

The Structures of some Ferric Chloride–Graphite Compounds

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The ferric chloride–graphite system containing 55.5% ferric chloride has been examined by high-resolution electron-diffraction techniques and by X-ray powder photography. The system is found to consist of about 17% free graphite and about 83% of a ferric chloride–graphite compound. The complementary use of the two techniques allowed a detailed analysis of the structure of this compound. Single-crystal electron-diffraction patterns were used to determine the structures of the component layers. X-ray powder patterns served to confirm these results, and provided information on the stacking of the layers. It was found that single layers of ferric chloride are parallel and lie between successive parallel planes of carbon atoms. The *c* axis (normal to the layers) is 9.41 Å. The translations of the layers relative to one another normal to the *c* axis are essentially random except that a partial coordination of chlorine and carbon positions gives rise to some short-range order. The ferric chloride layer, relative to a single layer in normal ferric chloride, is about 92% filled.

The ferric chloride–graphite systems containing less than 55.5% ferric chloride are similar. As the percentage of ferric chloride decreases, the percentage of free graphite increases and the fraction of ferric chloride per ferric chloride layer decreases. At about 39% ferric chloride the layer stacking sequence in the *c* direction becomes random.

Introduction

A number of substances, for example fluorine, bromine, potassium, oxygen, nitric acid, anhydrous ferric chloride, cause crystalline graphite to swell. Such swelling is the result of compound formation, i.e. the intercalation of these substances into the graphite lattice. Formerly, the ferric chloride–graphite compound was unique: it was the only known intercalated compound of graphite which showed high stability to heat and to a variety of reagents, and which decomposed thermally at relatively high temperatures to yield the intercalated substance in an unchanged form. In the past few years Croft (Croft & Thomas, 1951; Croft, 1953) has discovered a number of intercalated compounds of graphite with these properties. These compounds, besides being of fundamental interest, are of practical importance. For example, Croft (1952) has pointed to the feasibility of using graphite, with its ability to intercalate some substances, but not others, to effect certain analytical separations.

An investigation of the structures of some compounds of ferric chloride–graphite was carried out for two main reasons: first, it was hoped that from such structures an indication of the role which structure plays in determining which substances can be intercalated into the graphite lattice might be obtained; second, the earlier investigation of the ferric chloride–graphite system (Rüdorff & Schulz, 1940) carried out with X-ray single-crystal and powder techniques,

seemed to us to exhibit certain anomalies and inconsistencies, as noted below, and it was felt that a re-investigation of the system would be worthwhile.

The structures are of the layer type and are thus ideally suited to the technique of high-resolution electron diffraction. Crystals sufficiently large for single-crystal X-ray studies are obtained only with great difficulty, whereas very small crystals, giving good single-crystal electron-diffraction patterns, are obtained readily. The use of the electron-diffraction technique has the disadvantage, however, that the patterns which would give the most direct evidence on the stacking of the layers of atoms, namely patterns obtained with the electron beam very nearly in the plane of the layers, cannot be obtained because of the sheet-like form of the crystals. Information on the stacking sequence was derived more readily from X-ray powder patterns. The presentation of our results is designed to demonstrate how electron and X-ray diffraction observations may be correlated. The complementary use of the two techniques has led to a detailed picture of the structure which could have been obtained only with the greatest difficulty by the use of either technique separately.

Preparation and analysis

Ferric chloride–graphite compounds may be prepared by heating anhydrous ferric chloride and graphite together in a sealed tube for prolonged periods at elevated temperatures. The compounds are freed from any excess ferric chloride by washing. Ferric chloride content, which may vary between 0 and 56%, is

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dependent upon the initial ratio of ferric chloride to graphite, temperature, and duration of heating. Provided that ferric chloride is in excess, and that a temperature above 300° C. is maintained for a sufficient length of time (usually at least 24 hr.), a sample with 56% ferric chloride is obtained after washing. Samples with less ferric chloride may be obtained under different experimental conditions, or by the sublimation of ferric chloride from a 56% sample at elevated temperatures. The ferric chloride content is generally ascertained from the weight of ferric oxide obtained after digestion of the sample with concentrated sulfuric acid and subsequent ignition. Details of preparation and analysis are discussed in greater detail elsewhere (Thiele, 1932; Rüdorff & Schulz, 1940; Barker & Croft, 1953).

All samples used in this study were kindly prepared and analysed by Mr R. C. Croft of this Division. The specimens investigated contained the following percentages of ferric chloride: 55.5, 49.2, 43.4, 38.5, and 30.3. These samples also contained approximately 0.5–1.0% water. Samples were prepared from 325-mesh South Australian graphite, except that 48–65-mesh graphite was used in the preparation of the 43.4% sample.

Density measurements

Density determinations were first carried out by the flotation method. During initial determinations on the 55.5% sample, it became apparent that the sample was not of uniform density. For example, the sample was added to a solution of methylene bromide-carbon tetrachloride which had a density of 2.40 g.cm.⁻³ at 25±0.5° C. Even after long periods of centrifugation part of the sample remained afloat while the rest had sunk. At a liquid density of 2.20 g.cm.⁻³ the entire sample sank. Such observations are not in agreement with the density of 1.93 g.cm.⁻³ found by Rüdorff & Schulz (1940) for the 56% preparation.

In order to check the flotation measurements and to obtain average densities, pycnometric measurements were made. Reagent-grade xylene ($\rho = 0.852$ g.cm.⁻³ at 25° C.) was used as the pycnometric liquid, for it readily wetted the preparations. A sample was placed in a 2 cm.³ pycnometer, and was pumped under high vacuum for several hours. The xylene was then introduced in such a manner that no air was admitted. The pycnometer was then capped and weighed. No extrapolation to zero time was found necessary. All

Table 1. *Miscellaneous data for some of the ferric chloride-graphite preparations*

% FeCl ₃ in sample	Density (g.cm. ⁻³)	p	x_G	% FeCl ₃ in compound
55.5	2.42±0.02	0.92	0.17	66.9
49.2	2.36±0.02	0.88	0.26	66.2
43.4	2.23±0.02	0.80	0.32	64.0
0.0	2.25±0.01	(0.0)	(1.00)	(0.0)

measurements and weighings were carried out in a room constant in temperature to ±0.2° C. at 25.0° C. Determinations were always carried out in duplicate. Table 1 gives the results of these measurements.

The structures of graphite and of ferric chloride

The structures of graphite and of ferric chloride will be referred to often in the discussions below, and so these structures are reviewed very briefly at this point.

Graphite

Hexagonal,

$$a = 2.4612, \quad c = 6.7079 \text{ \AA} \quad (\text{Nelson \& Riley, 1945a}).$$

$$D_{6h}^4 - P6_3/mmc.$$

C atoms in (b) and (c).

$$Z = 4 \quad (\text{Bernal, 1924}).$$

Graphite consists of two sheets of carbon atoms displaced relative to one another by the translation $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$. A single sheet ($Z = 2$, C at 0, 0; $\frac{1}{3}, \frac{2}{3}$) is made up of carbon atoms arranged in an hexagonal array.

Ferric chloride

Trigonal,

$$a = 6.06, \quad c = 17.40 \text{ \AA} \quad (\text{Rüdorff \& Schulz, 1940}).$$

$$C_{3i}^2 - R\bar{3}.$$

Fe in (c) with $z \sim \frac{1}{3}$; Cl in (f) with $x = \frac{1}{3}, y = 0, z = 0.077$.

$$Z = 6 \quad (\text{Wooster, 1932}).$$

Ferric chloride consists of three layers displaced relative to one another by the translation $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$. A single layer consists of sheets of iron atoms in an hexagonal array (Fe at $\pm\frac{1}{3}, \frac{2}{3}$) between sheets of chlorine atoms also in an hexagonal array ($\pm\frac{1}{3}, 0, 0.077$; $\pm 0, \frac{1}{3}, 0.077$; $\pm\frac{1}{3}, \frac{2}{3}, 0.077$) in such a way that every iron is surrounded by an octahedron of chlorines. The a -axis dimension for ferric chloride of Rüdorff & Schulz given above, rather than that of Wooster ($a = 5.92, c = 17.26$ \AA), was confirmed in the present study.

Electron-diffraction observations on the 55.5% sample

Specimens were prepared simply by dipping 200-mesh nickel grids into the powder. The specimens were examined in the electron-diffraction camera (Cowley & Rees, 1953) under high resolution, using a finely collimated electron beam which was focused on the specimen. (The general techniques of structure analysis using high-resolution electron-diffraction methods have been described by Cowley (1953).) Zinc oxide smoke was used for purposes of calibration. The wavelength was 0.0577₅ \AA.

Diffraction patterns such as the one reproduced in Fig. 1 were obtained when the beam was normal, or nearly normal, to the layer planes. The pattern would, at first glance, seem to result from diffraction from a mixture of graphite and ferric chloride, with the respective a axes of the two lattices at 30° to one another in the a - a plane, and with their c axes parallel

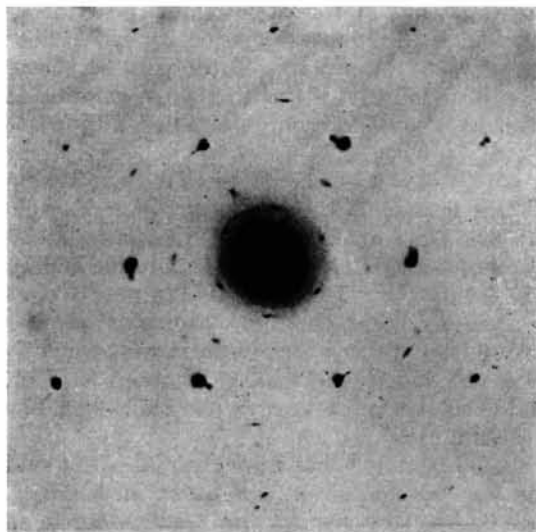


Fig. 1. Single-crystal electron-diffraction pattern ($hk0$ reflections) from 55.5% ferric chloride-graphite sample. The strong, widely spaced spots are given by carbon layers. The weaker, more closely spaced spots are given by FeCl_3 layers.

to one another and to the beam. However, the 100 and 200 reflections of ferric chloride are forbidden in the normal structure, and their appearance on the pattern suggests that normal stacking of the ferric chloride layers is not present. Moreover, tilted-crystal patterns show no extinguished reflections, but only changes in intensities. Such an observation requires disorder normal to the layer axis, but is not compatible with a simple mixture of the two substances.

For the measurement of intensities, an intensity strip was prepared from timed exposures of an off-centre, defocused beam. For a given reflection the intensity was obtained from the average of the visual estimates on all equivalent reflections. The structure amplitudes E_o given in Table 2 are the square roots of the respective intensities. The average lattice constants observed were

$$a_{\text{carbon}} = 2.46 \text{ \AA}, \quad a_{\text{FeCl}_3} = 6.06 \text{ \AA}.$$

The atomic scattering factors for electrons, f_e , were calculated from the corresponding X-ray form factors, f , from the usual relation

$$f_e = -\frac{2k\alpha}{s^2} \left(1 - \frac{f}{Z}\right), \quad (1)$$

where $k = 2\pi/\lambda$, $\alpha = -Ze^2/\hbar v$, and $s = (4\pi/\lambda) \sin \theta$.

Table 2. *Electron-diffraction structure factors*

(Values in Angström units)

Carbon lattice			
Reflection	100 E_o	100 E_c	100 $E_{\text{single layer}}$
100	134	-118	-136
110	95	97	126
200	59	-60	-50
210	33	-33	-30
300	51	64	48
220	33	31	37
Ferric chloride lattice			
Reflection	10 E_o	10 E_c	10 $E_{\text{single layer}}$
100	146	-142	-108
110	116	1	-22
200	22	-10	-50
210	36	-34	-36
300	146	148	216
220	58	27	-7
310	36	-41	-27
400	29	-35	-23
320	15	-11	-21
410	36	30	1
500	< 7	-7	-17
330	36	41	92
420	15	-17	-15
510	15	-12	-13
600	22	28	72
430	< 7	-14	-12
520	< 7	22	0
610	7	-13	-11
440	22	20	2
700	< 7	-10	-10

(Note that while f is in electrons, f_e is in \AA .) The form factor calculated by Hoerni & Ibers (1954) was used for carbon, and those calculated by James & Brindley (1931) for chlorine and iron.

Structure factors E_c were calculated for a single layer of carbon atoms. The quantities k and B in the expression

$$E_c = kE_o \exp(B \sin^2 \theta / \lambda^2) \quad (2)$$

were found by least squares. The value of B was -0.06 \AA^2 , and was thus taken to be zero. Comparison of observed and calculated structure amplitudes indicated small, but significant, differences. (The discrepancy factor $R = \sum |E_o - E_c| / \sum |E_o|$ was 0.13.) For structure amplitudes calculated for the two-layer graphite structure the R factor was 0.51. Likewise, the observed structure amplitudes from those reflections which correspond to the ferric chloride lattice are in better agreement with structure amplitudes for a single layer of ferric chloride than with those based on the normal structure. These facts, coupled with the disorder mentioned above, suggest that in the 55.5% sample single layers of carbon and ferric chloride are superimposed without any strong correlation in the a direction between successive layers.

It was thought likely that on a statistical basis chlorine atoms would prefer particular positions relative to the carbon ring. Since the ratio of the repeat distances along parallel directions in the ferric chloride

and carbon lattices is irrational, the chlorine atoms of a normal ferric chloride layer would not have any definite positions when referred to the average unit cell of the carbon layer lattice. If, however, the chlorines tend to take up preferred positions relative to the carbon atoms when this involves only small movements relative to the ferric chloride layer lattice, the carbon layer unit cell can be considered to contain fractions of chlorine atoms at the preferred positions, and the structure factors will be modified accordingly. Therefore, the signs of E_c were assigned to E_o , and a difference Fourier map, $E_o - E_c$, was computed in $\frac{1}{30}$ th's of the orthohexagonal cell edges. One-quarter of the difference Fourier map is shown in Fig. 2.

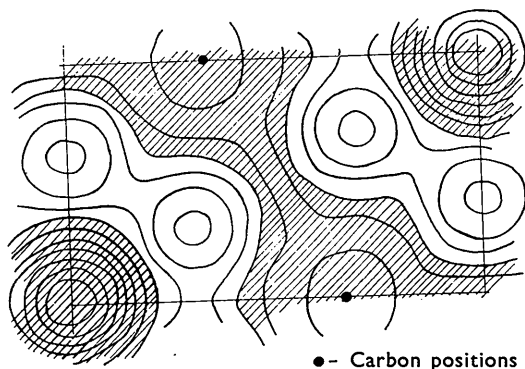


Fig. 2. Difference Fourier map derived from the carbon $hk0$ reflections from 55.5% ferric chloride-graphite sample by subtracting the contributions of carbon atoms at the positions indicated. One quarter of the orthohexagonal cell is shown. Negative regions are shaded.

Peaks are observed at $\pm\frac{9}{30}, \frac{9}{30}; \pm 0, \frac{9}{30}; \pm\frac{9}{30}, 0$ (all on the hexagonal unit cell), and are assigned to chlorine. The estimation of the number of chlorine atoms present per carbon atom is made difficult by insufficient knowledge of $f_{eCl}(0)$. The atomic scattering factors for electrons at zero scattering angle are indeterminate from equation (1), but may be determined approximately by extrapolation. In this way values of $f_e(0)$ for chlorine between 8 and 14 Å were thought possible. In order to estimate the number of chlorine atoms per carbon atom, that is, per quarter orthohexagonal cell, the assumptions were made that the scale of the difference Fourier map, based on the calculated structure factors for a single layer of carbon atoms, was correct (it was found subsequently to be correct to 1%), and that the hole at the origin in the difference Fourier map was due to $-f_{eCl}(0)$. The number of chlorine atoms per quarter orthohexagonal cell is found to be between 0.2 and 0.4. It is also possible from this number and from the peak heights, corrected for the origin term, to estimate the temperature factor to be applied to the chlorine atoms. The value $B = 1 \text{ \AA}^2$ was obtained in this way.

Structure factors for the hexagonal cell, which contains two carbon atoms, were computed for various

amounts of chlorine between 0.4 and 0.8 atoms. The value $B = 1 \text{ \AA}^2$ was applied to chlorine, but no temperature factor was applied to the carbon atoms. The best agreement with the observed structure amplitudes was obtained for 0.5 chlorine, where the R factor is 0.08. These structure factors are given in Table 2. Corresponding values of R are 0.10 for 0.4 chlorine, and 0.16 for 0.8 chlorine. Because of the uncertainties in the data and in the calculations, introduced primarily by the difficulties of intensity estimation and by insufficient knowledge of the atomic scattering factors, it is doubtful if the number of chlorine atoms per carbon atom has been determined to better than $0.2 \leq n_{Cl/C} \leq 0.3$.

It will be shown subsequently that there is one carbon plane between successive layers of ferric chloride in the 55.5% sample. The ratio of the areas of the unit cell of a single layer of ferric chloride containing two molecules to the unit cell of a single plane of carbon atoms containing two atoms is about 6:1. Accordingly, for every carbon atom in the compound there is 0.5 chlorine. Thus, only about half of the available chlorine atoms are in the positions indicated in the difference Fourier.

It should be noted that since the number of chlorine atoms per carbon atom can be at most 0.5, $f_{eCl}(0)$ cannot be less than 6.4 Å. This value is not in agreement with that of 2.65 Å obtained by Vainshtein (1952) from attempts to correlate $f_e(0)$ with atomic radii. It would seem that structure determinations by electron diffraction afford, at the present time, the best method for the determination of a reliable set of $f_e(0)$ values.

The reflections from a single layer of ferric chloride, depending upon their structure factors, may be grouped as follows:

- (1) $h-k \equiv 0 \pmod{3}$, $E = -f_{eFe}$;
- (2) $h-k \equiv 0 \pmod{3}$ and 3 does not divide h ,
 $E = 2f_{eFe} - 3f_{eCl}$;
- (3) $h-k \equiv 0 \pmod{3}$ and 3 divides h ,
 $E = 2f_{eFe} + 6f_{eCl}$.

Structure factors were computed for a single layer and compared with the observed, which, for purposes of this comparison, were corrected for scale and temperature factors by equation (2). These structure factors for a single layer are given in Table 2. Agreement is quite poor, but is significantly better for type-(1) reflections than for the others. This indicates that the iron atoms are approximately in their normal positions, but that the chlorine atoms are not. Structure factors for type-(1) and type-(3) reflections offer no problem of sign determination. However, structure factors for type-(2) reflections may be either positive or negative. The signs were taken to be positive, for it was assumed, and soon confirmed, that the chlorine atoms have high effective temperature factors. With the signs thus assigned, a Fourier projection in $\frac{1}{30}$ th's of the orthohexagonal cell edges was computed from the

observed structure amplitudes. No artificial temperature factor was needed. An estimate of $E(00)$ was made from an extrapolation to zero scattering angle of the iron and chlorine scattering factors.

The Fourier map (Fig. 3) indicates that the iron

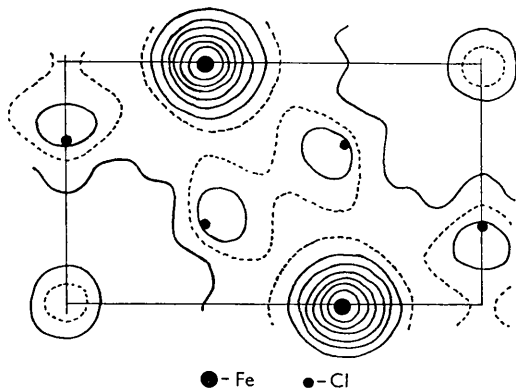


Fig. 3. Fourier map derived from the ferric chloride $hk0$ electron-diffraction intensities from 55.5% ferric chloride-graphite sample. The black dots indicate the atomic positions for a normal ferric chloride layer. One quarter of the orthohexagonal cell is shown.

atoms are in their normal positions, and that the chlorine atoms are diffuse and shifted by about 0.2 \AA ; that is, the chlorine triangles on either side of an iron atom are rotated approximately 3° about the c axis toward one another. The chlorine positions $\pm 0.36, 0.36$; $\pm 0, 0.36$; $\pm 0.36, 0$ together with the iron positions $\pm \frac{1}{3}, \frac{2}{3}$ (all on the hexagonal cell) and the temperature factor B of 6 \AA^2 for the chlorine atoms derived from the Fourier map were used to calculate the structure factors E_c given in Table 2. Agreement is good, and if the 110 reflection and unobserved reflections are omitted, the R factor is 0.12.

It can be seen from Fig. 1 that equivalent points are not of the same intensity. This is because the c axis of the crystal is inclined slightly (about 2°) to the electron beam. It will be shown below that the wider variation and general increase of intensity of the 110 and 220 reflections of ferric chloride are expected for small angles of tilt. The very high, incorrect structure amplitude for the 110 reflection, which was put into the Fourier map, does little but augment the iron peaks, and hence does not affect the conclusions reached above.

An estimate of the percentage carbon in the ferric chloride-graphite compound may be made from the respective areas of the carbon and ferric chloride lattices, the derived scale factors, and the estimated values of $E(00)$. The percentage obtained is consistent with one ferric chloride layer per carbon plane, but is not deemed sufficiently reliable to establish such a ratio definitely. All evidence from the electron-diffraction data supports the picture of a ferric chloride single layer intercalated between successive planes of carbon. However, it seemed desirable to obtain direct

evidence for this stacking order, i.e. to obtain the repeat distance in the c direction. For this purpose, and because it provided a useful check on interpretations given above, X-ray powder data on the 55.5% sample were collected.

X-ray diffraction observations on the 55.5% sample

X-ray diffraction powder photographs were taken in a 14.3 cm. diameter General Electric type camera, using Co $K\alpha$ radiation ($\lambda = 1.7902 \text{ \AA}$) filtered through 0.038 mm. of iron. Samples were made up in thin-walled uniform glass tubes of external diameter about 0.3 mm. Exposures were of the order of 240 mA. hr. Longer exposures were not useful because of the increase in the level of the background.

The positions of the rings were measured with a vernier scale. The intensities were estimated in the following way: On a Leeds-Northrup recording microphotometer tracings were made of the powder photographs. A smooth background was drawn in and then, after replotting on a linear scale, the areas under the peaks were found with the aid of a planimeter.

Table 3 lists, besides the positions and integrated intensities of the rings, the structures and the values of hkl to which these rings are assigned. The rings are of five types: (1) hkl rings of graphite; (2) $00l$ rings of

Table 3. X-ray diffraction powder data

d_o (Å)	d_c^* (Å)	Structure†	Index	Intensity (arbitrary scale)
9.2	9.41	F-C	001	399
5.17	5.25	F	10	~ 1000
4.65	4.71	F-C	002	411
3.33	3.35	G	002	172
3.12	3.14	F-C	003	229
2.90	3.03	F	11	~ 425
2.57	2.62	F	20	~ 205
2.11	2.13	C, G	10, 100	50
2.08	2.09	G	1, 0, $\frac{1}{3}$?
2.03	2.03	G	101	28
1.99	1.98	F	21	10
1.76	1.75	F	30	228
1.73	1.72	F-C	301	57
1.68	1.68	G	004	33
1.63	1.64	F-C	302	48
1.56	1.57	F-C	006	80
1.50	1.52	F	22	55
1.46	1.46	F	31	65
1.23	1.23	G	110	18
1.22	1.23	C	11	28
1.18	1.18	F-C	008	23
1.15	1.16	G	112	16
1.14	1.15	F	41	15
1.13	1.12	G	006	30
1.07	1.07	C, G	20, 200	13
1.01	1.01	F	33	28
0.993	0.992	G	114	88

* d_c is for normal reflections. In the case of the hk reflections from carbon and from ferric chloride, the d_c computed for the normal $hk0$ reflections should be too high.

† F-C is the ferric chloride-graphite compound; F is ferric chloride within the compound; C is carbon within the compound; G is free graphite.

ferric chloride-graphite; (3) hk rings of single planes of carbon; (4) hk rings of single layers of ferric chloride; and (5) hkl rings from ferric chloride-graphite.

(a) *The graphite rings*

A striking feature of the powder photographs is the appearance of rings which can only be assigned to the graphite lattice as hkl . The presence of $hk0$ rings is expected in view of the electron-diffraction observations, but the presence of rings for which $l \neq 0$ can only be explained on the basis of free graphite. The presence of graphite in these preparations had not been suspected previously, but is consistent with the observation noted earlier that the densities are non-uniform. Many of these same rings were observed by Rüdorff & Schulz (1940) on their powder patterns of 56% samples and were assigned by them to reflections from β radiation and to hkl reflections from ferric chloride-graphite. The radiation used in the present study was filtered with a thickness of iron sufficient to remove all but about 0.001% of the Co $K\beta$ radiation. Moreover, on photographs of natural graphite and of sodium chloride prepared with Co $K\alpha$ from the same tube, no extra lines are observed; the tube was thus free from foreign radiations. As is shown in detail below, these rings cannot be hkl reflections from the proposed structure of ferric chloride-graphite.

The presence of free graphite could well indicate a more complicated phase system for ferric chloride-graphite mixtures. Accordingly, X-ray powder photographs were taken of the 55.5% sample at $300 \pm 10^\circ$ C. in the same camera adapted for high-temperature photography. The photographs show none of the rings assigned above to free graphite, but show, in addition to the other rings already observed on the room-temperature photographs, rings at d values of 1.81₉, 1.80₁, 1.26₂, and 1.07₁ Å. The reason for the appearance of these extra rings is not known; they might result from a compound formed at elevated temperatures from the hydrolysis of part of the ferric chloride by the water known to be present, or possibly from a compound formed by the reaction of part of the ferric chloride with adsorbed oxygen. They are not due to a single layer of normal ferric oxychloride (Goldsztaub, 1935). It therefore appears that, whereas both our samples and those of Rüdorff & Schulz (1940), cooled after preparation with excess ferric chloride at 300° C. or more, contain free graphite and an enriched ferric chloride-graphite phase, heating of this mixture with zero partial pressure of ferric chloride results in the disappearance of the free graphite.

It is possible to determine the percentage by weight of free graphite x_G in the following way. Suppose p is defined as the ratio of ferric chloride in an intercalated layer to that in a layer in normal ferric chloride. Then, on the assumption that there is one ferric chloride layer per carbon plane (this is justified below), one finds readily that

$$\left. \begin{aligned} \rho &= 0.808 + 1.800p, \\ r &= (1 + 0.449/p)^{-1}, \end{aligned} \right\} \quad (3)$$

where ρ is the density of the ferric chloride-graphite compound and r is the percentage of ferric chloride in the compound. Then we have

$$(x/\rho + x_G/\rho_G)^{-1} = \rho_0, \quad xr = r_0, \quad (4)$$

where ρ_0 and r_0 refer to the mixture, i.e. they are the measured quantities. From the values $\rho_0 = 2.46 \pm 0.02$ g.cm.⁻³, $r_0 = 55.5\%$, and $\rho_G = 2.267$ g.cm.⁻³, one obtains $p = 0.91_5 \pm 0.020$ and $x_G = 0.17 \pm 0.02$. The compound thus contains 66.9% FeCl₃, as compared with 69% for one with completely filled layers.

The observed graphite intensities were adjusted by multiplicity, Lorentz and polarization factors, and corrected for adsorption. (The linear absorption coefficient μ for the mixture is 176 cm.⁻¹, and μr is approximately 6.) Structure amplitudes were derived from these intensities and were corrected for temperature effects, using the temperature factors of Bacon (1952). These structure amplitudes are compared in Table 4 with those calculated for the two-layer

Table 4. *Observed and calculated structure factors for graphite*
(Values in e^-)

Reflection	F_o	F_o (100% graphite)	F_c
002	27	16.4	-17.3
100	11*	3.6	3.1
1,0, ₃ ²	—	8.2†	-9.2
101	6	4.8	-5.2
1,0, ₃ ⁴	—	6.5†	-5.7
102	—	1.8	-2.7
004	17	10.4	10.1
103	—	2.8	2.4
110	5	7.2	7.8
112	5	6.3	-7.5
006	5	6.6	-7.3
200	5*	—	1.8
201	—	1.7	1.8
114	8	8.9	6.8

* These structure amplitudes were computed from intensities to which the carbon hk reflections had also contributed. In the case of the 110 reflection, the 11 ring of carbon can be resolved.

† Scale factor for these reflections is 13.0.

graphite structure from the Hoerni & Ibers' (1954) form factor. The observed structure amplitudes have been scaled, the scale factor being 1.05. The R factor is 0.35 for the six reflections. (In the calculation of the scale and R factors, the $hk0$ structure factors were omitted, since these are enhanced by the carbon hk reflections.) In view of the difficulty of an accurate measurement of the sample thickness and of the large effect of small changes in μr on the observed structure factors, and in view of the fact that most of the graphite reflections occur at relatively low values of d and are faint, this R factor cannot be considered too poor.

For the sake of comparison, structure factors derived in the same way (but with a negligible absorption correction) from a photograph of natural graphite (scale factor 3.74) are given in Table 4. The R factor in this case is 0.11. The sample contained about 20% of the rhombohedral three-layer form of graphite (Lipson & Stokes, 1942), as estimated from the respective scale factors of the rhombohedral and hexagonal reflections. Values between about 0 and 30% are found in natural graphite from various sources (Boehm & Hofmann, 1955). The R factor of 0.11 seems to result primarily from the limitations of the methods used for the estimation of intensities. The effect of the rhombohedral form on the observed intensities (enforcement of reflections of the type $h-k \equiv 0 \pmod{3}$), and the effect of preferred orientation (enforcement, in general, of the $00l$ reflections) are not observed.

(b) *The 00l rings of ferric chloride-graphite*

The electron-diffraction evidence suggests a structure for ferric chloride-graphite in which one ferric chloride layer is between successive planes of carbon. The predicted repeat distance for this model is of the order of $(\frac{1}{2}c_{\text{graphite}} + \frac{1}{3}c_{\text{FeCl}_3}) = 9.2 \text{ \AA}$. A series of rings are observed that can be indexed on the basis of $c = 9.41 \pm 0.02 \text{ \AA}$. (This value is obtained by extrapolation (Nelson & Riley, 1945b).) Rüdorff & Schulz (1940) find a c spacing of 9.37 \AA for the 56% preparation.

For the calculation of structure factors it was assumed that the iron, chlorine, and carbon layers are all planar. The perpendicular distance between iron and chlorine planes was taken to be 1.34 \AA , as in normal ferric chloride. The carbon plane was assumed to be midway between chlorine planes, and on this assumption the perpendicular distance between carbon and chlorine planes is 3.36_5 \AA . The percentage of ferric chloride per ferric chloride layer was taken to be 92%. Table 5 gives the calculated and the observed structure factors.

Table 5. *Observed and calculated structure factors for ferric chloride-graphite*

Reflection	(Values in e^-)	
	F_o	F_c
001	51	27.3
002	86	93.1
003	85	-82.2
004	< 23	22.1
005	< 29	-20.9
006	103	93.1
007	< 46	51.9
008	80	83.7
009	< 55	-4.9

The observed structure amplitudes were derived from the integrated intensities, adjusted by multiplicity, Lorentz and polarization factors, and corrected for absorption. No correction was made for extinction. The scale and temperature factors were

found by least squares to be $k = 2.47$ and $B = 5.9 \text{ \AA}^2$. These have been applied to the observed structure amplitudes in Table 5.

The agreement between observed and calculated structure amplitudes must be considered good ($R = 0.12$, with unobserved reflections omitted), particularly in view of the difficulties of estimating intensities of the weaker rings.

The data are not sufficiently reliable or numerous to allow one to detect either minor deviations from planarity of the layers or small variations in the Fe-Cl perpendicular distance. Rüdorff & Schulz (1940), on the basis of very rough intensities, state that the Fe-Cl distance is lengthened to 1.43 \AA , but there seems little justification for this conclusion.

It is possible to calculate from the scale factors of the graphite and the ferric chloride-graphite structure factors, and from the values of $F(000)$ for the two lattices, a value of x_G . One obtains x_G of 0.19, in excellent agreement with the value 0.17 ± 0.02 derived earlier from the density measurements and percentage ferric chloride. These two calculations are essentially independent, for p has little effect on x_G computed from the scale factors.

(c) *The hkl rings of ferric chloride-graphite*

The powder photographs reveal only two general hkl rings of ferric chloride-graphite, the 301 and the 302. If successive planes were completely random in translation parallel to the layers, no hkl lines would be observed. It is known from the electron-diffraction results, however, that some of the chlorine positions are correlated with carbon positions. Such a correlation will introduce some short-range order.

In Fig. 4 is drawn part of the carbon layer together with the positions in projection occupied statistically

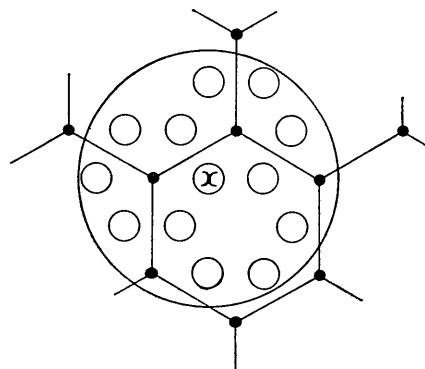


Fig. 4. The preferred chlorine positions (circles) relative to a carbon layer lattice.

by some of the chlorine atoms. Suppose for the moment that all chlorine atoms are in such positions, and that a particular chlorine atom is at the point x and is below the carbon plane. The circle of radius 1.91 \AA in Fig. 4 encloses an area in which there must be at least one chlorine atom. The positions within the circle

thus represent possible locations of a chlorine atom in the layer above the carbon plane. The probability that a chlorine atom in this plane is also at the point x is $\frac{1}{3}$, if it is assumed that this chlorine atom is not influenced by the one beneath the carbon plane. For the chlorine atom above the plane to lie also at x , it is necessary that the upper ferric chloride layer be shifted by one of the translations $a/3, 0; 0, a/3; a/3, a/3$ (a refers to the ferric chloride a spacing) relative to the lower layer. Such a translation will result in hkl reflections for $h-k \equiv 0 \pmod{3}$ and 3 divides h . No other hkl reflections will appear. Moreover, since the carbon a spacing is not a sub-multiple of the ferric chloride a spacing, none of the other possible positions for the upper chlorine atom leads to a translation which produces hkl reflections.

The preceding arguments are unaffected by the fact that not all chlorine atoms lie in the positions indicated in Fig. 4. All that is required is that enough chlorine atoms be in these positions to 'hold' the layers in position relative to one another. That such is the case is attested to by the fact that the a axis of ferric chloride is observed to make an angle of 30° with the a axis of carbon.

The $33l$'s are not observed, for they lie under the 330 peak.

It is possible in theory to compute the probability distribution from the observed intensities of the hkl reflections and so determine whether a chlorine atom in the upper plane is influenced by a chlorine atom below the plane. However, the limited number of hkl reflections observable and the limited accuracy possible in the measurement of their intensities make such a calculation fruitless.

(d) *The hk reflections from carbon and ferric chloride*

If we neglect the slight local ordering effect discussed in the preceding section, both the ferric chloride and the carbon components of the compound are in the form of equidistant and parallel layers with random translations normal to the layer axis (c axis). Diffraction of X-rays from such layers has been treated

theoretically (for example, Laue, 1932; Warren, 1941; Houska & Warren, 1954) and experimentally (for example, Biscoe & Warren, 1942; Franklin, 1951; Houska & Warren, 1954). Two types of reflection are observed: sharp, crystalline $00l$ reflections, and diffuse, two-dimensional reflections, hk .

Following Houska & Warren (1954), one finds that the relative intensity at θ of a two-dimensional reflection hk with Bragg angle θ_0 is

$$P'(2\theta) = k\tau^{\frac{1}{2}} \cdot F^2(hk) \cdot \varphi(\alpha) \cdot \frac{1 + \cos^2 2\theta}{2 \sin \theta \cdot (\sin \theta + \sin \theta_0)^{\frac{1}{2}}}, \quad (5)$$

where

$$\varphi(\alpha) = \int_{-\infty}^{\infty} \exp[-(\alpha - x^2)^2] dx, \quad \alpha = \tau\pi(\sin \theta - \sin \theta_0).$$

Here, τ is a function of the wave-length and of the particle dimensions. The structure factor $F(hk)$ is given by

$$F_{\pm}(hk) = \sum_n f_n \exp \left[2\pi i \left\{ hx_n + ky_n \pm \frac{2cz_n}{\lambda} (\sin^2 \theta - \sin^2 \theta_0)^{\frac{1}{2}} \right\} \right], \quad (6)$$

and, in general, the square of the structure factor may be written

$$\left. \begin{aligned} F^2(hk) &= F_+^2(hk) + F_-^2(hk) \quad (\theta > \theta_0), \\ F^2(hk) &= F_+^2(hk) = F_-^2(hk) \quad (\theta = \theta_0). \end{aligned} \right\} \quad (7)$$

If the layers are strictly planar, so that z_n is zero in equation (6), $F^2(hk)$ is a decreasing monotonic function. Hence, in the powder pattern, the intensity rises sharply to a maximum at an angle close to, but greater than, θ_0 and then falls off slowly on the high-angle side. The shift of the maximum from the Bragg angle depends primarily on the crystal size. The carbon hk reflections appear to have this predicted peak shape. This cannot be confirmed quantitatively, however, since the hk reflections occur at high angles and are weak and overlapped by other rings. Also, they very nearly coincide with the $hk0$ reflections of the free

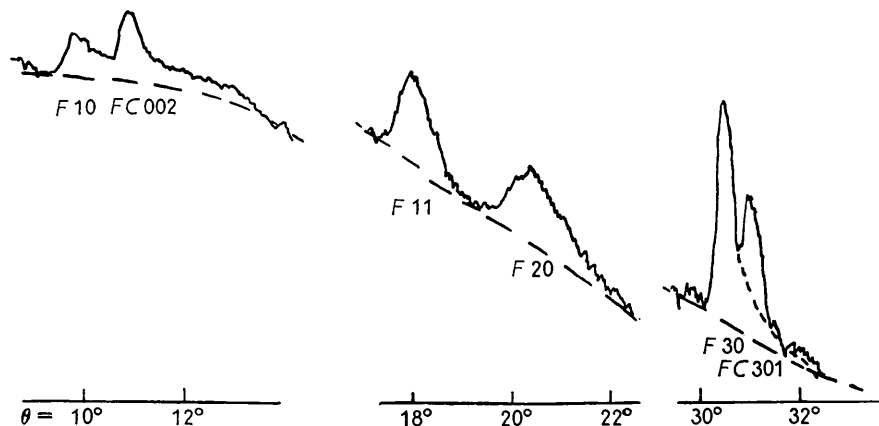


Fig. 5. Portions of the microphotometer trace of the X-ray powder pattern of 55.5% ferric chloride-graphite sample.

graphite. The 110 and 11 rings are resolved, and each has the expected shape.

The ferric chloride reflections for which $h-k \equiv 0 \pmod{3}$ should have very nearly this same peak shape, since, except for the small effect of the deviation of the chlorine atoms from their normal positions, only the iron atoms contribute to the structure factors. This is confirmed, for example, by the 10 and 20 peak shapes in the microphotometer trace (Fig. 5).

For the other types of ferric chloride reflections, $F^2(hk)$ does not decrease monotonically, and there are weak subsidiary maxima in the high-angle tails of the hk peaks. Calculation shows that these subsidiary maxima are too weak and too diffuse to be detected with any certainty. Reflections with $h-k \equiv 0 \pmod{3}$ and 3 divides h , such as the 30, give relatively sharp, almost symmetrical peaks with maxima very close to the Bragg positions. From the width of the 30 peak (see Fig. 5), ignoring instrumental broadening, the particle size was estimated to be 1000 Å. Using this value it is found that there should be a subsidiary diffuse maximum at $d = 1.14$ Å, of height 2% of that of the primary peak and width about 0.15 in $\sin \theta$. A slight increase in the background suggests that this peak may be present.

For a reflection with $h-k \equiv 0 \pmod{3}$ and 3 does not divide h , $F^2(hk)$ is very small at θ_0 but becomes large for higher angles. The maximum of the peak is therefore shifted appreciably from the Bragg position. For the 11 reflection the shift was observed to be 0.013 in $\sin \theta$, as compared with the calculated shift of 0.014. A broad subsidiary maximum of height less than 1% of the primary peak is predicted at $d = 0.94$, but this is not observable.

All the hk two-dimensional peaks for carbon and ferric chloride have therefore been shown to have the expected shapes, at least qualitatively, and it has been established that no observable rings result from the secondary maxima in the scattering function for the ferric chloride layers.

In reciprocal-lattice space, there are continuous lines of scattering power corresponding to the 11 and 22 ferric chloride reflections. The scattering power is very small at the $hk0$ position, but increases rapidly on either side of this position. Thus a single-crystal electron-diffraction pattern obtained with a tilt of 2° or so to the c axis may show strong 11 and 22 reflections. This effect is seen in the pattern (Fig. 1) and explains the discrepancies in Table 2.

The intensities of the ferric chloride hk reflections could not be measured with any accuracy because of their extended shapes and the uncertain background. However, they are seen to be in semi-quantitative agreement with the electron-diffraction intensities. It should be noted that information derived from the electron-diffraction $hk0$ intensities could not have been derived independently from the relatively inaccurate X-ray intensity measurements for the hk reflections.

Observations on other ferric chloride-graphite compositions

The electron-diffraction and X-ray patterns of the 49.2% and 43.4% samples are identical in detail with those of the 55.5% sample except for differences in the intensities of the free graphite reflections relative to the ferric chloride-graphite intensities, and for a weak extra ring at $d = 1.36$ Å. From the intensities, and independently from the densities and the known percentages of ferric chloride, values of p and x_G were derived. These are given in Table 1, together with the values derived earlier for the 55.5% sample.

The powder photographs of the 38.5% and 30.3% samples, on the other hand, are quite different from those of the 55.5%. No sharp $00l$ reflections of ferric chloride-graphite appear. Instead there are diffuse haloes in positions corresponding to d values of from 16.2 to 9.5 Å, from 4.8 to 4.5 Å and from 4.0 to 3.7 Å. These may be explained on the basis of a disordered stacking sequence with a more-or-less randomly varying number of carbon planes between successive ferric chloride layers. The relatively sharp hk ferric chloride rings and hkl rings of free graphite are present, although weak, together with some unexplained rings, notably one at $d = 3.23$ Å.

The structure of the ferric chloride-graphite compound

In a hypothetical structure in which all of the chlorine atoms take up the positions relative to the carbon atoms indicated in the difference Fourier map, several interesting features are observed. First, the angle between the respective a axes of the ferric chloride and graphite must be 30° , in agreement with experiment. Second, the chlorine atom configuration must be distorted so that some Cl-Cl distances are as short as 3.15 Å while others are as long as 4.2 Å, as compared with the normal distances of 3.40, 3.49 and 3.75 Å in the ferric chloride structure.

The actual structure apparently results from the simultaneous attempt of the chlorine atoms to occupy the preferred positions relative to the carbon lattice indicated in the difference Fourier map, and to maintain normal, or nearly normal, Cl-Cl distances. In view of the large distortions involved if all chlorines occupy the preferred positions, it is not surprising that only about half of them do. These will be distributed at random in the chlorine planes.

The slight rotation relative to one another of the chlorine triangles above and below an iron atom is such as to maintain approximately equal Cl-Fe distances.

It was noted earlier that the samples contained 0.5-1.0% water, i.e. one water molecule per 7-15 ferric chloride molecules. This water may be adsorbed on the surface of the particles, or may actually be intercalated with the ferric chloride, in which case its

presence may account for the fact that the ferric chloride layer is only 92% filled, and also may account for the 2% increase in the a axis over that observed by Wooster (1932) in normal ferric chloride.

The structures of the lower percentage samples are consistent with their preparation from the 55.5% material. As the latter is heated, the amount of ferric chloride is reduced partly by an increase in the amount of free graphite and partly by a reduction in p , i.e. in the amount of ferric chloride contained in each layer. When the total ferric chloride content becomes less than about 40%, the value of p becomes less than 0.80, and the ordered layer stacking sequence is unstable at room temperature. It is possible, of course, that some disorder in the stacking sequence exists for the higher percentage samples, but the effects of such disorder on the powder photographs are not readily detected.

The fact that the final percentage of ferric chloride is independent of particle size (Rüdorff & Schulz, 1940) suggests that the free graphite does not result from inadequate exposure to the ferric chloride. Some indication of the origin of the free graphite is given by observation of the occurrence of the rings corresponding to the rhombohedral form of graphite. Boehm & Hofmann (1955) have found that the rhombohedral form, present in the starting material, is absent from graphite recovered after intercalation with ferric chloride. In the patterns of the 55.5% sample, the rhombohedral $1,0, \frac{2}{3}$ line was found to be missing, or else very much weaker relative to the other graphite lines than in the pattern of pure graphite. This suggests that at the temperature of preparation all the graphite was involved in a single-phase system with the 55.5% ferric chloride intercalated, giving a p of 0.56. On cooling to room temperature this single phase dissociated to give free graphite and a compound with higher ferric chloride content (a p of 0.92). In the patterns from the 49.2%, 38.5%, and 30.3% samples the rhombohedral $1,0, \frac{2}{3}$ line did appear weakly, but its intensity relative to other graphite lines was less than that found in pure graphite. The $1,0, \frac{2}{3}$ line was normal in patterns from the 43.4% sample. This is not significant, however, for this sample was ground to reduce the particle size before the pattern was recorded, and Boehm & Hofmann (1955) have indicated that the rhombohedral modification is produced by grinding normal graphite. It therefore appears that in the 49.2 and 43.4% samples, as in the 55.5%, the amount of free graphite increases as the sample is cooled from the reaction temperature. The disappearance of the free graphite rings from the 55.5% pattern when the sample was reheated confirms this picture.

Comparison with the results of Rüdorff & Schulz

The conclusions reached in this paper are so different from those of Rüdorff & Schulz (1940) that a detailed

comparison would be too lengthy, and only a few of the major differences will be mentioned.

Rüdorff & Schulz (1940) find three types of ferric chloride-graphite 'compounds', designated types I, II and III, depending on the number of carbon planes between successive ferric chloride layers, and containing 56%, 44% and 30-37% of ferric chloride respectively. From the densities which they found for these 'compounds', one finds the fractions of ferric chloride present in the layers to be 0.50, 0.67 and 0.75. These fractions are difficult to reconcile with the evidence of an ordered structure of the layers. In the structures which Rüdorff & Schulz propose for these 'compounds', both the ferric chloride layers and the graphite layers are stacked in an ordered manner to give large three-dimensional unit cells. These structures are clearly inconsistent both with our data and with theirs.

It is possible that slight differences in the methods of preparation have prevented us from confirming the occurrence of the types II and III of Rüdorff & Schulz. Their observation that their 56% 'compound' decomposes directly and rapidly to the 30-37% (type III) 'compound', is not confirmed by the recent research of Croft (1955), who is able to obtain a continuously decreasing percentage of ferric chloride by heating the 56% material at about 320° C.

Conclusion

This investigation has revealed a rather interesting new type of structure for the intercalated graphite-ferric chloride compound. The observations on the occurrence of free graphite have indicated that the ferric chloride-graphite phase system is more complicated than previously supposed. In the limited composition range studied, there seems to be a single-phase region of variable composition at elevated temperatures, and a two-phase region at room temperature, the stable phases being free graphite and a ferric chloride-graphite compound with about 65% ferric chloride. A much more detailed investigation is obviously required in order to establish the exact form of the phase diagram.

It does not seem possible, from the evidence of this one structure, to draw any conclusions about the role which structure plays in the selectivity of graphite towards intercalation. Such information will presumably come only from comparison of the structures of a number of intercalated compounds.

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A Simplified Calculation for the Elastic Constants of Arbitrarily Oriented Single Crystals

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A simple, completely general, and easily remembered scheme is presented for solving problems involving the transformation of elastic constants from one orthogonal coordinate system to another rotated with respect to the first. Since the components of stress can be expressed as the elements of a second rank tensor, and the components of strain (if properly defined) can likewise be expressed as the elements of a second rank tensor, the elastic constants connecting stress and strain must be the elements of a fourth rank tensor. The method depends upon the simultaneous contraction of the fourth rank tensor and the quadratic products of the direction cosines connecting the two axis systems. The application of the resultant 'transformation matrix', instead of the conventional methods, reduces the number of steps to a minimum with a corresponding reduction in the chance for errors in the computation. The saving in time and labor is considerable, as is shown by typical examples.

1. Introduction

In many solid-state experiments on single crystals (e.g., the determination of elastic constants) it is necessary to express the elastic moduli or elastic constants in an axis system rotated with respect to an orthogonal system oriented along the principal

crystallographic directions of the crystal. The matrix of the direction cosines connecting an arbitrary axis system (primed) in the specimen with this crystal-axis system (unprimed) can usually be determined in a straightforward manner (e.g., by X-ray analysis). Then if a system of stresses is applied to the specimen and the resultant strains are measured, the elastic constants of the material (relative to the unprimed system) can be calculated.

Difficulties in practice often arise due to the necessity for contracting a fourth rank tensor, and the

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