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X-RAY DIFFRACTION STUDIES
ON
HEAVY METAL IRON-CYANIDES

by

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A Thesis

Presented to the Faculty of the
Rice Institute of Houston, Texas

in Partial Fulfillment of
the Requirements for the

Degree

of

Doctor of Philosophy

The Rice Institute

1941

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CONTENTS

INTRODUCTION	1
EXPERIMENTAL	
A. Isothermal rehydration Studies	3
B. X-ray Diffraction Studies	4
C. Density Measurements	7
DISCUSSION	
A. Isothermal Dehydration Studies	8
B. X-ray Diffraction Studies	9
C. Prussian Blue and Turnbull's Blue	14
SUMMARY OF RESULTS AND CONCLUSIONS	17
BIBLIOGRAPHY	20
TABLES	
DIAGRAMS	

X-ray Diffraction Studies on Heavy Metal Iron-Cyanides

I. Introduction

Various iron cyanides have been investigated by x-ray diffraction studies as to the arrangement of ions in the lattice and the nature of the bonds. From the study of the iron cyanide (1), it was concluded that all the iron cyanides are isostructural with the iron cyanide. The structure of the iron cyanide is a simple cubic lattice with the iron ions, cyanide ions and water molecules in the lattice. The structure of the iron cyanide is a simple cubic lattice with the iron ions, cyanide ions and water molecules in the lattice. The structure of the iron cyanide is a simple cubic lattice with the iron ions, cyanide ions and water molecules in the lattice. The structure of the iron cyanide is a simple cubic lattice with the iron ions, cyanide ions and water molecules in the lattice.

In the case of the iron cyanide, the structure of the iron cyanide is a simple cubic lattice with the iron ions, cyanide ions and water molecules in the lattice. The structure of the iron cyanide is a simple cubic lattice with the iron ions, cyanide ions and water molecules in the lattice. The structure of the iron cyanide is a simple cubic lattice with the iron ions, cyanide ions and water molecules in the lattice. The structure of the iron cyanide is a simple cubic lattice with the iron ions, cyanide ions and water molecules in the lattice. The structure of the iron cyanide is a simple cubic lattice with the iron ions, cyanide ions and water molecules in the lattice.

By a series of analyses on various iron cyanides, it was concluded that the iron cyanides are isostructural with the iron cyanide. The structure of the iron cyanide is a simple cubic lattice with the iron ions, cyanide ions and water molecules in the lattice. The structure of the iron cyanide is a simple cubic lattice with the iron ions, cyanide ions and water molecules in the lattice. The structure of the iron cyanide is a simple cubic lattice with the iron ions, cyanide ions and water molecules in the lattice. The structure of the iron cyanide is a simple cubic lattice with the iron ions, cyanide ions and water molecules in the lattice.

Wolfsberg, Milligan and Bates (2) obtained almost identical x-ray diffraction patterns for Prussian blue, Turnbull's blue, and the ferrous cyanide and ferrocyanide salts of divalent copper, cobalt, nickel, and manganese. It was assumed that these compounds are isostructural and that the relatively large iron-cyanide anions are so arranged as to give channels in which the smaller metal ions are produced.

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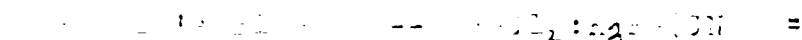
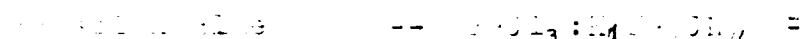
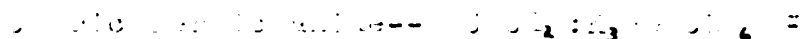
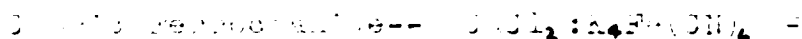
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II. Experimental

A. Isothermal degeneration studies

Small amounts of the ferrocene, nickel, cobalt, and manganese, plus lanthanum, cerium, and thorium salts were prepared by reacting mixtures of UO_2 and $UO_2 \cdot 2H_2O$ with UO_2 and $UO_2 \cdot 2H_2O$. The reaction conditions were varied as follows, in order to obtain mixtures of different compositions. The following mole ratios were used:



The samples were dried in a desiccator over $CaCl_2$ for 24 hours. The samples were then placed in a desiccator over $CaCl_2$ for 24 hours. The samples were then placed in a desiccator over $CaCl_2$ for 24 hours. The samples were then placed in a desiccator over $CaCl_2$ for 24 hours.

The isothermal degeneration of these samples was carried out in an apparatus previously described (12). The apparatus consisted of a fused silica spring balance (7). The general procedure was carried out under reduced air flow to avoid excessive loss of water vapor. Definite amounts of water vapor were introduced into the equilibrium vapor pressure corresponding to the composition was determined by means of a manometer filled with vacuum ampullae of $CaCl_2$ (0.5% $CaCl_2$). It usually required from two to three days for equilibrium to be established at each composition.

Fig. 1

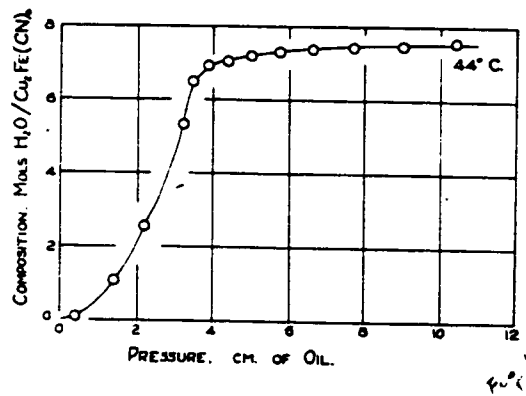


Fig. 1. Dehydration Isotherm for Cupric Ferrocyanide

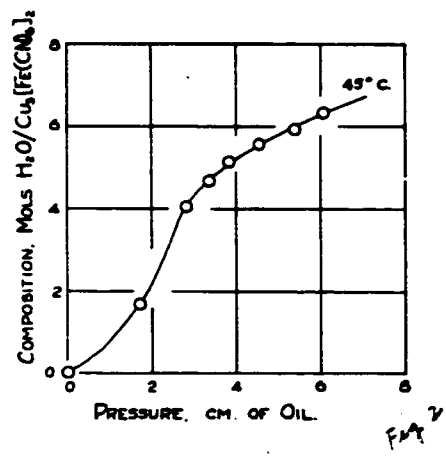


Fig. 2

Fig. 2. Dehydration Isotherm for Cupric Ferricyanide

Fig. 3

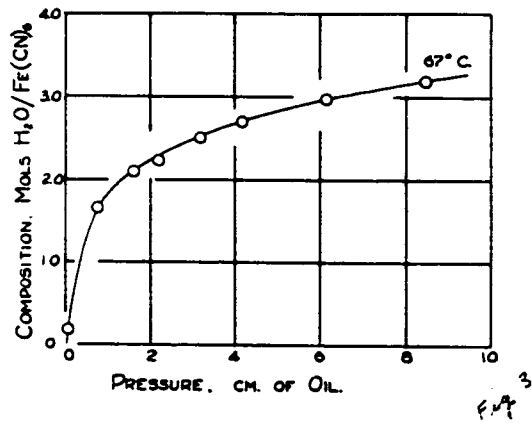


Fig. 3. Dehydration Isotherm for Prussian Blue

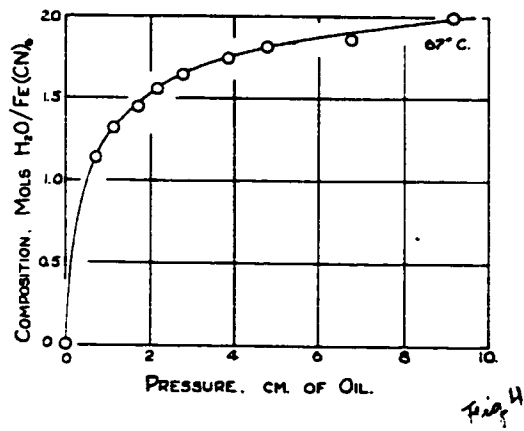


Fig. 4. Dehydration Isotherm for Turnbull's blue

ferrocyanide or potassium ferrocyanide with an excess of the metal chloride (except for cerium nitrate and scandium sulfate). The gelatinous precipitates were washed with distilled water by centrifuging until no chloride ion could be detected in the wash water, and were then dried in the air. As it is usually observed, the characteristic brown sol of ferric ferrocyanide was obtained; flocculation of this sol was effected by the addition of ethyl alcohol. A precipitate was obtained with chromium nitrate and potassium ferrocyanide only after the addition of acetic acid and several days of aging. The white iron cyanide sols of aluminum and indium which formed immediately, decomposed partially during the process of washing and air drying and took on a blue color. Other samples of indium ferrocyanide were prepared using the same method as above except that oxygen-free water and a nitrogen atmosphere were employed and (b) by using alcoholic solutions of indium chloride and hydroferrocyanic acid in a dry nitrogen atmosphere. These samples were nearly white, indicating but little decomposition. However, the x-ray diffraction patterns of these differently prepared indium ferrocyanide samples were identical, showing that any crystalline products of decomposition are present in an amount insufficient to be detected by x-ray diffraction methods.

The x-ray diffraction patterns of the air-dried gels of Prussian blue and Turnbull's blue consist of a few broad lines (see figure 5) indicating a small primary particle size. In order to obtain sharper x-ray diffraction patterns, an attempt

was made to increase the particle size of these iron-blue precipitates by recrystallization from hydrochloric acid solutions. The precipitates resulting from the slow cooling of hydrochloric acid solutions saturated at 100°C. with either Prussian blue or Turnbull's blue, give sharp but identical x-ray diffraction patterns. In Figure 5 this reprecipitated substance is referred to as "iron blue ex HCl".

The x-ray examination of these iron-cyanide compounds was made with Fe K α x-radiation filtered through manganese foil using a camera of 57.3 mm. diameter. In the case of the indium salts it was found that Co K α x-radiation (nickel foil filter) gave better results provided a sheet of thin aluminum foil was placed between the film and the sample in order to diminish the intensity of fluorescent x-radiation from the indium.

Diagrams of the x-ray diffraction patterns of $Tl_3 [Fe(CN)_6]_4$, $Pt [Fe(CN)_6]$, $In [Fe(CN)_6]$, $Fe [Fe(CN)_6]$, Prussian blue, Turnbull's blue, "iron blue ex HCl" $Al_4 [Fe(CN)_6]_3$, $Sc_4 [Fe(CN)_6]_3$, $In_4 [Fe(CN)_6]_3$, $Zn_3 [Fe(CN)_6]_2$, $Cd_3 [Fe(CN)_6]_2$, $Cu_3 [Fe(CN)_6]_2$, and $Cu_2 [Fe(CN)_6]$ are given in Figure 5. These patterns agree very closely as to the position and the relative intensities of lines.

In Figure 6 are given charts of the x-ray diffraction patterns of $La_4 [Fe(CN)_6]_3$, $La [Fe(CN)_6]$, $Nd_4 [Fe(CN)_6]$, $Fe [Fe(CN)_6]$ and Prussian blue. There is no similarity between the patterns of $La_4 [Fe(CN)_6]_3$, $La [Fe(CN)_6]$, $La-Fe(CN)$, and $Nd_4 [Fe(CN)_6]_3$, and the patterns of Prussian blue and $Fe [Fe(CN)_6]$.

Fig 5

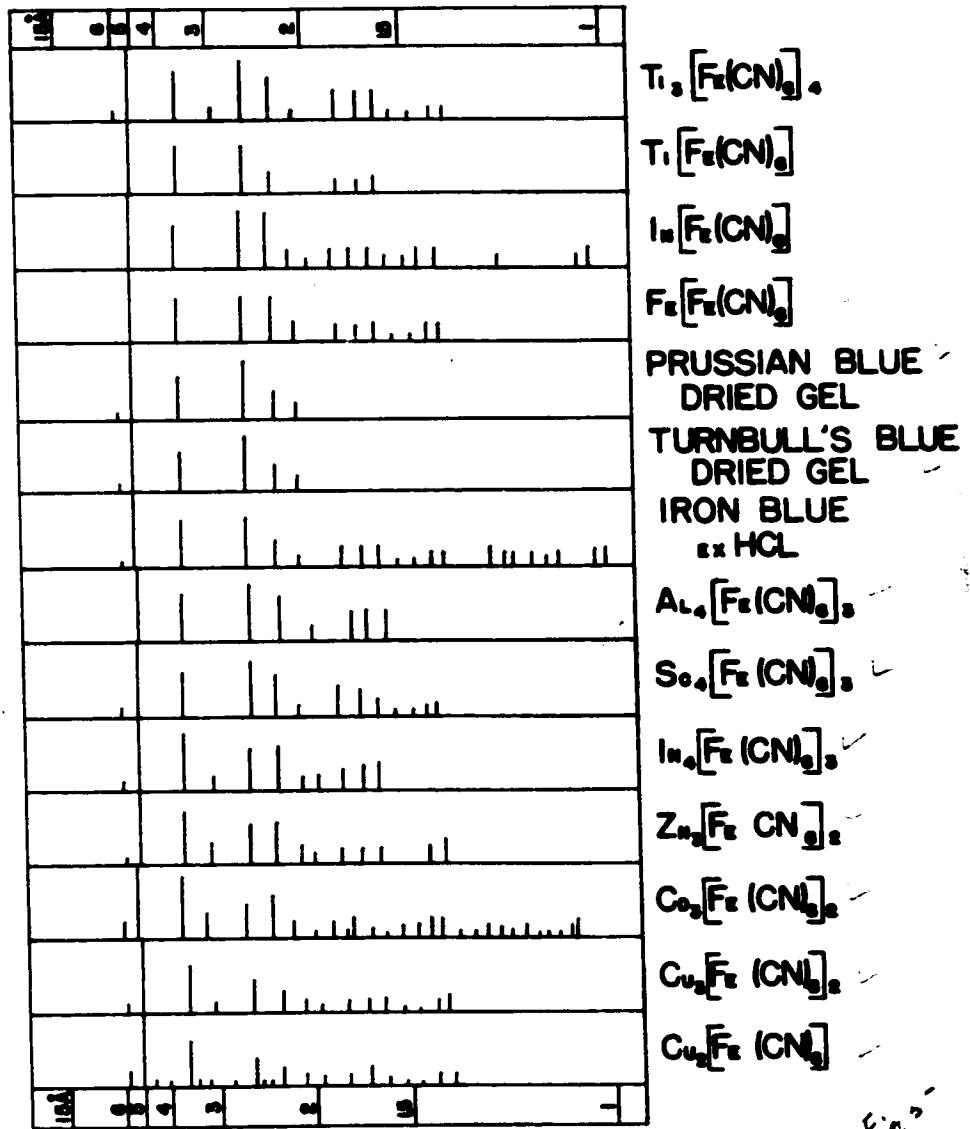


Fig. 5. Diagrams of the X-ray Diffraction Patterns of Various Heavy Metal Iron-Cyanide Compounds

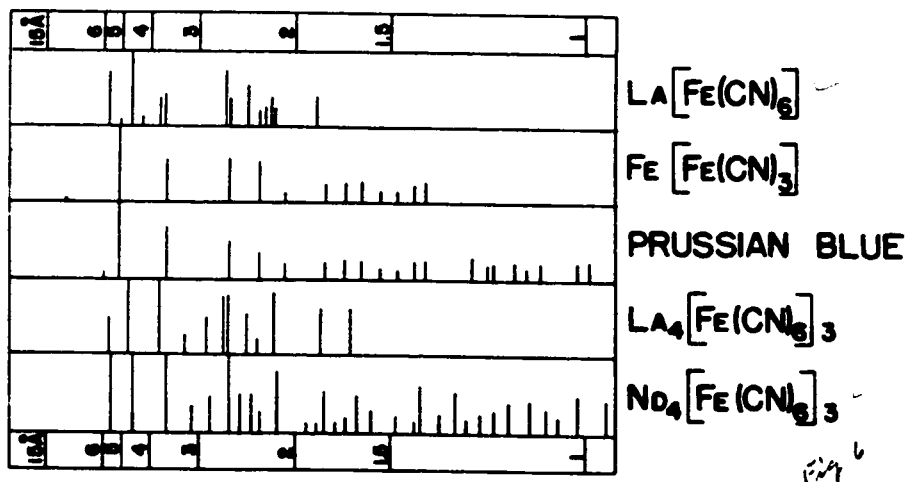


Fig. 6. Diagrams of the X-ray Diffraction Patterns of $La_4[Fe(CN)_6]_3$, $La[Fe(CN)_6]$, $Nd_4[Fe(CN)_6]_3$, Prussian blue, and Turnbull's blue

3. Density Measurements.

The same samples of Prussian blue and of Turnbull's blue as used in the isothermal dehydration studies were used in these density determinations. In measuring the density of these iron-blue powders, Gilbertson's method (1) was used with xylene as the pycnometric liquid. Before making the measurement, the adsorbed water was removed by subjecting the sample to the vacuum of a "Hyvac" pump at a temperature of 57°C for 72 hours. According to the dehydration isotherms already given, this is three times longer than was required to remove all the water from the same material. The density values obtained were:

Prussian blue---1.785 gms/cm³

Turnbull's blue---1.83 gms/cm³

III. Discussion

A. Isothermal Dehydration Studies

The continuous dehydration isotherms for the gels of cupric ferrocyanide, cupric ferricyanide, prussian blue, and Turnbull's blue indicate that these materials do not form definite hydrates. Most of the water present in the samples is adsorbed on the surface of the finely-divided crystals, but some may be held by the absorption forces within the channels in the lattice between the relatively large iron-cyanide ions, after the manner of certain zeolite crystals that do not contain water molecules in definite chemical combination (3).

Van Bever concluded from the observed intensity ratios of the 400 to the 600 or the 142 reflections, that water molecules should be placed at octant centers, i.e. the $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ positions. In intensity calculations to be discussed later (see figures 3 through 16), it can be seen that the calculated and observed intensity ratios of these reflections agree very well without assuming the presence of any water or other material in the $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ positions. Since the x-ray diffraction patterns of cupric ferrocyanide, cupric ferricyanide, prussian blue, and Turnbull's blue taken before and after the removal of all the water, agree not only as to the position of the lines but also as to their relative intensities (as indeed was observed by van Bever), the amount of diffracting material within the unit cell must be the same before and after dehydration. Therefore, it is assumed that the water in these hydrous iron-cyanides is not present as water of hydration.

* The symbols used throughout this paper are those of the Internationale Tabellen zur Bestimmung von Kristallstruktur.

TABLE I

SPACE GROUP	REASON FOR EXCLUSION
T^2	No set of 32 equivalent points
T^3_h	None
T^4_h	No set of 4 equivalent points
T^2_d	No set of 32 equivalent points
T^5_d	No set of 4 equivalent points
O^3	No center of symmetry
O^4	No set of 4 equivalent points
O^5_h	None
O^6_h	No set of 4 equivalent points
O^7_h	No set of 4 equivalent points
O^8_h	No set of 4 equivalent points

TABLE II
Crystal Structure Data

Space group: O_h^5 or T_h^3

4 $\text{Fe}(\text{CN})_6$ groups per unit cell

Atomic positions:

4 Fe at 4 fold 4(a) positions $(000, 0\frac{1}{2}\frac{1}{2} \rightarrow *)$

4 M at 4 fold 4(b) positions $(000, 0\frac{1}{2}\frac{1}{2} \rightarrow) + \frac{1}{2}\frac{1}{2}\frac{1}{2}$

0 to 4 M at 32 fold 32(f) positions $(000, 0\frac{1}{2}\frac{1}{2} \rightarrow) + (x_3, x_2, x_1, \bar{x}_3, \bar{x}_2, \bar{x}_1, x_3, \bar{x}_3, \bar{x}_2, \bar{x}_1, x_3, x_2, \bar{x}_3, \rightarrow)$

24 C at 24 fold 24(e) positions $(000, 0\frac{1}{2}\frac{1}{2} \rightarrow) + (x_1, 00 \rightarrow, x_1, 00 \rightarrow)$

24 N at 24 fold 24(e) positions $(000, 0\frac{1}{2}\frac{1}{2} \rightarrow) + (x_2, 00 \rightarrow, x_2, 00 \rightarrow)$

$x = 7/36 a_0$; $x = 11/36 a_0$; $x = 1/6 a_0$.

* \rightarrow cyclical change of coordinates

Fig. 7

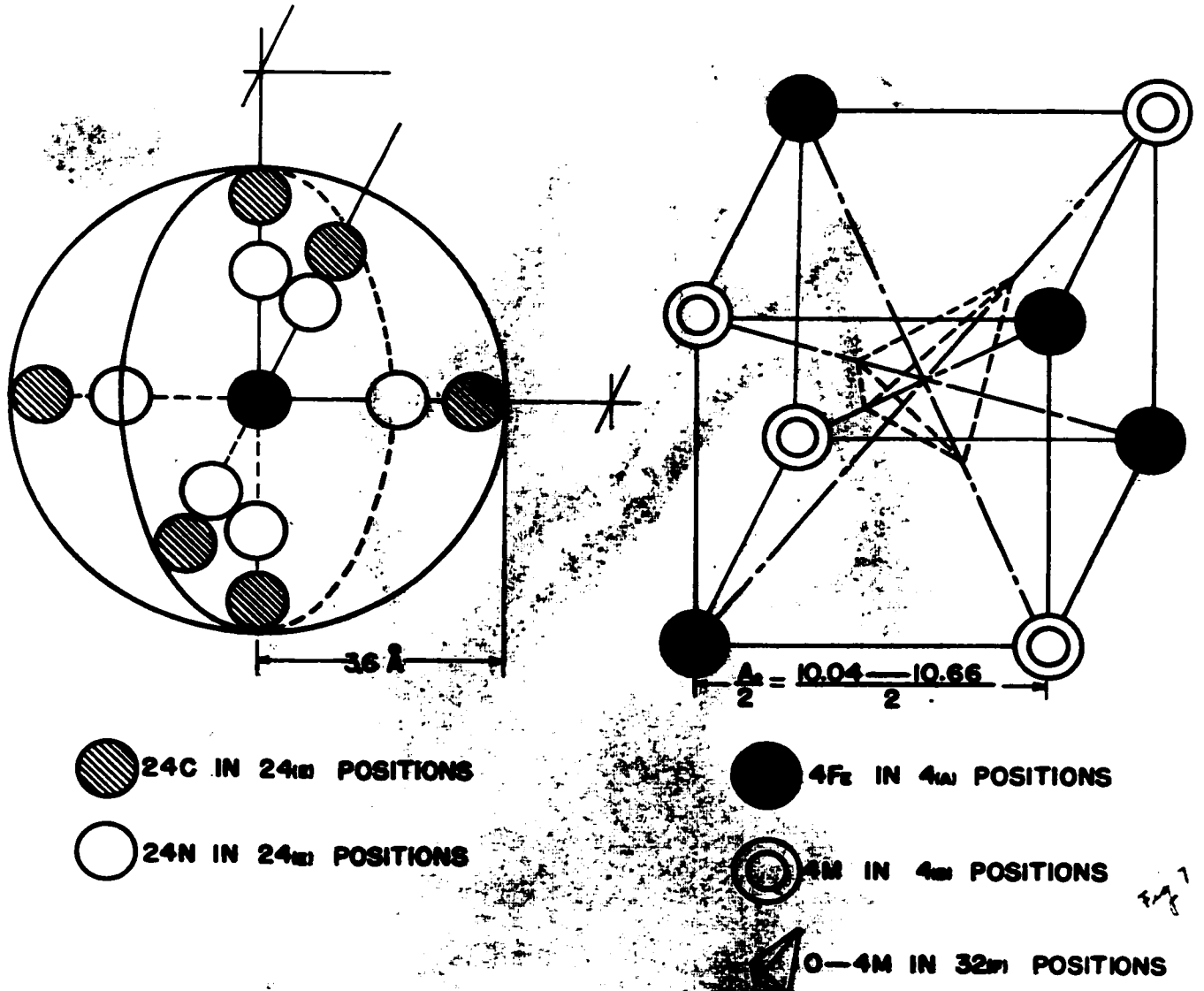


Fig. 7.

of the unit cell. For example, the observed intensity of $\alpha_3 [Fe(CN)_6]_2$ is 100% and the calculated intensity is 100%. The observed intensity of $\alpha_2 [Fe(CN)_6]_2$ is 100% and the calculated intensity is 100%. It has been shown that the intensity of certain x-ray reflections is dependent upon the relative positions of the atoms in the unit cell. This explains the varying number of reflections for the various positions along the long diagonal of the unit cell, i.e., the α_1 positions. The lattice constants were determined in the lattice in which these positions. The radius of the iron-oxalate ion was obtained from calculations based on the crystal structure of the compound.

In order to determine the relative intensities of the reflections, calculations were made on the intensity of x-ray reflections from these compounds. The relative intensities are listed in Table II. Calculations were made only for the following examples from the above list of divalent and tetravalent heavy metal ferrocyanides and ferricyanides: Prussian blue, Turnbull's blue, $Fe_3 [Fe(CN)_6]_4$, $Fe [Fe(CN)_6]$, $Fe [Fe(CN)_6]$, $Co_4 [Fe(CN)_6]_3$, $Co_3 [Fe(CN)_6]_2$, $Co_3 [Fe(CN)_6]_2$, and $Co_2 [Fe(CN)_6]$. The following equation was used:

$$I = k \cdot \frac{1/2 (1 + \cos^2 \theta)}{\cos^2 \theta \sin^2 \theta} \cdot j \cdot F^2$$

- I = intensity of x-ray reflections
- k = constant
- $1/2 (1 + \cos^2 \theta)$ = J.J. Thomson polarization factor
- $\cos^2 \theta \sin^2 \theta$ = Lorentz factor
- j = multiplicity factor
- F = crystal structure factor

The observed and calculated values for the relative intensities of

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... in between the large iron-cyanide ion.

... subtracting the radius of the iron-cyanide ion from half of the average a , an average value of 1.6 Å is obtained as the maximum radius of a heavy metal ion which will fit in the available space. It is not probable that the iron-cyanide ion is spherically symmetrical, but it is more likely that it bulges out along the cube edges. If this be the case, it would be expected that the a axis in between the large iron-cyanide ions are actually smaller than that with other axes. This is borne out by the following experimental evidence.

In table III is given a list of the ionic radii of the heavy metals studied. The divalent calcium and trivalent lanthanum and neodymium cations are considerably larger than any of the other cations. The dissimilarity between the patterns of $\text{La}_4[\text{Fe}(\text{CN})_6]_3$, $\text{La}[\text{Fe}(\text{CN})_6]$, $\text{Nd}_4[\text{Fe}(\text{CN})_6]_3$, and the patterns of Russian blue and $\text{Fe}[\text{Fe}(\text{CN})_6]$ shows that the lanthanum and neodymium compounds do

TABLE III

IONIC		RADII*	
ION	RADIUS	ION	RADIUS
T_1^{+4}	0.68 Å	Cd^{+2}	0.97 _a
L_a^{+3}	1.15	Mn^{+2}	0.80
Nd^{+3}	1.08	Cu^{+2}	-
In^{+3}	0.81	Fe^{+2}	0.75
Sc^{+3}	0.81	Zn^{+2}	0.74
Fe^{+3}	0.60	Co^{+2}	0.72
Al^{+3}	0.50	Ni^{+2}	0.70

* Pauling: "The Nature of the Chemical Bond",
P.346, Cornell University Press, Ithaca, New York (1940)

TABLE IV

CLASSIFICATION OF HEAVY METAL IRON - CYANIDE COMPOUNDS

Type of Compound	Number of Molecules Per Unit cell	Number of Metal ions Per Unit cell	Heavy Metal Iron-Cyanide
$A_3 X_4$	1	3	$Ti_3 [Fe(CN)_6]_4$
$A X$	4	4	$Ti [Fe(CN)_6]_4$, $Ln [Fe(CN)_6]$, $Fe [Fe(CN)_6]_4$
$A_4 X_3$	1 1/3	5 1/3	$Sc_4 [Fe(CN)_6]_3$, $In_4 [Fe(CN)_6]_3$, $Al_4 [Fe(CN)_6]_3$
$A_3 X_2$	2	6	$Zn_3 [Fe(CN)_6]_2$, $Cd_3 [Fe(CN)_6]_2$, $Cu_3 [Fe(CN)_6]_2$
$A_2 X$	4	8	$Cu_2 [Fe(CN)_6]$

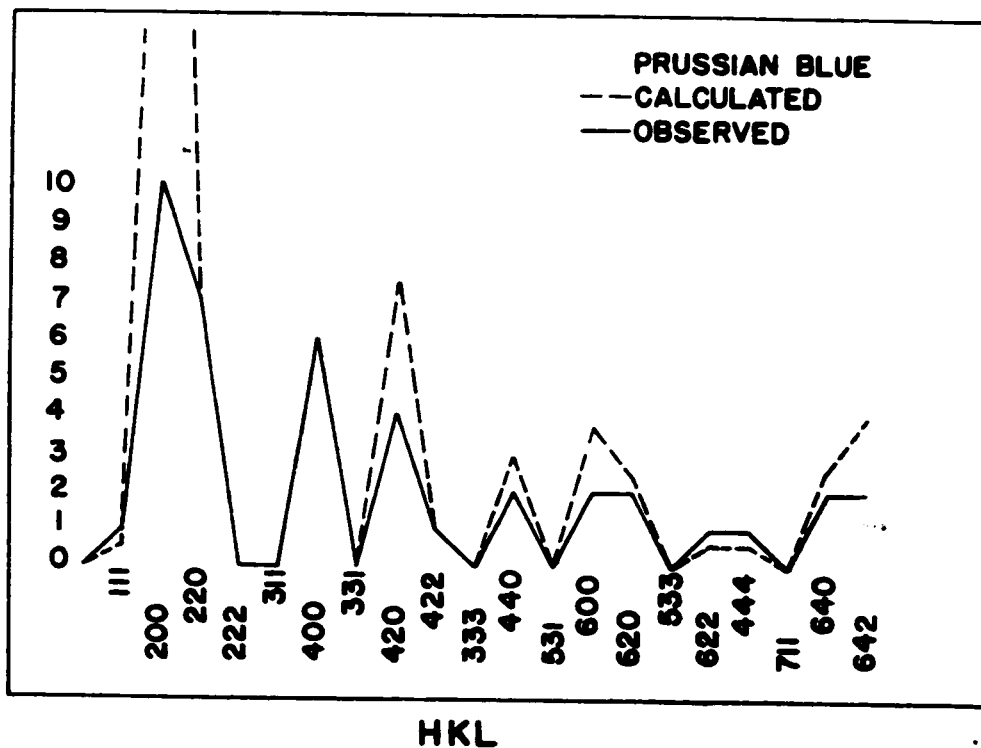


Fig. 8. Comparison of Calculated and Observed Intensities

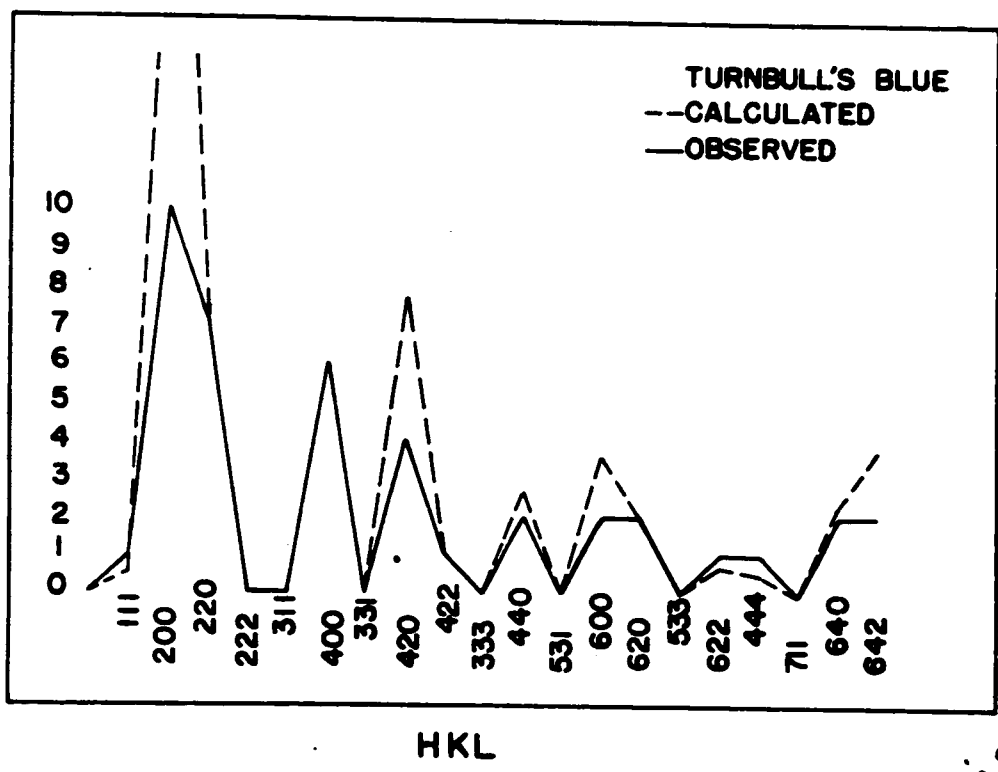


Fig 9

Fig. 9. Comparison of Calculated and Observed Intensities

Fig. 10

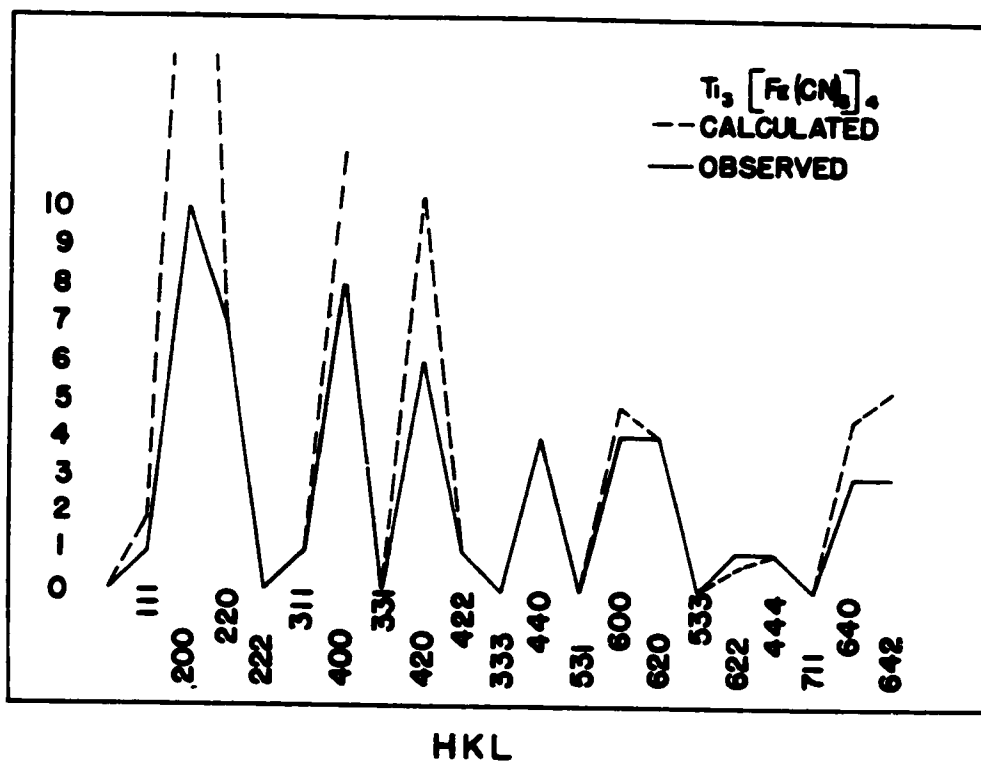


Fig 10

Fig.10. Comparison of Calculated and Observed Intensities

Fig. 11

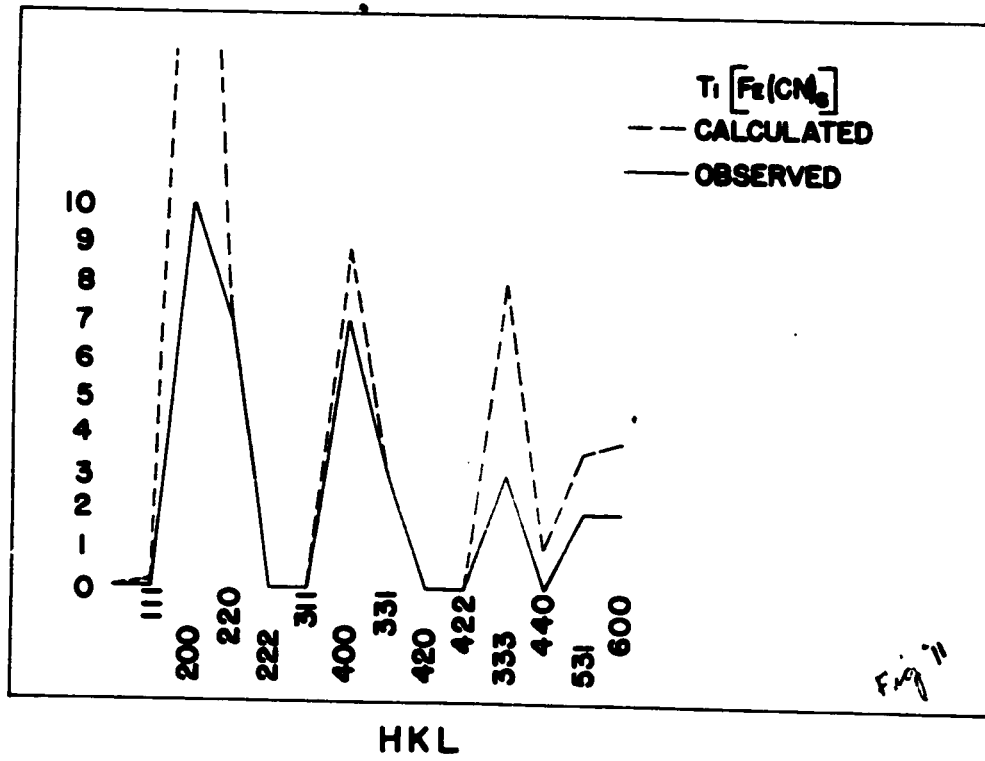


Fig. 11

Fig.11. Comparison of Calculated and Observed Intensities

Fig 12

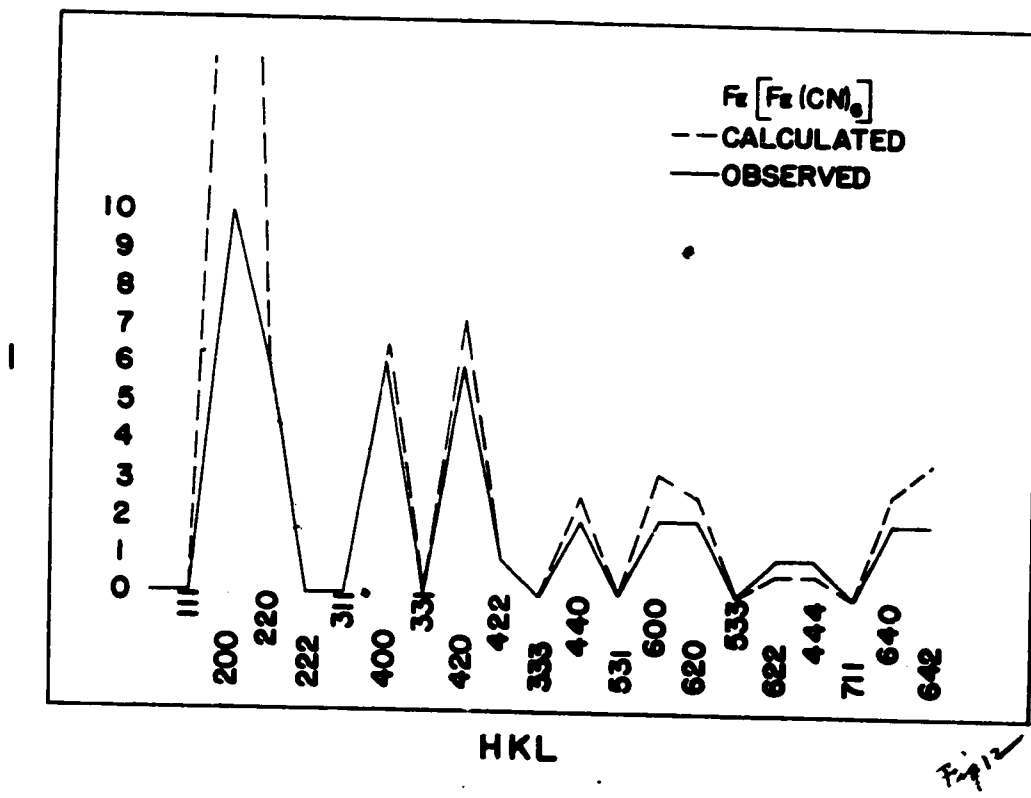


Fig 12

Fig.12. Comparison of Calculated and Observed Intensities

Fig. 13

Fig. 13

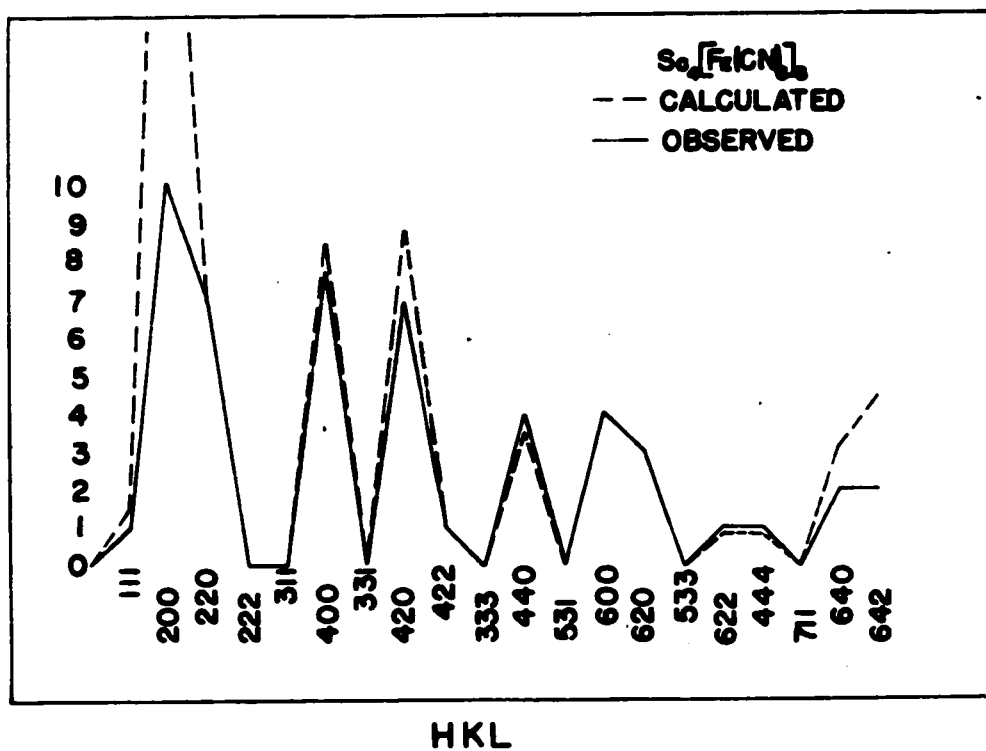


Fig. 13

Fig.13. Comparison of Calculated and Observed Intensities

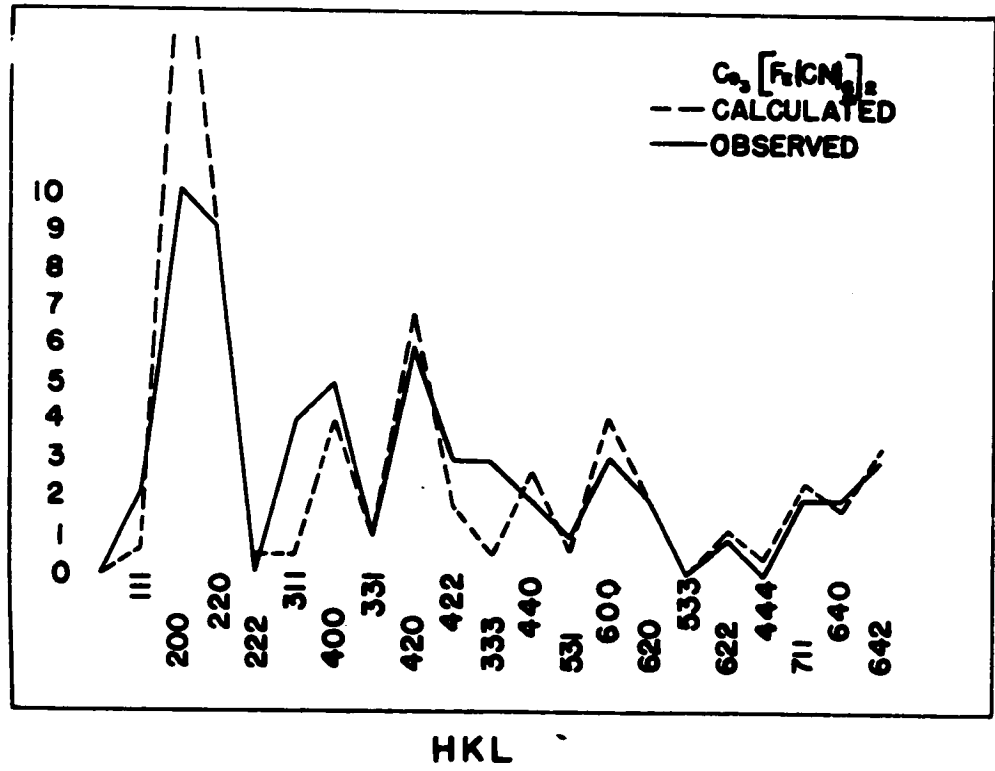


Fig 14

Fig.14. Comparison of Calculated and Observed Intensities

Fig. 15

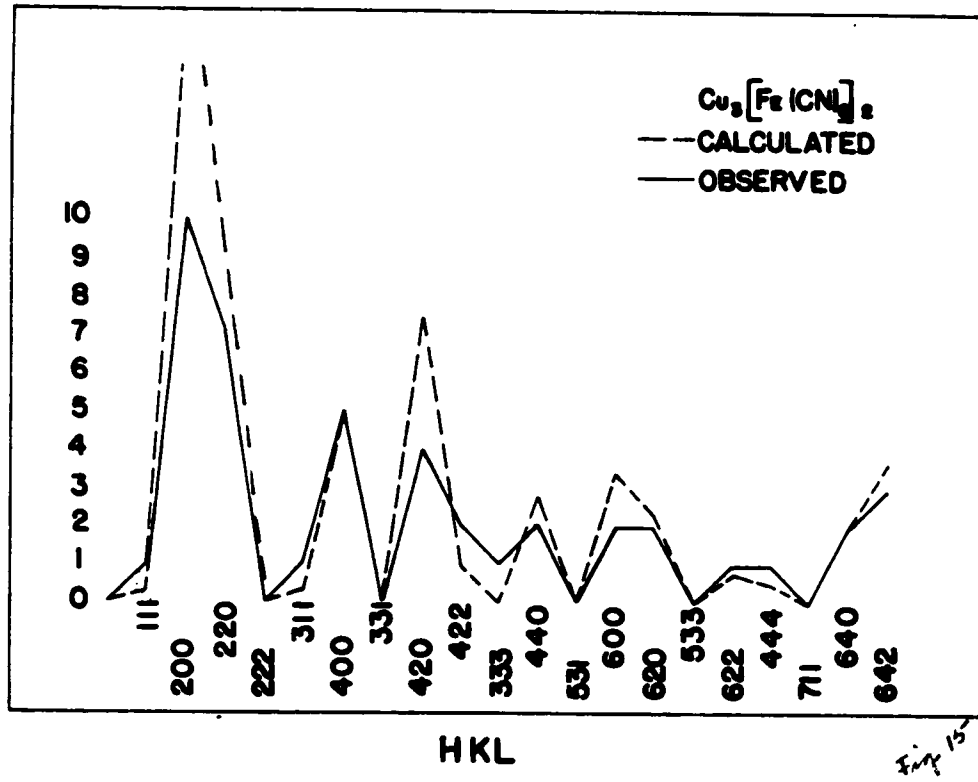


Fig. 15

Fig.15. Comparison of Calculated and Observed Intensities

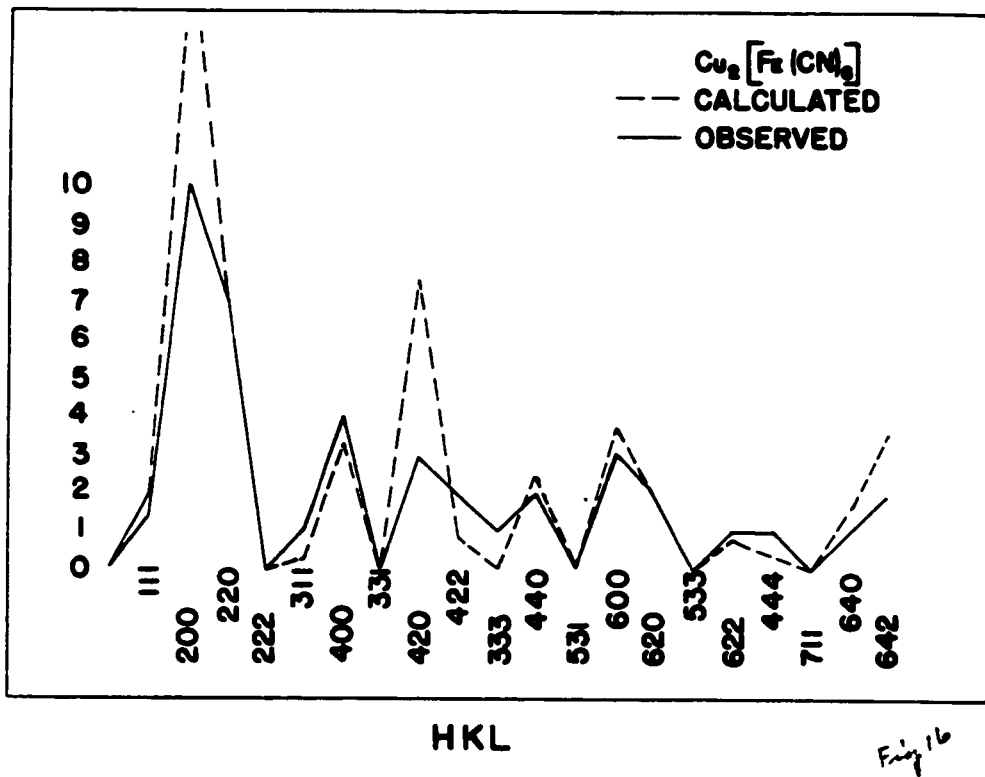


Fig.16. Comparison of Calculated and Observed Intensities

Fig. 16

is not possible to have a total number of transition line of
of $[Fe(CN)_6]$.

The two types of compounds which differ in the number of
 $3_3 [Fe(CN)_6]_2$ are considered in the present paper. The two
isomeric iron-oxalate compounds are written as $3_3 [Fe(CN)_6]$
as well as $3_3 [Fe(CN)_6]_2$ to show the presence of six of the
oxalate iron-oxalate ion bonds studied. This indicates that the
oxidation number of iron is +2 in both cases. This is
the largest number of iron ions = 0. 3, which is the
number of iron ions in the unit cell. The number of iron ions
in the unit cell = 1.1, which is the number of iron ions
in the unit cell.

Many other iron-oxalate compounds of this type series
may be classified into several types. Table IV shows a
classification together with the number of molecules and the
number of metal ions per unit cell for each type of compound. The
number of metal ions per unit cell varies from one to four.
 $1_3 [Fe(CN)_6]_4$ is the same for $3_2 [Fe(CN)_6]$. The structure of these
compounds is assumed to depend on the size of the large metal
ions. Metal ions within a certain size and polarization range can
fit into the remaining channels and interstices in the lattice
to satisfy the valence requirements.

A possible decision between the S_h or F_h space groups, will
be the main test of the proposed structure, which will be
prepared in large crystals of the heavy metal ion-oxalate
which will make possible the application of the single crystal
method of x-ray analysis.

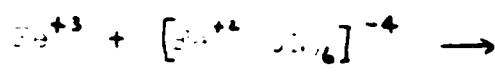
TABLE V

Theoretical and Calculated Molecular Weights of Prussian
Blue and Turnbull's Blue

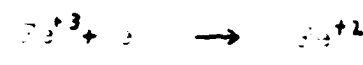
<u>Material</u>	<u>m</u>	<u>Calculated</u>	
		<u>Mcl. Wt.</u>	<u>Formula</u>
Prussian	1	1139	
Blue	1 1/3	854	
1.785	2	569	
gms./cm.	3	379	$\text{Fe}_4 [\text{Fe}(\text{CN})_6]_3$
Turnbull's	1	1142	
Blue	1 1/3	856	
1.790	2	571	
gms./cm.	3	381	$\text{Fe}_3 [\text{Fe}(\text{CN})_6]_2$

is obtained. The reaction is: $3Fe^{+3} + 4[Fe^{+2}(CN)_6]^{-4} \rightarrow Fe_3[Fe^{+3}(CN)_6]_2 + 2[Fe^{+3}(CN)_6]^{-3}$.
 The reaction is reversible, and the equilibrium constant is $K = \frac{[Fe_3[Fe^{+3}(CN)_6]_2][Fe^{+3}(CN)_6]^{-3}}{[Fe^{+3}]^3[Fe^{+2}(CN)_6]^{-4}}$.
 The reaction is not reversible, and the equilibrium constant is $K = \infty$.
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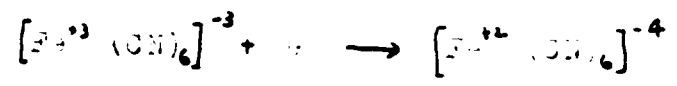
There are several lines of evidence which indicate that the reaction is reversible. The reaction is reversible, and the equilibrium constant is $K = \frac{[Fe_3[Fe^{+3}(CN)_6]_2][Fe^{+3}(CN)_6]^{-3}}{[Fe^{+3}]^3[Fe^{+2}(CN)_6]^{-4}}$.
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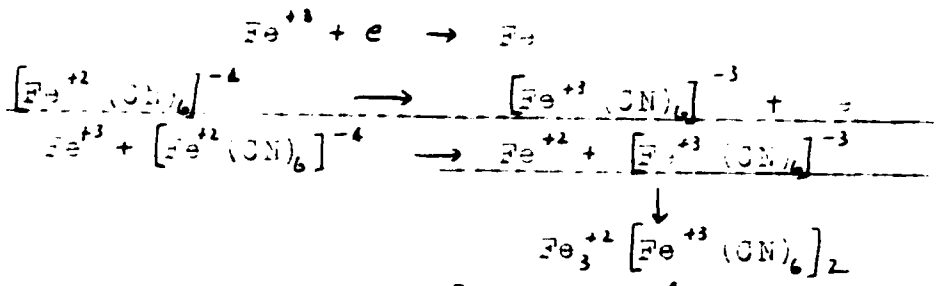
the reaction is reversible, and the equilibrium constant is $K = \frac{[Fe_3[Fe^{+3}(CN)_6]_2][Fe^{+3}(CN)_6]^{-3}}{[Fe^{+3}]^3[Fe^{+2}(CN)_6]^{-4}}$.
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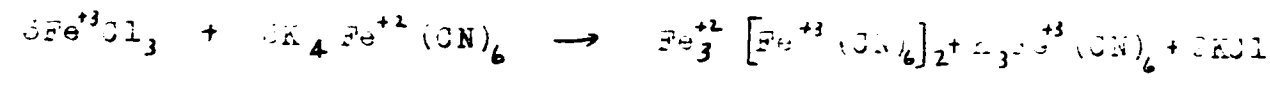
is 0.418; the potential of



is 0.480, with respect to the standard hydrogen electrode. The reaction for the hypothetical cell with electrodes of Fe^{+3} , Fe^{+2} and $[Fe^{+3}(CN)_6]^{-3}$, $[Fe^{+2}(CN)_6]^{-4}$ is:



If, then, on mixing Fe^{+3} with $[Fe^{+2}(CN)_6]^{-4}$ a precipitate of $Fe_3[Fe^{+3}(CN)_6]_2$ is obtained, the entire reaction must be:



This shows a molar ratio of $\frac{1}{2} \text{K}_3 \text{Fe}^{2+} (\text{NO}_2)_6$ which is obtained for every mole of $\text{Fe}_3 (\text{NO}_2)_6$ and is in agreement with the results obtained by the approximate calculations, an analysis of the experimental data showed it to contain some $[\text{Fe}^{2+} (\text{NO}_2)_6]^{-3}$ ions as indicated by the above formula. The slight deviation could be expected because of the complex formation of the iron(II) ions with the nitro groups and the nitro groups. In the case of the iron(II) ions, the experimental results are in agreement with the results obtained by the approximate calculations. In the case of the iron(III) ions, the experimental results are in agreement with the results obtained by the approximate calculations. As mentioned above, the discrepancy between the experimental results and the theoretical results is due to the complex formation of the iron(II) ions with the nitro groups and the nitro groups. However, since the complex formation of the iron(II) ions with the nitro groups is limited by precipitation, the above formula for the reaction reaction looks like.

TABLE VI

Ferrocyanide and Ferricyanide Ions in the Supernatant Liquid

(millimoles)

<u>Amounts Mixed</u>		<u>Calculated</u>		<u>Observed</u>	
<u>$K_4Fe(CN)_6$</u>	<u>$FeCl_3$</u>	<u>$K_4Fe(CN)_6$</u>	<u>$K_3Fe(CN)_6$</u>	<u>$K_4Fe(CN)_6$</u>	<u>$K_3Fe(CN)_6$</u>
170	99.7	70.3	33.2	40.6	19.8
194	49.8	144.2	16.6	114	12.1

CONCLUSION

The results of this investigation are summarized as follows:

1. The infrared transmission isotherms obtained for the salts of cupric ferrocyanide, cupric ferricyanide, potassium blue, and Turnbull's blue indicate that these compounds are not definite hydrates.
2. The x-ray diffraction patterns of cupric ferrocyanide, cupric ferricyanide, potassium blue, and Turnbull's blue obtained before and after rehydration are identical; however, the data indicate that these cyanide compounds are not definite hydrates.
3. The electron diffraction patterns obtained for the compounds obtained in a similar manner to that of the x-ray diffraction pattern of the potassium blue is not a definite hydrate.
4. Since the x-ray diffraction patterns of $M_3[Fe(CN)_6]_4$, $M[Fe(CN)_6]$, $M_2[Fe(CN)_6]$, $M_3[Fe(CN)_6]$, potassium blue, Turnbull's blue, "iron blue ex HCl", $Al_4[Fe(CN)_6]_3$, $Se_4[Fe(CN)_6]_3$, $In_4[Fe(CN)_6]_3$, $Zn_3[Fe(CN)_6]_2$, $Cr_3[Fe(CN)_6]_2$, $Co_3[Fe(CN)_6]_2$, and $Cu_2[Fe(CN)_6]$ are similar, these compounds are of the same crystalline symmetry and therefore isomorphous with each other.
5. The systematic extinctions occurring in the x-ray diffraction data of these ⁽¹⁰⁰⁾ cyanide compounds are characteristic of face-centered cubic symmetry. Of the space groups possessing this symmetry, both the O_h^5 and F_d^3 space groups have the required number of sets of equivalent points as demanded by chemical evidence and the in-

analysis studies of certain x-ray diffractions.

8. The x-ray diffraction studies of the Prussian blue structure may be summarized as follows:

- a. $Fe_4[Fe(CN)_6]_3$ at 50°C. (10.7 Å) conditions
- b. $Fe_4[Fe(CN)_6]_3$ at 25°C. (10.7 Å) conditions
- c. $Fe_4[Fe(CN)_6]_3$ at 25°C. (10.7 Å) conditions
- d. $Fe_4[Fe(CN)_6]_3$ at 25°C. (10.7 Å) conditions
- e. $Fe_4[Fe(CN)_6]_3$ at 25°C. (10.7 Å) conditions

9. Since the x-ray diffraction patterns of $Sc_4[Fe(CN)_6]_3$, $La_4[Fe(CN)_6]_3$, and $Nd_4[Fe(CN)_6]_3$ differ from patterns of Prussian blue and $Fe_4[Fe(CN)_6]_3$, the latter must be recognized as having a different crystal structure as described in no. 5 above, and are, therefore, not isomorphous with the other heavy metal ferricyanides investigated.

10. There is some difference in the relative intensities of the lines of x-ray diffraction patterns of $Sc_3[Fe(CN)_6]_2$ as compared with the patterns of the other isomorphous compounds. This observation and the large lattice constant of $Sc_3[Fe(CN)_6]_2$ indicates that ions as large or larger than cadmium (radius = 0.97 Å) modify or disrupt the lattice, described in no. 5 and 6 above.

11. Since x-ray diffraction studies show that definite trivalent heavy metal ferricyanides (eg. $Sc_4[Fe(CN)_6]_3$) and definite divalent heavy metal ferricyanides (eg. $Zn_3[Fe(CN)_6]_2$) have the same face-centered crystal symmetry, this method cannot give any indication as to whether the composition of Prussian blue and Turnbull's blue is represented by the formula, $Fe_4[Fe(CN)_6]_3$ or the formula, $Fe_3[Fe(CN)_6]_2$.

12. Since the divalent heavy metal ferricyanides and tri-

valent heavy metal ferrocyanides have nearly the same number of metal ions per unit cell, it cannot be determined from density measurements whether Prussian blue and Turnbull's blue have the composition represented by the formula $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ or $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$.

11. The electrode potential theory applied to the mixture of Fe^{+3} and $[\text{Fe}(\text{CN})_6]^{-4}$ indicates that the reaction would go to produce $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ in the following way.



An analysis of the supernatant liquid showed that an appreciable amount of $[\text{Fe}(\text{CN})_6]^{-3}$ was formed during the precipitation of $\text{K}_4\text{Fe}(\text{CN})_6$ with FeCl_3 in accordance with the above equation.

12. It is concluded that Prussian blue and Turnbull's blue may be represented by the formulation $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$.

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