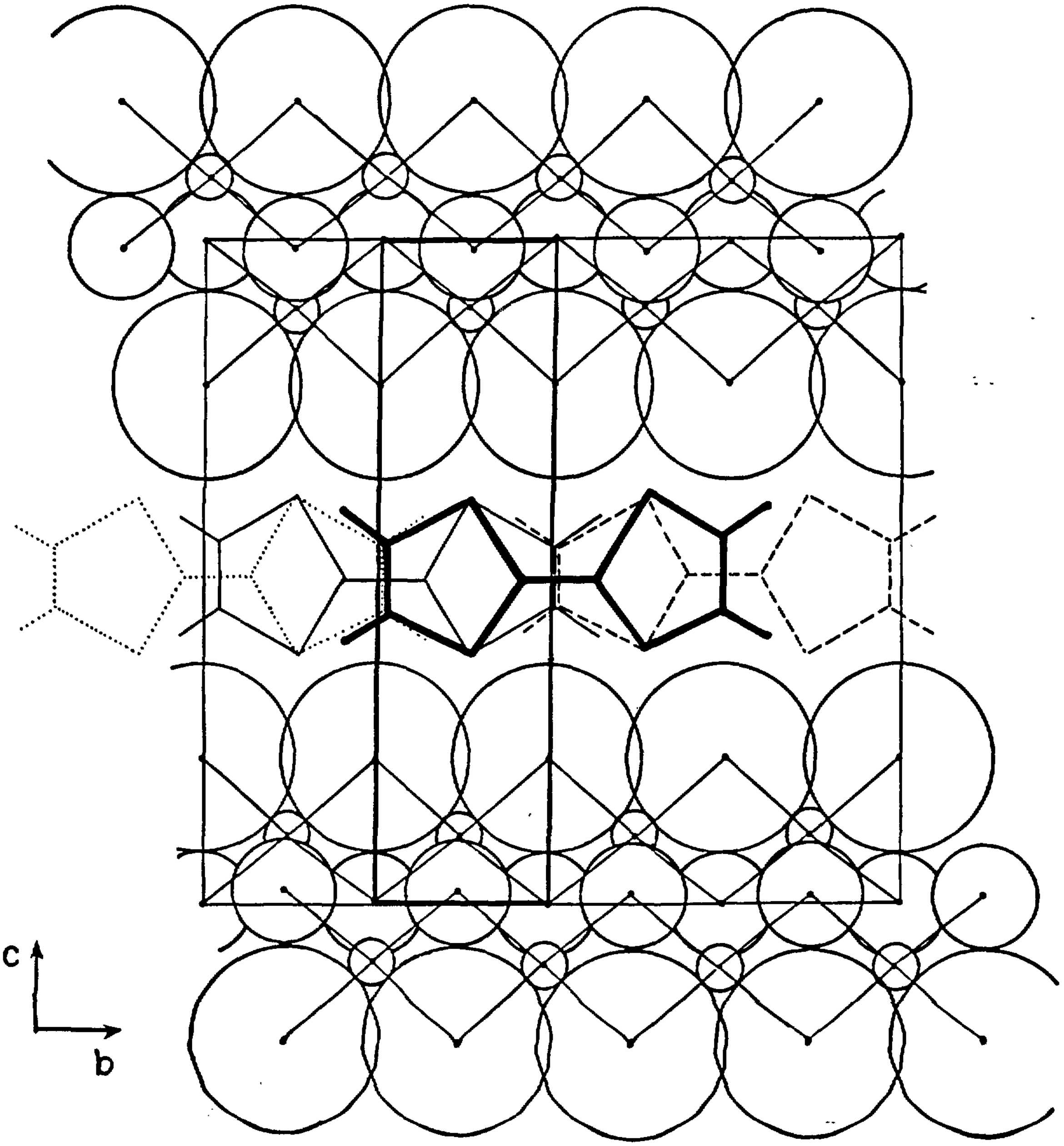

Fig. 8