Miscellaneous notes.

K. Krishnan

Giauque : Pronounce "Joke"

Nature, Vol. 163, April 23, 1949. p.624.

Fission Products.

The isotopes which are known to undergo fission with slow neutrons are uranium-233, uranium-235 and plutonium-239; others (thorium-232, ionium-230, protoactinium-231, uranium-238 and neptunium-237) require fast neutrons, and less information is available on the fission products*.

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* The information contained in this article is drawn largely from declassified reports issued by the United States Atomic Energy Commission, the Division of Atomic Energy of the National Research Council and the Division of Atomic Energy of the Ministry of Supply.

Cholesterylene

a = 15.88

b = 7.66

c = 19.25

State

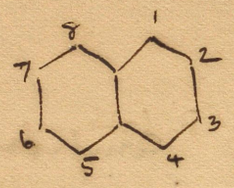
Some heterocyclic compounds

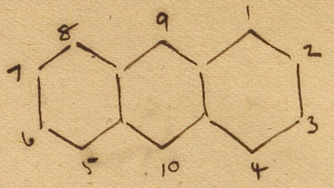
which may be studied by

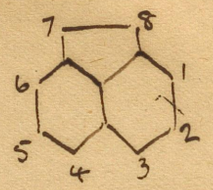
1. crystal structure by X-rays
2. magnetic and optical anisotropies in cryst. state
3. Pleochroic absorption. Cryst.

and in liquid state or state of soln. by

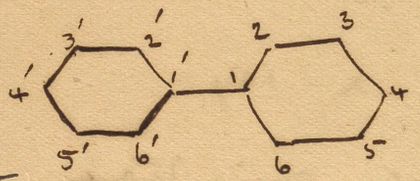
1. absorption
2. magnetic double refraction.

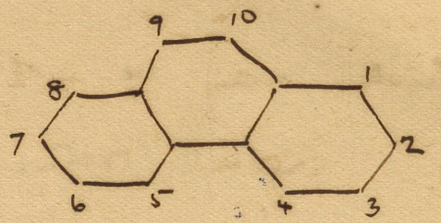


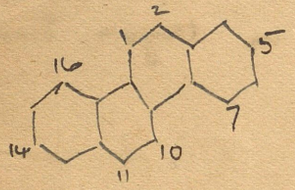


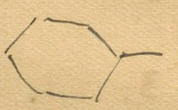


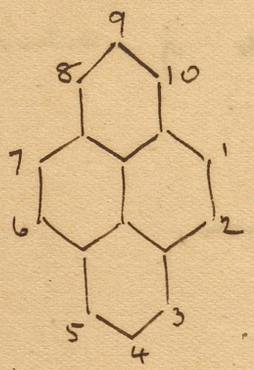
acenaphthylene

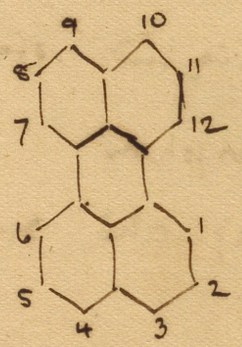












Non benzenoid aromatic systems

Cyclooctatetraene, tetraphenylene, pentalene, azulene, and diphenylene. Wilson Baker's lecture Feb 23, 1945 Tilden Chem Soc

+ Soc C.I.

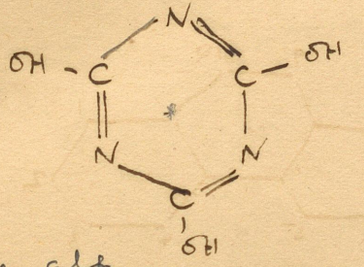
Cyclobutatriene

Heterocyclic compounds

1. Cyanuric acid (dihydrate)

Substance available

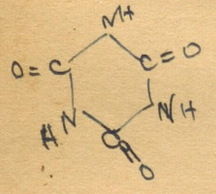
For cryst. data see Gr III 563.



$+ 2 H_2O$

See also ~~According to~~ Wiebenga + Moerman, Nature 141 122, Jan 15, 1938, and paper by them to appear in Zs Kr.

Cyanuric acid anhydrous $(HCNO)_3$: obtained by sublimation in vacuum x-ray studies by Wiebenga + Moerman, Zs. Kr. A99, # 217-29 (1938)

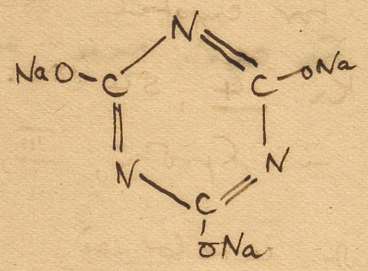


$a = 7.90$, $b = 6.74$, $c = 9.04$ Å $\beta = 90^\circ$ $Z = 4$

Molecular planes $\parallel^l$ to (101)

Double refn. $-^{ve}$.

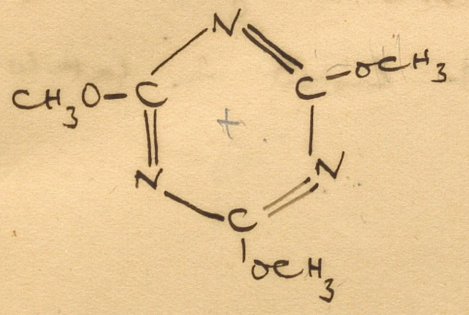
Trisodium cyanurate



no cryst. data.

Substance not listed in catalogues.

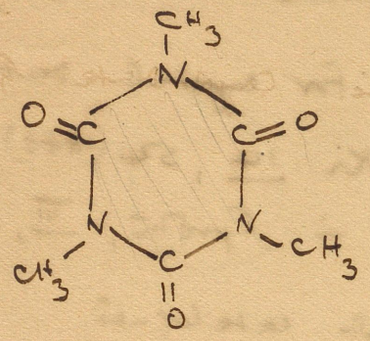
Trimethyl cyanuric ester (Cyanuric trimethide)



Rhombic. For crystal data see Fock, Z. Kr. 14, 54 (1888), quoted partially in Groth, III, 562.

Subst. not catalogued.

Methyl isocyanuric ester (Methyl tricarbimide)



Monocl. prisms. Cryst. data Groth III, 585.

Substt. not listed in catalogues.

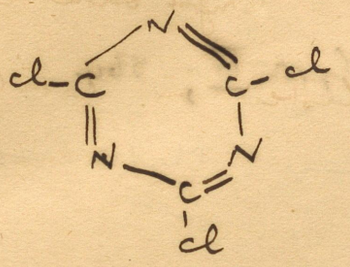
Ethyl isocyanuric ester

Cryst. data see Groth III, 586.

Substt. not listed in catalogues.

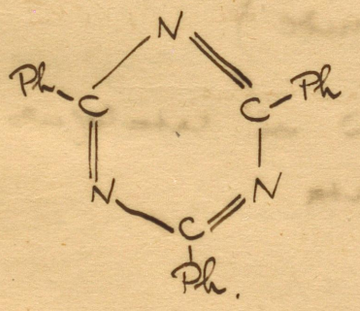
Tricyanogen chloride

Substance available. (sent to Jagadish Shanker)



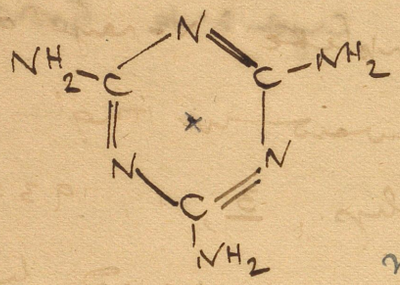
Monocl. prisms. Cryst. data Groth III, 564.

Triphenyl cyanidine (Cyanphenine)



no cryst. data.
substance not listed in catalogues.

Melamine (cyanuric triamide)



Substance available.

Cryst. data Groth III; 564.

According to Bajrekar (Mata Prasad's student)

monocl. prism

$a = 10.52$ A

$b = 7.44$

$c = 7.33$

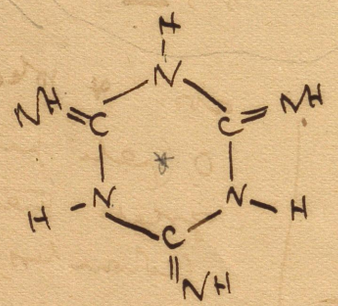
$\beta = 111^\circ 47'$

$\rho = 1.57$

C_{2h}^5

$Z = 4\left[C_3N_3(NH_2)_3\right.$

Isomelamine (Isocyanur triimide)

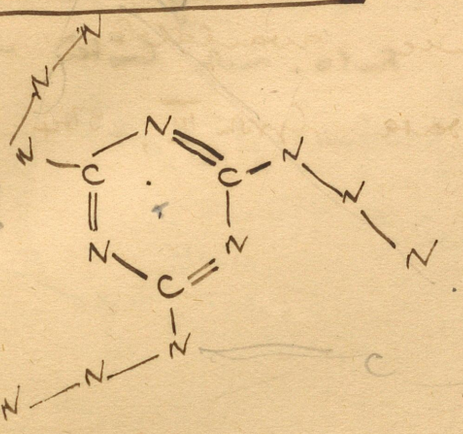


Subs. not listed in catalogues

no cryst. data.

Cyanuric triazide

explosive !!



W.H.
See Bragg, Nature, July 28th 1934.
I. E. Knaggs, Proc. R.S. A, 150, 576 (1935)
For complete x-ray analysis see Edward W. Hughes, Journal Chem. Phys., 3, 1, 1935.
material was prepared by him

"by the action of aqueous sodium azide on cyanuric tribromide. The resulting azide was recrystallised several times from purified acetone." m.p. 93°.5 C. For structure see p. 4.

Hexagonal $H6_3/m$. $a = 5.70$ $c = 5.58$ Å 2 mols in unit-cele.

$\rho = 1.71$ Sutton
1.72 x-ray. According to T.C. Sutton (Phil Mag., 15 1001, 1933)

cryst. optically negative

$\lambda =$	5791	5461	abn. of polarisation:
	1.862_4	1.871,	O (pale pink)
ω			greater than E
ϵ	1.378_3	1.380_5	(colourless).

Is it optically active ! The structure will seem to suggest it.

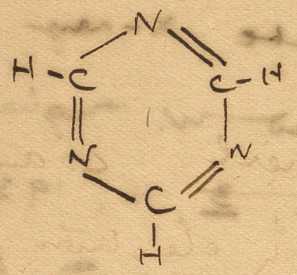
according to Mrs Lonsdale quoted by Knaggs

$\chi_{\parallel} = -102 \times 10^{-6} (\pm 1.5)$ $\chi_{\perp} - \chi_{\parallel} = 21.8 \times 10^{-6} (\pm 2)$

$\chi_{\perp} = -80 \times$ "

Pyrazine (para diazine)

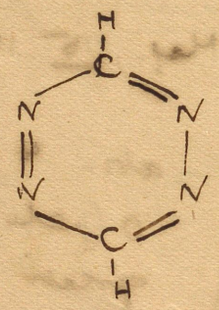
no cryst data
Subs. not listed in catalogues.



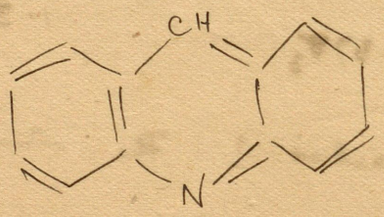
colourless prisms. m.p. 47°

Sym. tetrazine

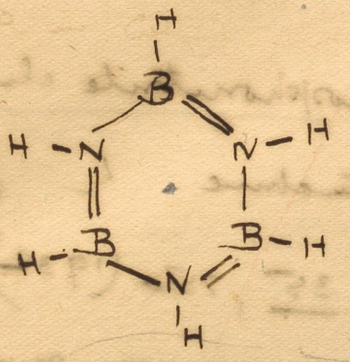
no cryst- data - Subst- not listed in catalogues.



Acridine



Heterocyclic Inorganic compounds



$B_3N_3H_6$

Liquid at ord. temps.

See Stock and Wiel Z. an. chem., 203, 228 (1931) by electron diffraction obtained patterns similar to those of benzene. N–B dist = 1·47 ± ·07 Å.

BH = pseudo Kohlenstoff (Grimm)

See also E. Wiberg, Ind. Eng. chem. News ed. 16 582 (1938) where the substance is referred to as inorganic benzene.

By $(PNCl_2)_3$ and $(PNCl_2)_4$

Triphosphonitrile chloride — Tetraphosphonitrile chloride

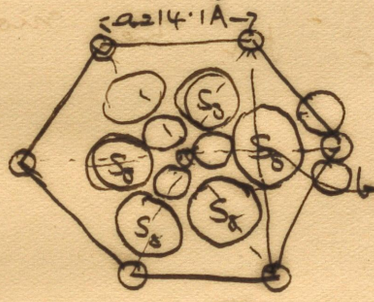
recently studied by crystal structure by Jaeger and Beintema, Proc. Amst. Acad. 35, 756 (1932). They suggest a plane cyclic structure for the molecules.

~~write to Prof Jaeger~~

$CHI_3 \cdot 3S_8$

Studied by x-Rays. by Hertel, Zs Ph. Chm. B, 15, 51 (1931-2)

Trigonal. Unit cell contains only one molecule of $CHI_3 \cdot 3S_8$



c = 4.44 Å.

Cryst prepared by dissolving CHI_3 and S in suitable proportions in CS_2.

o c ○ I (S8)

Extraordinarily interesting compound for study of magnetic and optical anisotropies.

The compound $AsI_3 \cdot 3S_8$ has a very similar structure. Trig. Z=1

a = 14·2
b = 24·6
c = 4·48 Å.

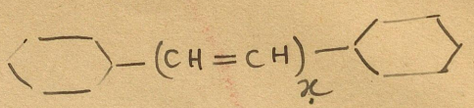
The S_8 groups have a cyclic structure.

Other Compounds of interest—

Hengstenberg and Kuhn
Zs. Kr. 75, 301 (1930)

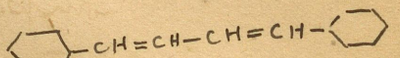
See Wyckoff 16 Suppl. p. 149.

Diphenyl Polyenes



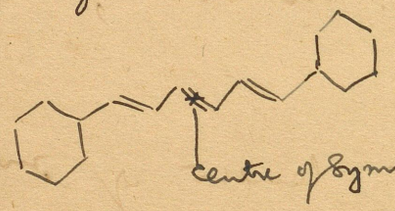
x = 1: (Stilbene) sym. Diphenyl ethylene

x = 2. Diphenyl-butadiene (Diphenyl-diethylene)



		Z	a	b	c	β
Monocl. prism.	(?) C_{2h}^2 (or C_{2h}'?)	4	7.71	11.70	$\frac{13.31}{\sin 97°} = 13.41$	97°

x = 3 Diphenyl hexatriene C_{2h}^5 2 6.33 7.43 14.43 90°



x = 4 = Diphenyl ~~octatriene~~ octatetraene C_{2h}^5 2 6.25 7.44 16.03 90°

also rhombic

Rhombic Polyenes

x = 5 Diphenyl decapentaene V_h^{15} 4 10.26 7.66 ~~23.58~~ 21.2

x = 6 Diphenyl dodecahexene ? 4 10.20 7.60 23.58

x = 7 Diphenyl tetradeca heptaene 4 10.2 7.57 25.95

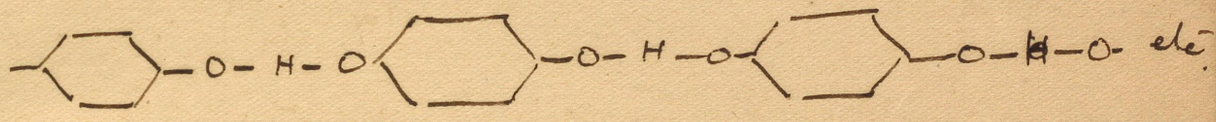
Write to Kuhn or Winterstein.

For the chemistry of these compounds see Winterstein and Kuhn Helv. chim. Acta 11, 87 (1928). See also Zechmeister, Chem. Rev. April 1944 p. 335.

magnetic measurements made already.

Quinhydrone

~~No~~ Probably not a molecular compound but a chain polymeride; Monocl. C_{2h}^5 — Each unit cell contains 1 molecule of quinone and one of quinol



See O. R. Foz and J. Palacios, Anal. Fis Quim, 30, 421 (1932).

Vibrations $\parallel^l$ to length of molecule (completely absorbed; black). ⊥ vibrations transmitted almost.

Mon. C_{2h}^5 $\left.\begin{matrix} a = 3.85 \\ b = 6.04 \\ c = 10.9 \\ \beta = 90° \end{matrix}\right\}$ $Z = 1$.

For chloranil and bromanil see p. 36.

B. J. Quinhydrone

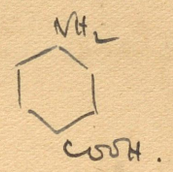
Hexa ethyl benzene

Subst. available - no cryst data.

Hexamethylene tetramine

X-ray cryst. data by Dickinson + Raymond, J. Am. ch. Soc. 45 22 (1923). Cubic

~~[illegible]~~ m- diphenyl benzene Subst. avail. no cryst. data.



p- aminobenzoic acid

monocl. prismc. C^5_{2h} Z = 4

Prasad + others J.I.C.S.

a = 12·26 A a : b : c = 1·424 : 1 : ·7316

b = 8·61 " Growth 1·4403 : 1 : ·7312

c = 6·30 ρ = 1·393.

β = 100° 10′ (goniometric)

in the form of plates ∥ to (10$\bar{1}$) ; (100) + (101) also developed

O- diphenyl benzene Subst. available – no cryst. data

Hexaphenyl benzene

(β)
1,2 - Naphthoquinone Subst- + Cryst- data available.

Caspari Proc. R.S., A 136, 82 (1932)

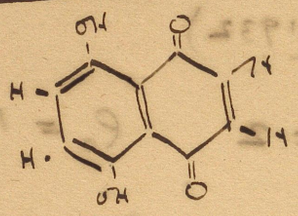
Monocl. $a = 3.84$ A $Z = 2$ $\rho_0 = 1.450$ (x Rg)
$b = 8.10$
$c = 13.40$ Sp. Gr. C_s^2.
$\beta = 118^\circ 40'$

For the x-ray crystallographic data of some β-derivatives of naphthalene [OH, NH_2, CH_3, Cl.]
see Neuhaus Zs. Kr. 101, 177 (1939).

magnetic measurements made already

Naphthazarin 5,8 dioxy-1,4-naphthoquinone

(Alizarin Black)



Cryst. data from x-rays

J. Palacios and R. Salvia

Anales de la Societad Espafiola de Fisica y Quimica, 32, 497 (1934).

monocl. $a = 3.85$ C^5_{2h} 2 centro-symmetric molecs in unit cell.

$b = 8.02$

$c = 14.5$

$\beta = 97° 6'$

? wd be if it is 4,8-dioxy-1,5-naphthoquinone

magnetic measurements made already

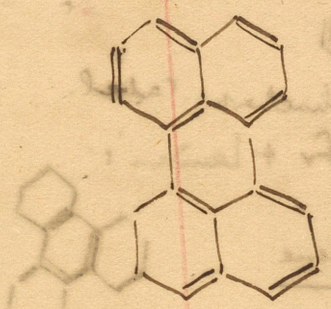
Alizarin 1:2-Dioxyanthraquinone $C_{14}H_6(OH)_2O_2$

Orthorhombic. $a : b : c = 0.8071 : 1 : ?$

Polynuclear compounds

1) **Perylene** (Thank Prof Dadieu for subst.)

magnetic measurements made.



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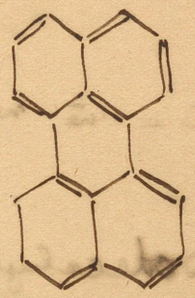


II

Form. I suggested by Clar Ber 65 B, 846 (1933)

Possibility of II not excluded by him.

See also Konrad Funke Monat. 62, 13 (1933).

Subst available — large crystals. no cryst. data.

write to him for pure substance

M. P. of pure perylene crystallised from acetic acid (pale bronze leaflets) 273-4° C. [G. T. Morgan and J. G. Mitchell, J.C.S. 1934 p. 536]

Cryst. str. by x-ray methods by Hertel + Bergk, Zs. Ph. ch. B, 33 319 (1936)

Monocl. $a = 10.3$ Å $\rho = 1.35$

$b = 10.8$ $Z = 4$.

$c = 13.6$.

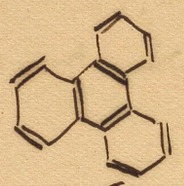
$\beta = 126.5$.

magnetic measurements made already

2. **Triphenylene** Subst available, no cryst data.

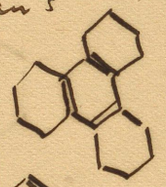
(Thank Prof Clar for subst)

9,10- Benzophenanthrene



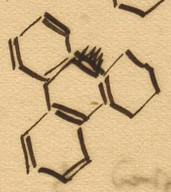
ordered for 20 gms 14 5/36 { Listed in the new (1936) T. Schuchart catal. 25 gms. 5 Marks.
also in Fr + Landau's

Dodecahydrotriphenylene

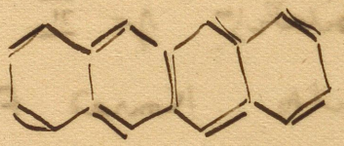


Mannich, Ber 40 153 (1907)
Diels + Karstens, Ber 60, 2323 (1927)
Bergman J.A.C.S. 59 1441.
Write to Ernst Bergmann
Daniel Sieff Research Institute,
Rehovoth, Palestine.
wrote to him on 16 9/37 for dodecacompd.

Tetrahydrotriphenylene



Naphthacene



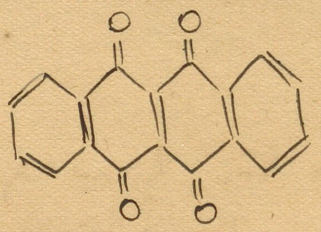
(Thank Prof. L. F Fieser for subst.)

2,3- Benzanthracene.

ordered for 20 gms. 14 5/36 { Listed in the new Schuchart catal.
10 gms. 3·35 M. + also in Fr. Land's
x-ray studies by Hertel + Bergk, Zs. Ph. Ch. B, 33, 319 (1936).

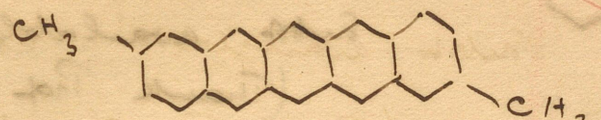
Monocl. $a = 7{\cdot}94$, $b = 6{\cdot}02$, $c = 13{\cdot}48$; $\beta = 112^\circ$ $Z = 2$

Naphthacenediquinone



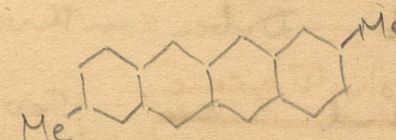
See J.A.C.S. 58, 1054, 1936.

Write to Prof. L. F. Fieser.

3) 

Subst. available
(Thank Prof Clar for subs)
no cryst data.

2,6 - Dimethylnaphthacene



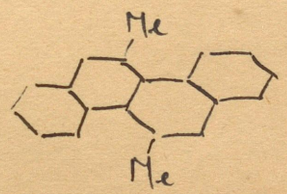
EA Coulson. J.C.S 1934, p. 1460.

write to Prof Morgan for substance.

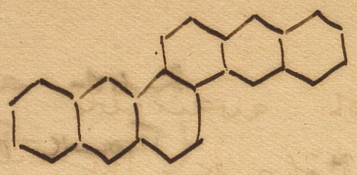
Golden orange flakes; m.P. 365° (it heated slowly darkens, partly sublimes and melts at 350°-60°. Sparingly soluble in common solvents, yielding orange solns with marked green fluorescence. Soluble in boiling acetic acid.

Symmetrical Derivatives of Chrysene J.C.S. 1938 p. 397

write to Prof Simonsen.



J. C. S. 1938 p. 1854.

4) 

Subst available
(Thank Prof clar for subst)

no. cryst data.

1:2:5:6 - Dibenzanthracene : For method of purification of the compound see Cook + others, Proc. R.S. B 111, 455 (1932).

magnetic measurements made already

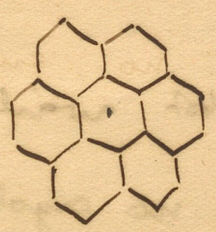
Dianthracene $(C_{14}H_{10})_2$ Hengstenberg + Palacios, Anals Soc. Espan phys quim 30, 5 (1932)

Orthorh. V_h^{15} a = 8.18, b = 12.15, c = 18.75 Å Z = 4

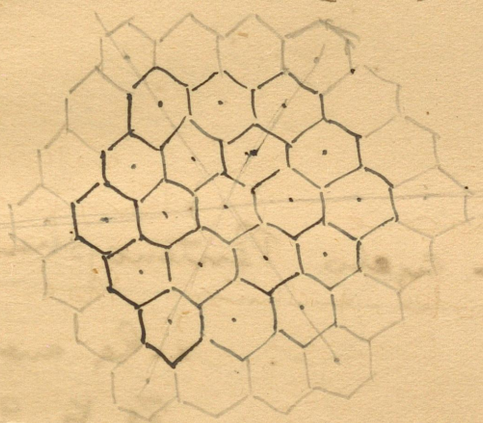
min. molec. Sym. C_i

Coronene

Subst available
(Thank Prof Scholl for subst.)
no cryst data.



"New synthesis of Coronene" By M.S. Newman, J.A.
C.S. 62 1683 (1940). Write to him for the substance.



Number of rings round the central one: *
6, 12, 18 etc.

Their formulae would be

$n =$

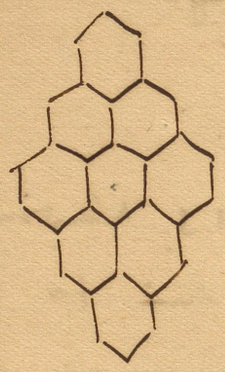
1. $C_6 H_6$
2. $C_{24} H_{12}$ (Coronene)
3. $C_{54} H_{18}$
4. $C_{96} H_{24}$

etc.

General formula
$C_{6n^2} H_{6n}$

In each hexagonal sector } No. of C atoms = 1, 3, 5, 7 etc.
H " 1, 2, 3, 4 ---

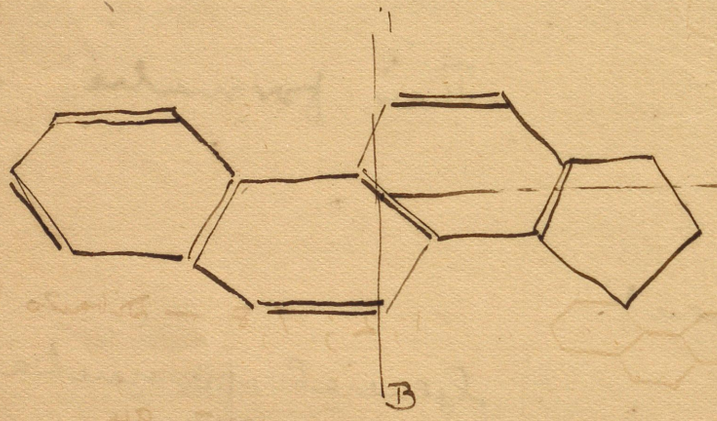
~~Anti D~~ Anti diperi dibenz coronene



Substance available (thanks Prof Schlenk for it)

no cryst data.

1:2- cyclo Pentenophenanthrene



X-Ray analysis by J. Iball
Zs Kr. 92, p. 293 (1935)

$a = 18.38$ Å
$b = 5.83$ $\beta = 114°3'$
$c = 23.61$

dens = 1.23 $Z = 8$.

and $\beta - b$ to 'a'

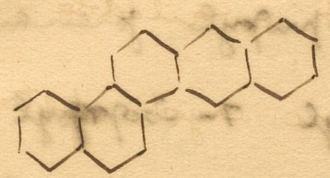
length of molec at- b to 'c' / and plane at- $30° - 35°$ to 'b' ax.

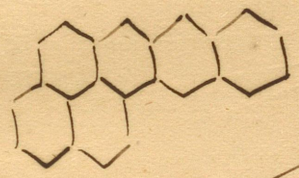
For cryst structure of 2 of the derivatives of this compound see Iball Zs Kr. 93, 47 (1936).

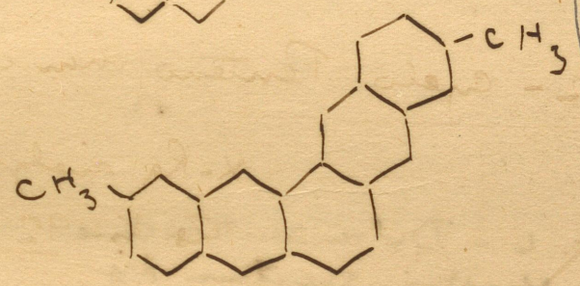
Other polynuclear compounds available

(from Prof Clar)

no cryst. data for any of them.

1) 

2) 

3) 

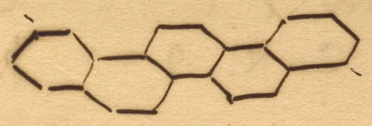
1-8 Dimethyl picene: 2 methyl groups at probably the positions marked:

Giacomello: Ze. Kr. A 99, 88 (1938)
+ Rend. Cont. Acad Lincei 27, 574 (1938)

a = 8.16 A d = 1.316
b = 6.36 M = 308.7
c = 15.01 Z = 2
β = 96° Space gr. $P2_1$.

write to either Ruzicka or Giacomello.

4) Picene
$C_{22}H_{14}$



1, 2; 7, 8 — Dibenzo phenanthrene

write to Prof L. Ruzicka (Zurich)

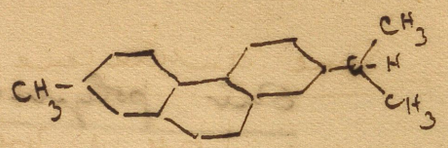
X-ray data Bernal & Crowfoot, J.C.S. 1935, 94

Rhombic Sp Gr. Aba a = 8.21 A Ref ind a = α
b = 6.16 b = β
c = 28.8 Z = c = γ.

Not the same [check whether Th. Sc's black compound (Picein) is the same.

See Ruzicka and Hösli Helv. chem. Acta, vol. 17, p. 470 (1934)
for Absorption spectrum see W.V. Mayneord & E.M.F. Roe, Proc. R.S.A
152 p. 299 (1935). $CHCl_3$ suitable solvent.

Retene $C_{18}H_{18}$

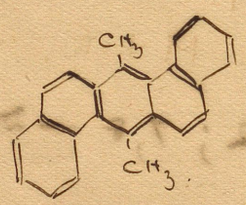


Bernal and crowfoot J.C.S 1935, 94 suggest the above formula (2-methyl 7-isopropyl phenanthrene)

Richter's book gives 1-methyl 7-isopropyl.

According to B and C orthorhombic Sp. Gr. Aba $a = 8.54$ Å, $b = 6.25$, $c = 23.4$ | $a = \alpha$, $b = \beta$, $c = \gamma$.

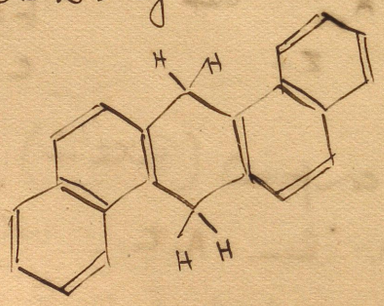
9:10 – Dimethyl – 1:2:5:6 – Dibenzanthracene



Absorption spectrum by Mayneord & Roe, Proc. R.S.A 152, p320 (1935)

For preparation and properties see Cook, J.C.S p. 489 (1933)

9:10 – Dihydro – 1:2:5:6 – Dibenzanthracene



Cook, J.C.S 1592 (1933).

Absn. sp. M & R. loc. cit

for X-ray analysis of its crystal structure see Iball J.C.S. 1938 p. 1074–77

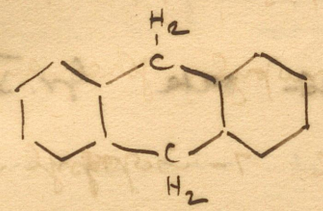
2 cryst. forms (i) monocl. $a = 14.24$, $b = 5.27$, $c = 24.90$ $\beta = 130°.2$ $Z = 4$

(ii) " $a = 9.49$, $b = 6.76$, $c = 24.38$ $\beta = 111°.4$ $Z = 4$

Some anthracene derivats

(all of them available)

magnetic measurements made already.



Abell: J.C.S. (1938) 1074; monocl.
a = 7.90, b = 6.21, c = 11.09; β = 113° Z = 2.
Cryst. data Gr. V 439.

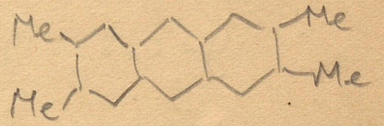
2:6- Dimethyl anthracene



Morgan + Coulson, J.C.S. 1929, p. 2203.

M.P. 250° Crystallises out of CS_2.

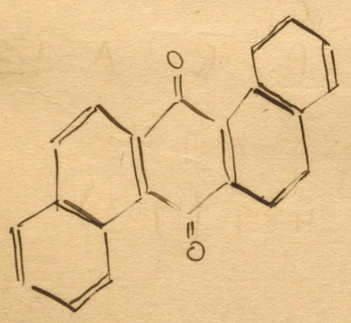
2:3:6:7 Tetramethyl Anthracene



Write to G.T. Morgan

Morgan + Coulson, J.C.S. 1931, p. 2323.
M.P. 308°. Pale yellow rhombic plates. Soluble in benzene + acetic acid, freely in CS_2.

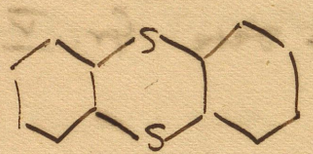
1:2:5:6- Dibenz-9:10- Anthraquinone



(1935)

See Cook, J.C.S. p 1477 (1932)
also sp. M + R. loc. cit.

(A magnetic measurements made already) 2) Thianthrene Diphenylene disulphide. (Subst available)



Cryst. data Gr. V, 34.

magnetic measurements made already.

For other compounds of this structure see Campbell & others J.C.S. 1938, 404.

1,2-Naphthoquinone Caspari Proc. R.S. A 136, 82 (1932)

Monocl. $a = 3.84$ Å $\rho_{x\text{-Ray}} = 1.450$

C_s^2 $b = 8.10$

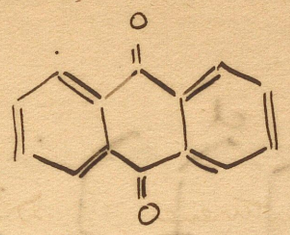
$c = 13.40$

$Z = 2$ $\beta = 118°40'$

magnetic measurements made already

meso-

3) 9,10- anthraquinone



(data available)

Cryst. data ~~available~~ cospari Z = 8.

1,4- Naphthoquinone

cospari loc. cit.

a = 13.50 Å

b = 7.74

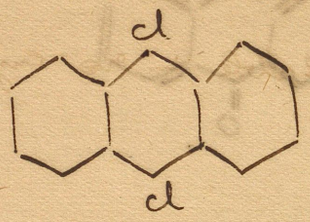
c = 8.25

β = 125° 10'

ρ_{x-ray} = 1.422

C_{2h}^5

Z = 4.



Subst available – no cryst data

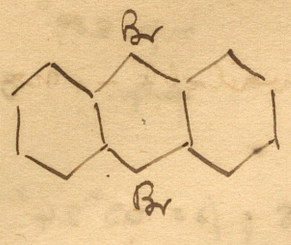
1·2 – Anthraquinone Caspari loc. cit.

$a = 11.41$ Å $\rho_{X\text{-Ray}} = 1.480$

$b = 11.56$ C_{2h}^{5}

$c = 9.30$ $Z = 4$.

$\beta = 130° 30'$



Subst. available — no cryst. data.

1,4-Anthraquinone Caspari loc. cit.

1st modin.

$a = 4.19$ Å $\rho_{x\text{-Ray}}$ 1.477

$b = 5.81$

$c = 19.62$ $Z = 2$

$\beta = 101° 30'$

2nd Modifn.

$a = 13.82$ $\rho_{x\text{-Ray}}$ 1.461

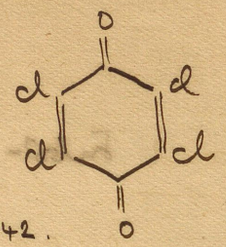
$b = 9.54$

$c = 7.31$ $Z = 4$.

$\beta = 100° 50'$

magnetic measurement made already

Chloranil (2,3,4,5-Tetrachloroquinone)



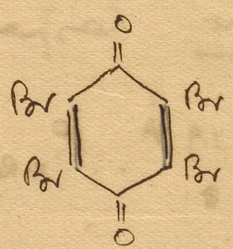
m.p. 289°
Sp. Gr. 1.933

Good Crystals available. Cryst. data Gr. IV, 142.

monocl. pris. a : b : c = 1.5179 : 1 : 2.9658 ; β = 103° 24′.

magnetic measurement made already.

Bromanil
(2,3,4,5 – Tetrabromoquinone)



m.p. 300°.

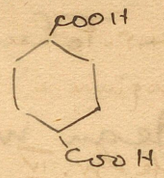
Good crysts. available

Cryst. data Gr. IV, 144. Monocl. prism. a : b : c = 1.3904 : 1 : 2.8895 ; β = 102° 3½′

$SO_2 \cdot 3\,C_6H_4(OH)_2$ —— 3 moles of above formula in unit cell. All the benzene rings oriented ‖l

Palin & Powell : Nature 156, 334, 15 9/45.
Structure according to them similar to that of β-quinol (Caspari J.C.S. 130 1093 (1927).

Terephthalic Acid



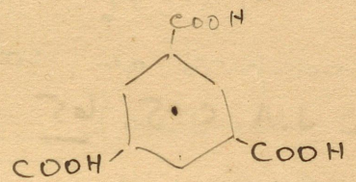
Powder, insoluble in alcohol and water. Sublimes unchanged.
no cryst. data. (listed in catalogues)
Cryst. data available for $C_6H_4(COO\cdot CH_3)_2$. Rhombic

Trimesic acid

(Benzene 3-tricarboxylic acid)

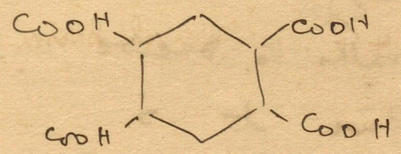
T.3.

m.P. 375°-80°.



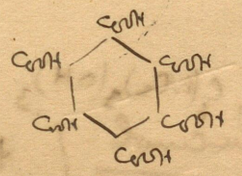
no cryst. data. — data available for $C_6H_3(COO\cdot C_2H_5)_3$ - Hexag.

Pyromellitic acid



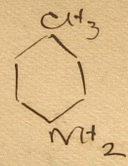
Crystallizes with 2 mol. of H_2O. Triclinic — (Ggr. IV, 760).

Mellitic Acid



Crystal data available for $C_6(COOK)_6 \cdot 9H_2O$ and $C_6(COO\cdot NH_4)_6 \cdot 9H_2O$ Ggr. IV, 763. Both rhombic Latter uniaxial for green.

magnetic measurement made already ~~A-toluidine~~ ✓ p-Toluidin



mp. 45°

Orthorhombic Jean Wyart, C.R. 200, p. 1862 (27th May 1935)

$a = 5.98$ A
$b = 9.05$
$c = 23.3$

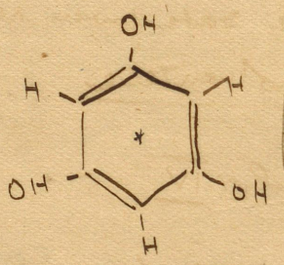
$Z = 8$. For Molecular orientations in the unit cell see p 1862 of paper.

Hexahydroxybenzene $C_6(OH)_6$ Crystallises in colourless prisms. no definite m.p. decomposes at 200°. Its K compound $C_6(OK)_6$ is explosive See J.A.C.S. 65 1770 (1943).

Tetrahydroxybenzene

magnetic measurement made already ✓ Phloroglucinol

good crystals available



I

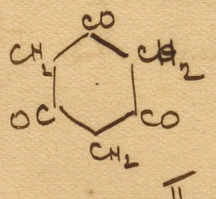
$+ 2H_2O$ Rhombic

Crys. data Gr. IV, 89.

According to Baeyer (?) it would be impossible to decide whether by formula it is

(a) 1,3,5-trihydroxybenzene

or (b) Triketohexamethylene II



II

$C_6(NO_2)_3(OH)_3$

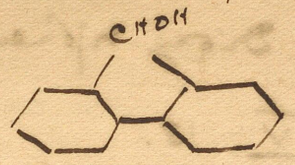
2,4,6 — Trinitrophloroglucinol / Hexag (cl) C^3_{3v} or D^4_{3d}

$a = 13.4$ $c = 9.6$ Å $Z = 6$.

Hertel & Schneider, Zs. Phys. Ch. 12 B p. 139 (1931)

magnetic measurements made already

Fluorenol.



(Fluorene alcohol)

Hexagonal $a : c = 1 : 0.631$ (See Gr. V, 429)

Thin tables $\parallel^l$ to c (0001)

Double refn. +ve extraordinarily strong.

p-iodoaniline - S-Trinitrobenzene (molecular compound) monoclinic

All the benzene planes nearly $\parallel^l$ to (100) 3° to it (Powell & others J.C.S 1943 p.153)

Crystals elongated along 'a' axis. Crystal double refn -ve a acute bisectrix

$a = 7.43$ $b = 7.39$ $c = 28.3$ A $\beta = 103° 25'$ $P_2 2_1/c$.

Complete data given re ~~molecular~~ atomic positions.

magnetic measurements made already

1,3,5 - (S-) Trinitrobenzene m.p. 121°-2° $\rho = 1.687_8$

Cryst. data Gr IV, 15. Rhombic pyr. .9487 : 1 : .7269.

1,2,4,6 - (D) Tetranitrobenzene orthorh. V^4

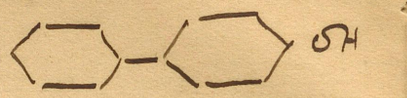
$a = 12.4$, $b = 6.15$, $c = 13.1$ Å. $Z = 4$.

Hertel + Römer, Zs. Phys. chem. 22 B, 267 (1933)

Styphnic acid $C_6H(OH)_2(NO_2)_3$ Hex. (cl.) C^3_{3v} or D^4_{3d}

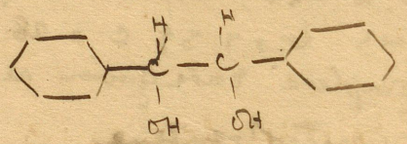
$a = 12.7$ $c = 10.0$ Å $Z = 6$.

has same cryst. structure as 2,4,6 trinitrophloroglucinol.

γ - Biphenol p-p'- Dioxydiphenyl 

Cryst. data Lyr. V, 18.

Rhombi - very difficult to crystallize.

Isohydrobenzoin 

Cryst. data see Landolt Tables.

monocl. probably C_2^2 Z = 2

a = 12.4₀ , b = 7.9₂ , c = 5.8₁ Å β = 92° 53'

molec. symmetry C_1 Polymerism excluded.

Cis- Azobenzene $C_{12}H_{10}N_2$

a = 7.57
b = 12.71
c = 10.30

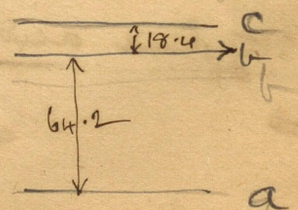
Orthorhombic - Space gr D_{2h}^{14} (P b c n)

Z = 4

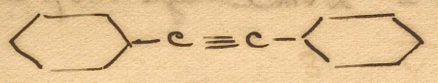
J.M. Robertson J.C.S. 1935 p. 232.

$\chi_a - \chi_b = -108\left[\cos^2 27\tfrac{1}{2}^\circ - \cos^2 146^\circ\right] = -64.2$

$\chi_a - \chi_c = -108\left[\cos^2 27\tfrac{1}{2}^\circ - \cos^2 81\tfrac{1}{2}^\circ\right] = -82.6$



For the preparation of the compound see Hartley (J.C.S. 1938, p. 633).

Tolane 

Monod. prism. cryst data Ztr. 5, 193.

Write to Weissenberger for substance

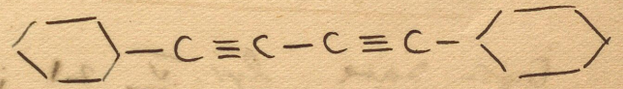
for discussions about the structure of the molec. read Weissberger Q.C.S. 1935, p. 855 and the papers referred to there.

The Dyson Perrin's Laboratory, Oxford.

or Brieglob or Kambeitz. Institut für physikalische chemie und Elektrochemie der Technischen Hochschule Karlsruhe.

Zs. Phy. ch. B, 4 305 (1936)

or Bergmann.

1,4 – Diphenyl butadiin – 1,3 

or Diphenyl diacetylene 

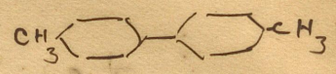
See Wiebenga Nature 143, 981 (June 10, 1939)

Monod. prism. $a = 6.61$ A $\quad b = 6.04 \quad c = 14.92 \quad \beta = 105^\circ$

$Z = 2 \quad \rho = 1.16_3$

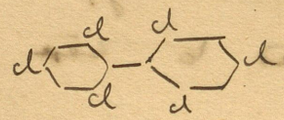
Sp. Gr. C_{2h}^5 $(P_{21/c})$

Wrote to Miss Pickett for compound on 7 12/36

p-p' Bi-tolyl (4, 4'- Dimethyl biphenyl) 

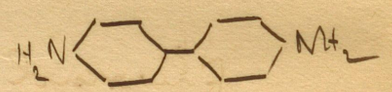
Cryst. data Gr. 5, 24.

Wrote to Miss Pickett for compound on 7 12/36

2, 4, 6, 2', 4', 6' — hexachlorobiphenyl 

a = 15.82 Å, b = 8.42, c = 21.50 β = 91° 49' Z = 8 C^6_{2h} [Pickett, J. Am. ch. Soc. 58, 2295, 1936]

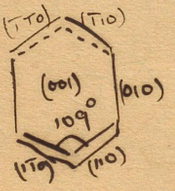
optically −ve into small axial ∠le.

Benzidine (4, 4'- Diaminobiphenyl.) 

Cryst. data Gr. V 21; triclinic a : b : c = 1.3276 : 1 : 0.7471
α = 119° 57', β = 93° 14', γ = 99° 34'.
Mieleitner

~~Triclinic~~.

According to H. Steinmetz, Zs Kr. 56 157 (1921) the crystal (obtained out of a warm aqueous soln.) is monoclinic



optically the plate shows a biaxial interference figure: Brief. +ve and acute bisectrix at 30° to the normal to the plate. [i.e. opt. ax. plane ⊥r to 'b' ax: — the description in the paper would seem to imply otherwise!]

ie β = b γ ax. makes 60° into 'a' magnetically |θ| std ve = 30°

According to Bajrekar (Mata Prasad's student)

a = 9.78 Å
b = 15.83
c = 11.51

Z = 6 !

He was not aware of the possibility of twinning suggested by Steinmetz.

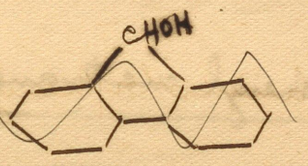
1, 3, 5 – Benzoltricarbonsäuretriethylester

$C_6H_3(COOC_2H_5)_3$

Hexagonal pyramidal $a = 11.3$ Å $c = 20.1$ $Z = 6$.

See Hertel & Dumont, Z. P. C., 29, 112 (1935).

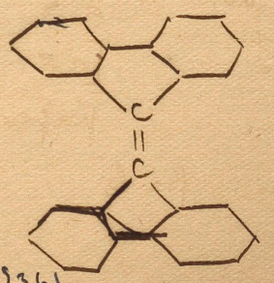
Fluorenol



Hexag.

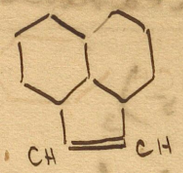
Bifluorene

Gr. V, 431



Dibiphenylenethylene $C_{26}H_{16}$ & its difluoro derivative studied by X-ray methods W. H. Taylor Ze. Kr. 93 151 (1936) & related compounds

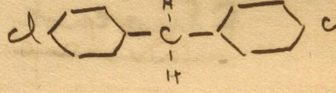
Acenaphthylene



Rhombic. Cryst. Structure very similar to that of acenaphthene

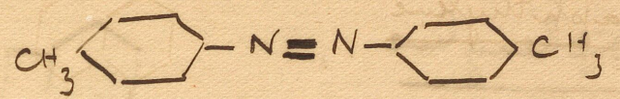
Lw. V, 421.

4,4'- Dichloro diphenyl methane



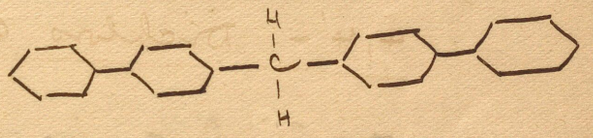
Monocl. prism Cryst. data Lw V, 97.

Azotoluene



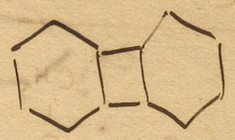
Monocl. prism Cryst. date lyr. V, 66.

Di biphenyl methane



Monocl - prism. lyr. V, 343

o-Diphenylene

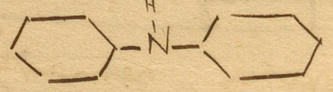


$C_{12}H_8$

Dobbie, Fox and Hyffmeister, Trans. Ch. Soc. 99, 683 (1911)
← Fox's letter: See also W.C. Lothrop, J.A.C.S.
63, 1187, May 1941 ← for abs. spectrum ibid p. 3231 Nov. 1941.

See p. 56.

Diphenyl amine



for V, 41.

Methyl bixin

$$CH_3-O-CO-CH=(CH-\overset{CH_3}{\overset{|}{C}}=CH-CH=)_4\,CH-CO-O-CH_3$$

Chemical Structure see Helv. Chem. Acta 11, 427 (1928).

Cryst. Structure see Waldmann & Brandenberger, Zs. Kr. 82 77 (1932)

Earlier x-ray Monel. work by Hengstenberg and Kuhn, Zs. Kr. 76, 174 (1931).

$a = 10.5_6$
$b = 13.4_0$
$c = 20.6_2$
$\beta = 121°$

$C_{2h}^5 - P2_1/a$

$Z = 4$ (moles of $C_{26}H_{32}O_4$)

Opt. properties remarkable

$\alpha = 1.44$
$\beta = 1.649$
$\gamma \geqslant 2.63$

Appr. by Prof Dr R. Kuhn Heidelberg for publ.

Structure of Isatin: See Cox & Stiles Proc. R. S., A 157, 399 (1936).

Phthalocyanine and its Cu, Ni & Pt derivatives

X-ray data by J. M. Robertson, J.C.S. 1935 p. 615.

See also Linstead and Dent, J.C.S 1934, p. 1016.

Try also magnetic anisotropy of manganic acetyl acetone. ($Mn^{+++}(CH_3 \cdot CO \cdot CH \cdot CO CH_3)_3^{'''}$) L. C. Jackson, Proc. Phys. Soc. Lond, 47 1029 (1935)

p-Dicodobenzene

Orthorhombic V_h^{15} $a = 17.00$ $b = 7.38$ $c = 6.21$ Å

$Z = 4$. Min mol. fg. C_2.

Hendricks, Maxwell & Jefferson, J. ch. 1, 549, 1933.

Hexabromohexamethyl benzene $C_6(CH_2Br)_6$

Rhombohedral $a = 9.621$ Å $\alpha = 116° 36'$ [crystals

hexag. cells: ~~a = b~~ $a = 16.373$ Å $c = 5.377$ Å $c/a = .328$]

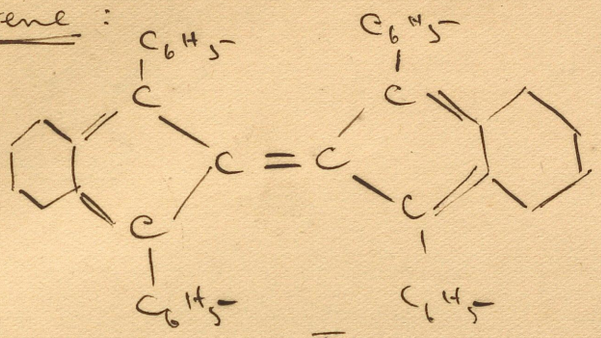
$Z = 3$.

X-Ray data by J. Beintema, P. Terpstra and W.J. VanWeerden,
Rec. Trav. chem. Pays-Bas [4] 54 962-9 (1935)
Str. Ber. cr. Band III p. 755 & 679.
Orientations of all the 3 benzene rings are given H^l 45 (111) plane

Technique for transferring monomolecular films of various long chain compounds:

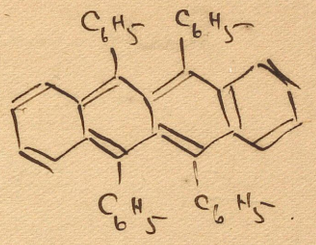
See Blodgett and Langmuir, J. A. C. S. 56, 495 (1934) and J. Fran. Inst. 218, 143 (1934); also Clark and another J. A. C. S. 57, 330 (1935)

Rubrene :



I

or



II

X-ray analysis by W. N. Taylor Zs. Kr. A 93, 151 (1936)

monoclinic $a = 17.9$ Å $\quad C_{2h}^5 \quad Z = 2$.

$b = 10.1$ plane of molec. nearly $\perp$ to (010)

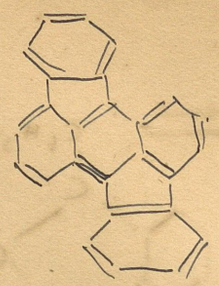
$c = 8.8$

$\beta = 120°$

T prefers I. Bergmann & Herlinger J. c. Phys. 4, 532 (1936) give evidence for structure II

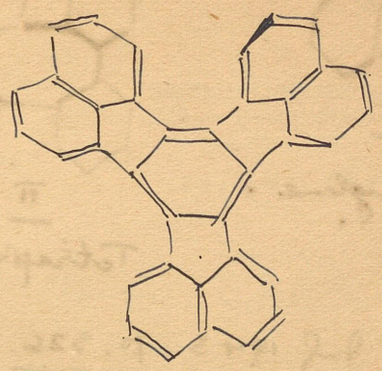
Dufraisse + Compagnon (C. R. 207, 585 (1938)) ~~prefer~~ give the II structure.

Rubricene $C_{26}H_{14}$



See Randall & others
Proc. R.S. 165 p. 441 (1938)

Decacyclene $C_{36}H_{18}$

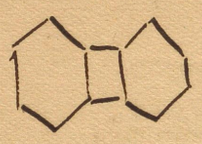


Randall & others
Proc. Roy. Soc. A 165 441 (1938)

See also Truxene, Trimethyl truxene, (p 441)

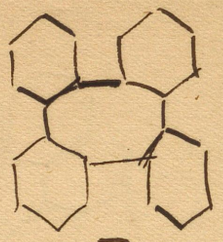
Tricyclomethylene benzene } (443)
octohydroanthracene }

Tribenzoylene benzene. 444



I

Diphenylene



II

Tetraphenylene

Central ring in II Octagon

J.C.S. Jnly 1943 p. 326.

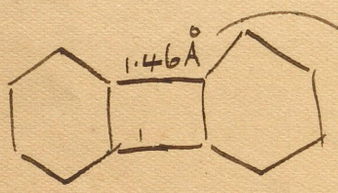
by Rapson + Shaw, Univ of Cape Town, South Africa.

See also Lothrop J.A.C.S. 63, 1187 1941), Baker Nature 150, 210 (1942)

II monoclinic C_{2h}^{6} N A 2/a

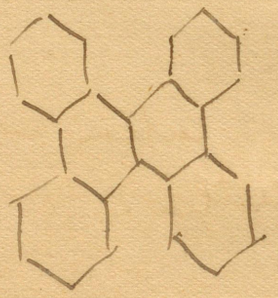
a = 16.35 A
b 13.16 β = 160° 40'
c = 15.60 Z = 8.

See also J.A.C.S. 65 1451 Aug 1943. Elec. diffraction studies & calculations of resonance energies.



all other distes 1.41 Å.

Tetra benz naphthalene



Write to Bergmann J.A.C.S. 66 183 (1944)

DAVY FARADAY RESEARCH
LABORATORY.

DIRECTOR: SIR WILLIAM BRAGG.

TELEPHONE:
REGENT 0669.

THE ROYAL INSTITUTION,
21, ALBEMARLE STREET,
LONDON, W.1.

21. 6. 1939.

Substances available with Mrs Lonsdale

Diphenyl diacetylene

Diphenyl butadiene

Cinnamylidene acetic acid

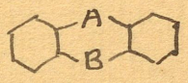
Crotonic acid (volatile)

Tiglic acid

$(CH_3)_2C:CH.COOH$

Sorbic acid

α-methyl cinnamic acid

Thiazan 

A	B
S	S
Se	Se
S	NH
N	N
S	O
Te	O

The value for $NiCl_2$ solns which we have been using [corresponding to a magnetic moment of 16·05 Weiss magnetons for the moment of Ni^{++}] will give

$$10^6\chi = \frac{10030}{T}x - 0{\cdot}720(1-x) = -0{\cdot}31\,x$$

per gm of soln.

A solution containing a weight fraction x of $NiCl_2$ has a susceptibility per

$$10^6\chi = \frac{10030\,x}{T} - {\cdot}720(1-x)$$

Professor Sugden's values for the suscept. of nickel chloride solutions

see p. 147 of these notes.

For the structure of pyrrhotite see Ze Kr. 56 202 1921 [abstract of a paper by Allen, Crenshaw and Larsen, Jr. Am. Journ Sc. 33, 168-236 (1912) and Zs. anorg. ch. 76, 201-273 (1912)]

α - Pyrrhotite : Rhombic (?)

a : b : c = ·5793 : 1 : ·9267
or ·5793 : 1 : ·9927

β - P Hexagonal

a : c = 1 : 0·8632 or 1 : 0·8742.

See Sidhu and Hicks, Phys. Rev. 52 667 (1937)

Graphitic acid

1) See Hoffmann (for a general survey of the reactions of graphite) Koll. Z. ~~1934~~ 69 351 (1934); A.; 1935 p. 163
Hoffmann, Frenzel & Csalan, Annalen 510, 1 (1934); A, 1934 p. 64
cf. H Thiele Z. Elektrochem., 40, 96 (1934); A. 1934 p. 262

2) A series of graphite sulphates has been prepared with SO_4 groups below every 2, 4, 6 etc graphite planes.
see Frenzel & Hoffman ibid p. 511; A. 1934 p. 978

3) Carbon subfluoride CF is also a graphite compound which has largely lost its metallic character. See
O. Ruff & O. Bretschneider (with F. Ebert) Z. anorgan. chem. 217, 1 (1934); A. 1934 p. 378.

See also Hoffmann & Rudorff, Trans. Farad. Soc. 34, 1017 (1938). See also papers by Riley ibid p. 1011, Ruff (p. 1022) Thiele (p. 1033) & Berl (1040) and the discussion.

Structure of products of action of alkali metals on graphite

A. Schleede + M. Wellmann
Z. Phy. Ch. 18 B, 1 (1932)

		a	c	
Hexagonal	KC_8	4.94	21.34	With an
"	RbC_8	"	22.73	
"	CsC_8	"	23.76	
Hexagonal	KC_{16}	"	17.45	
	RbC_{16}	"	17.95	
	CsC_{16}	"	18.51	

Graphite $a = 2.46 = \frac{4.92}{2}$

$c = 6.7$

$C_6H_9(SH)_3 \cdot 2NH_3$

Nature 163 721 (1949)

Boric Acid H_3BO_3

X-Ray analysis by W. H. Zachariasen, Zs. Kr. 88, [illegible] (1934)

~~Crystals pseudo-hexagonal~~

Triclinic $a : b : c = 0.9990 : 1 : 0.9228$ $\alpha = 92°30'$, $\beta = 101°10'$, $\gamma = 119°51'$

X-Ray: $a = 7.04$ Å, $b = 7.04$, $c = 6.56$

$\alpha = 92°30'$, $\beta = 101°10'$, $\gamma = 120°$

$\rho = 1.46$, $Z = 4$.

According to Zachr. Crystals pseudo-hexagonal, 'c' axis being the pseudo-hexag. axis. [Should not the p.h. axis be ⊥ (001)?]

R = For D, $\alpha = 1.340$, $\beta = 1.456$, $\gamma = 1.459$

α ax. exactly ⊥ to (001)

γ nearly along 'b'

Crystals prepared from aqueous soln. — 2 distinct types:—

(1) Plates ∥ to (001)

(2) needles along 'c' axis.

BO_3 plane structure ∥ to (001).

Cryst. structure of KNO_2 (Ziegler, Phy. Rev. 49, 884, 1536)

$NaNO_2$ (

Cryst structure of $Zn(SbO_3)_2$. (Zn meta antimonate)

by L. Clark and D. A. Reynolds. Z. Kr. 98, 185. (1537)

Tetrag. $a = 6.585$ Å $c/a = .783$. $Z = 2$ $\rho = 6.1$

Space Gr. $D_{2d}^8 - P\bar{4}n2$

SbO_3 group evidently planar.

Crystal structure of the rare earth ethyl sulphates

J. A. A. Ketelaar, Physica 4 615-30 (1937).

Finds that there are two rare earth ions in the unit cell, i.e. two moles of $M(C_2H_5SO_4)_3 \cdot 9H_2O$ the dimensions of the unit cell being roughly

$a = 14.0$ Å $\quad c = 7.1$ Å (hexagonal)

and nearly the same for all the ethyl sulphates.

The symmetry of the Cryst. field acting on the rare earth ion is probably C_{3h} [i.e. possesses at least a three fold axis, intersected by a plane at right angles.]

Abs. spectra: Freed Phys. Rev. 38, 2122, 1931
Proc. Amst Acad. 35, 979, 1932

Spedding + Bear Phys. Rev. 46 308, 1934

Merz Ann. der Phys. 28, 569, 1937.

AgN_3 X-Ray analysis of Cryst. Structure by Bassière

C. R. 201, 735 (1935).

$a = 5.58$ Å $\quad Z = 4.$

$b = 5.93$

$c = 6.04$

Rotation of Molecules in Crystals

Pauling : Phys. Rev. 36, 430 (1930)

Stern : Proc. R.S. A 130, 551 (1930):

Fowler " 149, 1 (1935-)

Nielsen J. Chem. Phys. 3, 189 (1935-)

Euler's formula connecting the no. of edges E, faces F, and vertices V of a polyhedron

$$E + 2 = F + V.$$

What is Cauchy's extension of this formula?

Only polyhedra having faces 4, 6, 8, 12 or 20 faces exist.

For cryst. structure of monazite see Wyllie Nature 161 97 (1948). [from Division of Chem. - CSIR, Melbourne.

Th Silica and thoria and other constituents probably part of the structure (ionic sizes suitable) and not impurities.

Free Radicals

$NH_4Cl \cdot NiCl_2 \cdot 6H_2O$ Mellor, 15, 418.

Green oblique prisms:

Either orthorhombic $a : b : c = .9786 : 1 : .68672$

or monoclinic $a : b : c = 1.02293 : 1 : .70928, \beta = 89°50'$

Sp. Gr. 1.645

(Moehle) $\chi = 2.001 \times 10^{-6}$ per gm., which will correspond to 465.2×10^{-6} per gm. molec., which is only a tenth of the normal value for Ni^{++}.

Is $\chi = 20.01 \times 10^{-6}$ and misquoted as 2.001×10^{-6} in Mellor?

According to W. L. Bragg (Z. Kr. 74, 237 (1930)) in the
$(Mg,Fe)_2SiO_4$. olivine.

olivine group Mg_2SiO_4
(orthorhombic) Fe_2SiO_4 / Fayalite (iron olivine)
Mn_2SiO_4 Tephroite. Six o atoms round the metal
etc.

phenacite group Be_2SiO_4
Hexagonal. Zn_2SiO_4
Dioptase H_2CuSiO_4 / 4 Oxygen atoms around the metal.

Find whether any Co or Ni silicates are known belonging to either of these groups.

Should be Diamagnetic

In titanite $CaTiSiO_5$ (Monoclinic C_2^6)
Ti at the centre of 6 oxygens.

Mg lies between (1) 4 oxygens in spinel + in melilite group
(2) 6 " in olivine, chondrodite, pyroxene & amphibole groups.
(3) 8 oxygens slightly [nearly two groups of 4 at different distances] in garnets.

Rhodonite

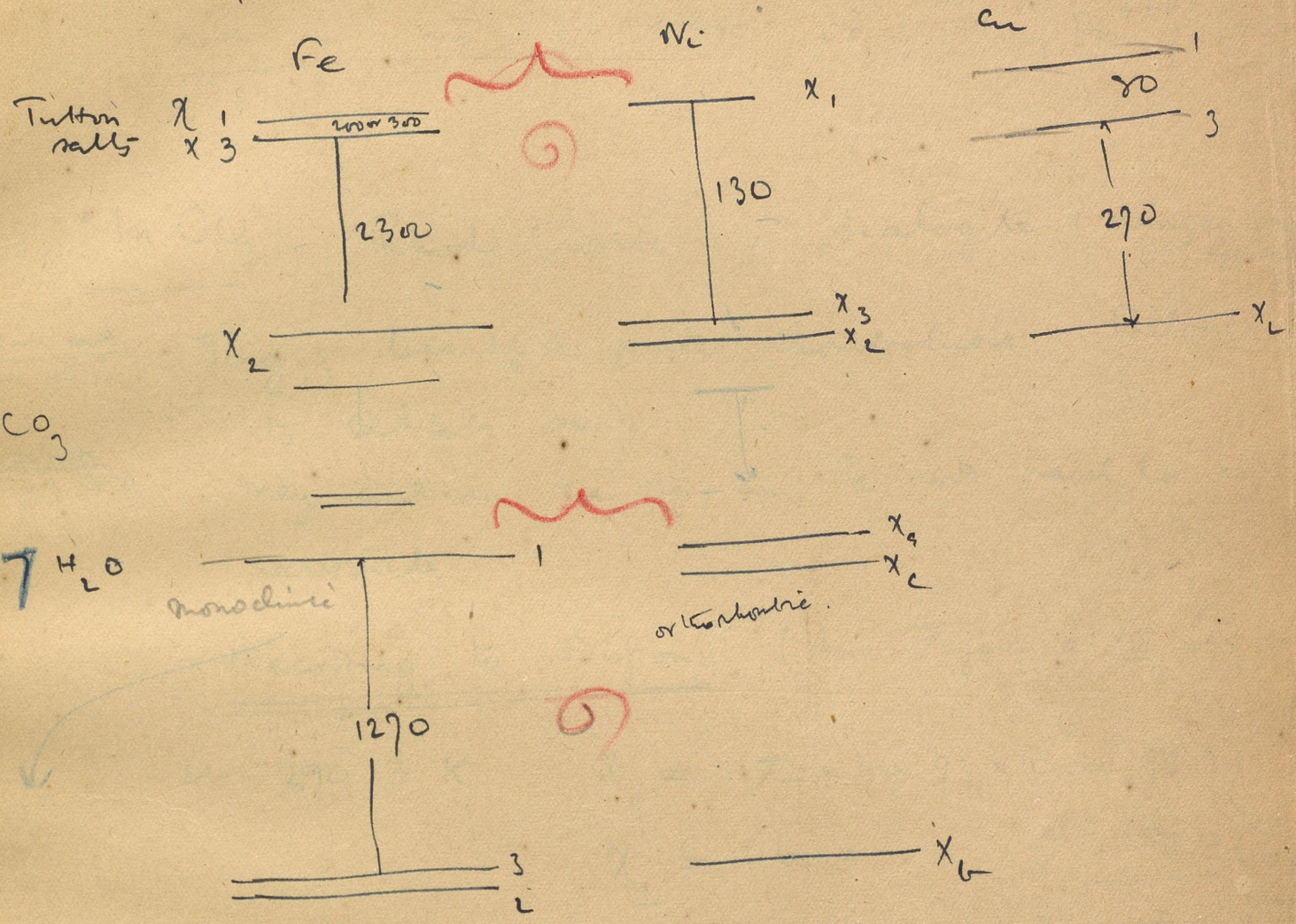
Triclinic $a : b : c = 1.07285 : 1 : 0.6213$

$\alpha = 103^\circ\ 18'$; $\beta = 108^\circ\ 44'$; $\gamma = 81^\circ\ 39'$.

commonly tabular $\parallel c\,(001)$

optically $-^{ve}$. $\beta = 1.73$.

Is it a general rule that Fe + Ni are inverted?
Try thin crystals of Fe + Ni



CO_3

= 7 H_2O

6 H_2O

5 H_2O

Some crystals whose paramagnetic ions are all in the S-state i.e. of Mn^{++}, Fe^{+++}, Gd^{+++}.

$MnCO_3$ Rhodochrosite or dialogite (mangan spar German)

Trig.; beautiful pink rhombohedra. Belongs to calcite series

may contain Ca, Mg, Zn, Fe and rarely Co as carbonates.

Ziconrhodochrosite may contain 45% $ZnCO_3$.

manganocalcite large % age of $CaCO_3$

According to Dupouy (Ann Physique 15, 495, 1931)

at 290°.3 K

$\chi_{\parallel} = 1.72 \times 114.93 \times 10^{-6} = 197.7$

$\chi_{\perp} = 1.61 \times$ " " $= 185.0$

$\chi = 189.2$ } $\times 10^{-6}$ per gm mol. of $MnCO_3$

[Corresponds to 3.8 Weiss magnetons]

per c.c. $\chi_{\parallel} = 1.72 \times 3.69 \times 10^{-6}$

$= 6.4 \times 10^{-6}$!!.

According to Sucksmith (Proc. R.S. A 133, 179, 1931)

at room temp. K (18°C? actual value not mentioned) ~~has~~ artificially prepared $MnCO_3$ (not the mineral) has a mean χ Anisotrop.

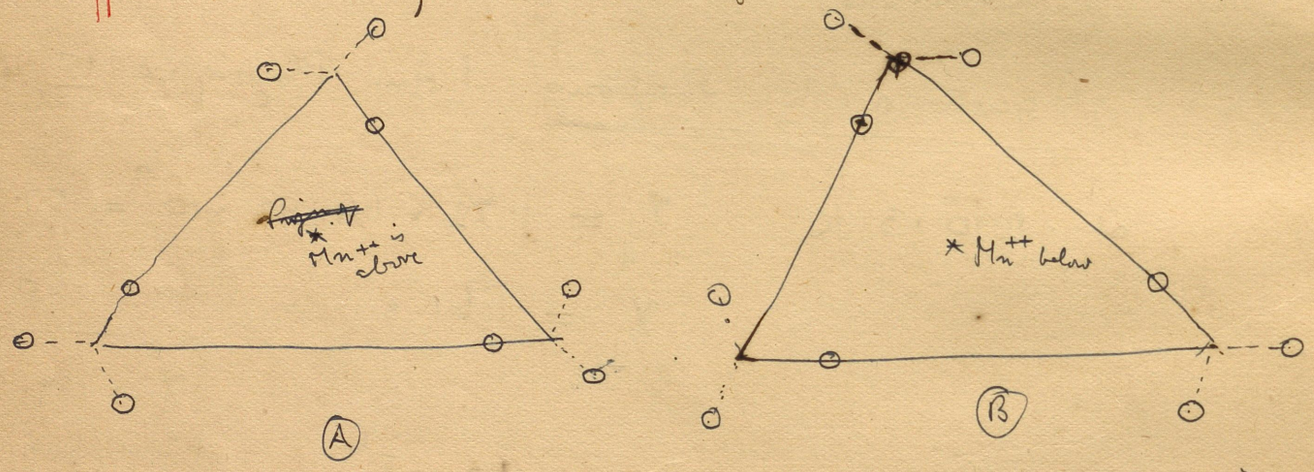
96×10^{-6} per gm. which corresponds to

$11,040 \times 10^{-6}$ per gm. mol. (Calcd. value for 5 magnetons =

which again corresponds to 25.7 Weiss magnetons as against 29.4 reqd by theory for $^6S_{5/2}$ state. It is however much nearer to the correct value than Dupouy's.

Measure the princip. susceps. of the new crystal of $MnCO_3$, and also ~~of~~ the mean for artificially prepared powder.

Study also its pleochroism ~~with~~ spectroscopically.



In the crystal of $MnCO_3$, each Mn^{++} ion is surrounded by six equally distant centres of CO_3 groups. If we imagine ~~Δ~~ the triangle (A) to be below & (B) to be above Mn^{++}. The dist. from Mn to centre of CO_3 group about = 2.9 Å. the distribution about Mn^{++} is trigonal ~~[illegible]~~, if the O's are omitted. Taking them into acc. There will be ~~[illegible]~~ another trigonal component, (but feeble) of cryst field superposed on it.

In siderite $FeCO_3$ the field acting on Fe^{++} will leave the same symmetry.

Prepare $(NH_4)_3 FeF_6$ 5 spins : known to obey curie law. If crystal not cubic (The cryst is cubic) study anisotropy : whether characteristic T^* of Simon small.

Ferric acetyl acetone $Fe(C_5H_7O_2)_3$ Z = 16.

orthorhom. a = 15.74, b = 13.68, c = 33.0 } Z = 16 Astbury P.R.S.A 112 448 (1926)

Structure & isotrimorphism of tervalent metallic acetyl acetones.

$$M^{+++}\left\{\begin{matrix} O-C(CH_3) \\ O=C(CH_3) \end{matrix}\right\}CH\Big\}_3$$

Cr^{+++}, Mn^{+++} & Co^{+++} acetyl acetones monoclinic

Z = 4

M =	a	b	c	β
Cr	14.2	7.62	16.5 A	99° 8'
Mn	14.1	7.68	16.5	99° 24'
Co	14.2	7.50	16.4	98° 38'
Al	14.1	7.42	16.5	98° 54'

For mixed crystals of chlorides of iron group (including ferric) crystallographic & other data see A. Neuhaus Zs. Kr. (A) 97, 28 & 98, 112 (1937)

Especially $FeCl_3 \cdot 2NH_4Cl \cdot H_2O$.

& $CoCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 2H_2O$ } are the cations four-coordinated?

also $CoCl_2 \cdot 2NH_4Cl \cdot 2H_2O$

Ni " " "

In $CrCl_3 \cdot 2H_2O$ is Cr^{3+} four coordinated? Then it ought to be strongly anisotropic magnetically.

Study some paramagnetic four coordinated nickel salt. It shd be strongly anisotropic, in contrast with the six coordinated nickel salts. [Many of the ordinary four coordinated nickel salts are diamagnetic.]

L.O. Brockway in his discussion on recent advances in the organic chemistry of the metals (Lectn B. of the British Assn. meeting at Cambridge: reported in Nature Oct. 15th 1938 p. 710) mentions "The 4-covalent metals in the copper & nickel groups have a planar configuration in the divalent state (eg. cupric & argentic picolinates, & the Ni, Rd & Pt. dioxime derivatives) & a ~~tetr~~ tetrahedral configuration in other valency states.

$(Co\ 2Py\ Cl_2)$ bispyridyl cobaltous chloride

Structure suggested by Barkworth & Sugden Nature Feb. 27, 1937

μ_B spin only value = 3.87 (s = 3/2)

Violet form stable at room temp. $\mu_B = 5.34$ $[Co\ 4Py]^+ + [CoCl_4]^=$

Blue form unstable at room temp. obtained from violet form by dissolving in $CHCl_3$ + ppting by dilution with ligroin. $\mu_B < 4.6$ $[Co\ 2Py\ Cl_2]$

3.87 spin-only value

The structures suggested by B & S correspond to 4 coordination of Co in both the compounds, the coordination being symmetrical in the former compound & unsymmetrical in the latter.

? One shd have thought that a symmetrical 4 coordination compound will give μ_B closer to spin only value than the asymmetrical one.

Can it be that in violet form Co is six-coordinated, and in blue form 4 coordinated?

Mn^{++++} and Cr^{+++} salts shd be isotropic like Ni^{++}.

Prepare some salt and verify; ~~while~~ Mn^{+++} may be anisotropic.

Soln. of $CoCl_2$ in pyridin

−45° to 0° C.	$CoCl_2 \cdot 6Py$	colour red at 0°
23° to 65°	" $\cdot 4Py$	violet at 25°
75° to 88°	$\cdot 2Py$	dark red at 50° & blue at higher temps.
91° to 110°	$CoCl_2$	

Crystal structure & absn. spectra of Cobaltous compounds R. Hill & O. Rhys Howell Phil Mag. 48, 833 (1924)

In Blue compounds, Co^{++} is 4-coordinated

in Red " " " 6- "

Gives several examples of blue & red compounds.

See also ~~paper by~~ Pearce & Dawson, J. Chem. Phys., 6 128 1938; Mellor and Coreyell, J. Am. Ch. Soc. 60, 1786 (1938) think that in cobaltous pyridine chloride Co' is ionic, and the distribution of negative charges about it should be octahedral in the α-form and tetrahedral in the β-form.

Coordination numbers of diff. metal atoms in the silicate: W.L. Bragg, Z. Krist. 74 237 (1930).

Some Crystals for magnetic study

1. Marcasite FeS_2
2. Löllingite $FeAs_2$
3. Arsenopyrite FeAsS
4. Gudmundite FeSbS
5. Goethite $Fe_2O_3 \cdot H_2O$
6. Diaspore $Al_2O_3 \cdot H_2O$.

For their structures see Barger Z. Kr. 95, 83.

Co in $Co(SCN)_4$ may be 4- coordinated.

Stereochemistry of complexes: D. P. Mellor Chem. Rev. Oct-1943 33 137.

Polarisation of Resonance Radiation

Steinhauser: Zs P. 45 669 (1935)

Pringsheim + Saltmarsh: (Hg 2537) P.R.S. A 154, 90 (1936)

$[Co(CN)_6]^{3-}$ ion is diamagnetic. many rare earth salts containing this ion have been measured for their mage. susceps. at 3 temp (1) room temp. (2) about 80° K. and (3) some intermediate temp. [see Karantassis & others C.R. 208 1720 (1939).]

p. 169. $CuCl_2 \cdot 2H_2O$ ✓ ‡

171 $Ca_2Fe(CN)_6 \cdot 12H_2O$ triclinic; first test — whether it is dia-, or para-, magneti

whether dia

174 ~~$K_2CuCl_4 \cdot 2H_2O$~~

~~$(NH_4)_2CuCl_4 \cdot 2H_2O$~~

Done by Ashu

$(NH_4)_4Fe(CN)_6 \cdot 2NH_4Cl \cdot 3H_2O$: is it diamagnet

177 $(NH_4)_2MnF_5$ ✗

" $K_3Cr(CN)_6$

" $K_3Mn(CN)_6$

178 $K_3Rh(CN)_6$

$CuTiF_6, 4H_2O$.

$Cu(MoOF_5), 4H_2O$.

$Cu[WO_2F_4], 4H_2O$

180-1

$FeSiF_6 \cdot 6H_2O$	
$NiSiF_6$	"
$CoSiF_6$	"
$CuSiF_6$	"
$MnSiF_6$	"
$MgSiF_6$	"

p. 205 $Co(ClO_4)_2 \cdot 6H_2O$

" $Ni(ClO_4)_2 \cdot 6H_2O$

p. 211 $CoN_2O_6 \cdot 6H_2O$.

"

p.

$(Fe)F_2 \cdot (Be)F_4$

Fe/BeF_4

BeF_2

K_2F_2

K_2BeF_4

Sc. 3295 Z

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TÉL. : ODÉON 01-38

Paris, le *193*

From Professor Trombe

end of May 1939

his fractionation number.

Gd_2O_3 (14).

impuretés Y_2O_3 . # 1,3 a 1,5 %.

$Eu_2O_3 < 10^{-3}$ gr. par gr.

Sa_2O_3 - 0.

Tb. - 0

yttrium (diamagnetic)

and not the rare earth ytb (ytterbium)

Sc. 3295 Z

The specimen of Gd_2O_3 presented by Professor Trombe (Institut de chemie, 11 rue Pierre Curie, Paris 5e), according to the data supplied by him, contains

Fractionation no. 14 Trombe

Impurities	Y_2O_3	1·3 to 1·5 %
	Eu_2O_3	$< 10^{-3}$ gm. per gm.
	Sa_2O_3	0
	Tb	0

yttrium
Y^{+++} diamagnetic

The ~~oxalates~~ of Ce, Pr, Nd, Sm and La presented by Prof Trombe (1 gm. of each) are all of purity > 99·9 %.

magnetic properties of Sb

Trig. $\chi_{\parallel}$ suscep. along axis } per gram
$\chi_{\perp}$ " "

Temp. °K	$\chi_{\parallel} \times 10^6$	$\chi_{\perp} \times 10^6$	authority
290° K	−1.13	−0.63	(1) M & C.
"	——	−0.66	(2) H & A
"	−1.42	−0.55	(3) S & U $\frac{1}{3}(\chi_{\parallel}+2\chi_{\perp}) = -.84$
(?)	−1.38	−0.497	Nusbaum Phys Rev. 29, 905 1927
90° K	−1.13	−0.63	(1) "
"	——	−0.65	(2)
"	−1.72	−0.55	(3)
4° K.	−1.78	−0.55	(3)

(1) McLennan & Cohen, Trans. Roy. Soc. Canada, 23 159 (1929)
(2.) de Haas & van Alphen, Leiden Comm. No. 225 b (1933) &
(3) Shoenberg & Zaki Uddin, Proc. Camb. Phil Soc. 32, 499 (1936)

Owen Honda. room temp. mean χ = −.82

& at m.p. 630° χ_{solid} = −.55
χ_{liquid} = −.49 (.049 ?)

Mott & Jones in their book p. 211 give value as 0.04 !

Hart : Phys. Rev. 52 130 July 15 1937.

$\chi_{\parallel}/\chi_{\perp}$ at room temp = 2·52 as against 2·56 (or 2·58?)

of Shoenberg & Z. Uddin

The two principal susceps tend to reach ~~the~~ at absol. zero, the values

$$\chi_{\parallel} = -1.76 \times 10^{-6} \text{ per gm}$$

$$\chi_{\perp} = -0.55 \times 10^{-6} \quad ''$$

These values would correspond to

$$-214 \times 10^{-6}$$

$$\& \quad -67 \times 10^{-6} \quad \text{respy per gm atom}$$

(121·77 gms)

$$\chi_e = -147 \times 10^{-6}$$

Magnetic properties of Bi

Honda - Owen (quoted by Stoner)

at m.p., 271°C, $\chi_{solid} = -213$, $\chi_{liq} = -16.7$ } $\times 10^{-6}$ per gm atom (209 gms)

Curie's values (also taken from Stoner) are of the same order

	Temp.	$-\chi \times 10^6$
solid	20°C	257
solid	273°	181
Liquid	273°–405°	7·3

For single crystals, according to Goetz and Focke (Phys. Rev. 45, 170, 1936) (Table III)

T in °C	$-\chi_{\parallel} \times 10^6$	$-\chi_{\perp} \times 10^6$	$-\chi \times 10^6$
−185°	256	406	323
−84°	231	354	313
22°	222	310	281
126°	193	258	236
268°	159	193	181

Kapitza's relative values (see P.R.S. 131, 234, 1931) using Sy. + F's $\chi_\perp$ at room temp. $= -310 \times 10^{-6}$, give

T	$-\chi_{\parallel} \times 10^6$	$-\chi_\perp \times 10^6$
17° C	225	(310)
−188° C	270	424.

At room temp. ~~Sy + F's~~

$\chi_\parallel / \chi_\perp$ = 0.71 Sy + F

= 0.72 K.

= 0.67 Hankel (quoted in Graetz's Handbuch IV 836)

0.71 Tyndall (Magnecrys. action)

$\chi_\parallel = -1.13$
$\chi_\perp = -1.32$
} pr gm. Nusbaum Phys. Rev 29, 905 (1927)

$\chi_{\perp}$ and $\chi_{\parallel}$ have been measured by Shoenberg and Uddin (Proc. Roy. Soc. A. 156, 687-720, 1936) over an extensive range of temps. from 4° K to about 400° K. with Hilger's Bi No. 10,283 - spectroscopic purity 99.998%).

and also for several alloys of Bi with traces of other metals. For details refer to original paper.

The two principal suscep. tend to reach at absolute zero the values

$$\chi_{\parallel} = -1.2 \times 10^{-6} \times 209.0 = -251 \times 10^{-6}$$

$$\chi_{\perp} = -1.76 \times 10^{-6} \times 209.0 = -368 \times 10^{-6}$$

As by Haidinger

Herapathite (Named after Herapath, who discovered this remarkable quinine compound, in 1851.)

$4\,Qu \cdot 3\,H_2SO_4 \cdot 2\,HI \cdot I_4 \cdot 6\,H_2O$.

~~Remarkable for its dichroism~~. — Crystallizes in small hexagonal plates: Remarkable for its peculiar dichroism one vibration completely absorbed and the other almost completely transmitted.

Refs.

Phil. Mag. 3 161 (1852)
6 346 (1853)
7 352 (1854)
9 366 (1855)

For Land polarizer see Nature Aug. 22nd 1936, p. 311.

Brit. Pat. nos. 412,179 Dec. 16 1932
433,455 Jan 15, 1934
442,825 June 17, 1935

~~See~~ For photoanisotropy see Freundlich, Photographic Journal, 76 395 (1936)

N.	State	Examples.
19	$^2D_{3/2}$ $l=2$ $s=\frac{1}{2}$	V^4 Ti^3
20	$^3F_2$ $l=3$ $s=1$	V^3
21	$^4F_{3/2}$ $l=3$ $s=\frac{3}{2}$	V^2, Cr^3, Mn^4
22	$^5D_0$ $l=2$ $s=2$	Cr^2, Mn^3
23	$^6S_{5/2}$ $l=0$ $s=5/2$	Mn^2, Fe^3
24	$^5D_4$ $l=2$ $s=2$	Fe^2, Co^3
25	$^4F_{9/2}$ $l=3$ $s=\frac{3}{2}$	Co^2
26	$^3F_4$ $l=3$ $s=1$	Ni^{2+}
27	$^2D_{5/2}$ $l=2$ $s=\frac{1}{2}$	Cu^2

centre

four-coordinated Co^{++} & Cr^{3+} salts
Optical behavior

λ (constant of spin orbit coupling)

Cr^{+++}	$+87\ cm^{-1}$
Co^{++}	-180
Ni^{++}	-335

According to Pauling Zs Kr. 72, 482 (1930)

$NiSnCl_6 \cdot 6H_2O$ (large deliquescent rhombohedra) has the structure

$$[Ni(H_2O)_6]^{++} \quad [SnCl_6]^{--}$$

A large no. of isomorphous crystals listed on p. 490 of this paper.

$M\,SiF_6 \cdot 6H_2O$. M = Mg, Zn, Mn, Fe, Co, Ni, Cu,

$M\,ZrF_6 \cdot 6H_2O$ M = Ni, Zn.

$M\,SnCl_6 \cdot 6H_2O$ M = Mg, Mn, Co, Ni

$M\,PtCl_6 \cdot 6H_2O$ M = Mg, Mn, Fe, Ni, Co, Cu, Zn, Cd

$NiPtBr_6 \cdot 6H_2O$

$NiPtI_6\,6H_2O$

$M\,TiF_6 \cdot 6H_2O$. M = Mg, Mn, Zn.

$M\,SnF_6\,6H_2O$ M = Mg, Mn, Co, Zn, Cd.

See also Hoard & Vincent, J. Am. Ch. Soc. 61, 2849 (1939).

It is probable that the following complex cyanides investigated by Steinmetz Zs. Kr. 57, 233, 1922 belong to the same series.

$A(NH_3)_6 \cdot B(CN)_6$

A	Co	Co	Co	Cr	Cr	Cr	Cr
B	Co	Fe	Cr	Co	Mn	Fe	Cr

Theory in particular

A:	Co	Co	Cr	Cr
B:	Co	Cr	Co	Cr.

$CrSO_4 \cdot 7H_2O$ Isomorphous with $FeSO_4 \cdot 7H_2O$

Also $CrSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

" K_2 " "

Rb_2

" Cs_2 " " Known.

See Mellor XI p. 435.

Chromous acetate most stable of the Cr^{++} salts.

PCl_5 : Tetrag. crystal $a = 9.22$ $c = 7.44$ A.
4 molecals of PCl_5 in unit-cell.

$PCl_4^+ + PCl_6^-$ in the form of distorted form of CsCl structure

P.Cl dist = 2.06 A in PCl_6 + 1.98 A in PCl_4.

$Mg\,SO_3 \cdot 6H_2O$
$Co\,SO_3 \cdot 6H_2O$
$Ni\,SO_3 \cdot 6H_2O$

Trigonal ; for preparation & cryst. data see Klassen + Mis Zs. Kr. 94, 1-6, 1936.

No corresponding Ferrous compound seems to be known.

Hexahydrated perchlorates $R''(ClO_4)_2 \cdot 6H_2O$ and fluoborats $R''(BF_4)_2 \cdot 6H_2O$ of Mg, Mn, Fe, Co, Ni + Zn (an isomorphous series of 12 hydrats) have been studied by Weil- (Zs. Kr. 91 480, 1935). Hexagonal crystals, many of them deliquescent.

$CrCl_3 \cdot 6H_2O$
$AlCl_3 \cdot 6H_2O$

Hexag. Zs. Kr. 87, 446, 1934

$K_4\ Fe(CN)_6$

Mn

Cr

Zs. Kr. 73, 360 (1930).

$Ni\ (CH_3 \cdot COO)_2 \cdot 4\,H_2O$ (Ni acetate) Zs. Kr 96 319 (1937)

Find whether corresp. Ferrous compound is known & is isomorphous with it.

According to Van Vleck the arrangement of levels as split by the crystalline field will be inverted for the following pairs of ions:-

Co^{++} Ni^{++}

Fe^{++} Cu^{++}

Co^{++} Cr^{+++}

Ni^{++} V^{+++}

Mn^{++} Fe^{+}

V^{+++} and should show a large anisotropy + should deviate from Curie law from spin-only value. for moment.

$\lambda S(2L+1) = \Delta\nu.$

Configuration d^z	Term	atom or ion	$\Delta\nu$ separation overall ~~splitting~~ cm^{-1}	Constant of spin orbit coupling λ in cm^{-1}
d^1	$^2D_{3/2}$ $L=2, S=\frac{1}{2}$ $\lambda = \Delta\nu \cdot \frac{2}{5}$	K	2.7	1.1
		Ca^+	60.8	24.4
		Sc^{++} X	197	79
		Ti^{+++}	384.5	154
d^2	$^3F_2$ $L=3$ $S=1$ $\lambda = \Delta\nu \times \frac{1}{7}$	Sc^+ X	184.9	26.4
		Ti^{++} X	421.9	60.3
		V^{+++}		
d^3	$^4F_{3/2}$ $L=3$ $S=\frac{3}{2}$ $\lambda = \Delta\nu \cdot 2/21$	Ti^+	307.6	29.3
		V^{++}	580	55
		Cr^{+++}	912	87
		Mn^{++++}	1270	121
d^4	$^5D_0$ $L=2$ $S=2$ $\lambda = \Delta\nu \cdot 1/10$	V^+	339.3	33.9
		Cr^{++}	566	57
		Mn^{+++}	852	85
Mn^{++} Fe^{+++} d^5	$^6S_{5/2}$			
d^6	$^5D_4$	Mn^+	635.3	64
		Fe^{++}	998	100
		Co^{+++}		
d^7	$^4F_{9/2}$ $L=3$ $S=\frac{3}{2}$ $\lambda = \Delta\nu \times 2/21$	Fe^+	1244.9	119
		Co^{++}	1890	180
d^8	$^3F_4$ $L=3$ $S=1$ ~~λ~~ $\lambda = \Delta\nu/7$	Co^+	1650	236
		Ni^{++}	2347	335
d^9	$^2D_{5/2}$ $L=2$ $S=\frac{1}{2}$ $\lambda = \Delta\nu \times 2/5$	Ni^+	1530	612
		Cu^{++}	2130	852

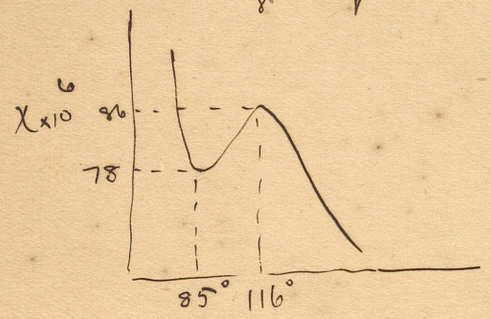
Mn^{+++}

The mean suscep. of manganic acetylacetone $Mn(\cdot CH_3 \cdot CO \cdot CH \cdot COCH_3)_3$, has been studied in the powder state by L.C. Jackson (Proc. Phys. Soc. 47 1029-32) over the range 16°.9 K to 292°.2 K.

$\chi(T+5.5)$ is roughly constant down to about 70°K the constant corresponding to a magnetic moment of 4.98 Bohr magnetons, as compared with the spin-only value of 4.90 ($=\sqrt{24}$) for the $^5D_0$ state. At lower temps. the ~~co~~ suscep. increases more rapidly with fall of temp. than is suggested by the formula. $\chi(T+5.5) = C$.

Growing large optically clear sodium nitrate crystals = See Journ. Frank. Inst. May 1938 p. 586.

The magnetic susc. of MnO has been studied over a wide range of temps by Tyler [Phys. Rev. 44 776 (1933)]



Discontinuity in sp. heat at 117° [Millar J.A.C.S. 50 1875 (1928)], but more at 85°

From 116° K to room temps. χ obeys the Curie-Weiss law $\chi = \frac{.0575}{T+548^\circ}$ per gm. The curie const. of .0575 corresponds to 5.7 Bohr magnetons as compared with 5.92 for the ^6S state of Mn^{++}.

More or less similar results obtained by Bizette & Wins [C.R. 207, 449 (1938)] (in the form $\chi = C/T-\theta$) C corresponds to 4.40 Bohr magnetons and $\theta = -610^\circ$. Maximum χ at 117°; but the min at 85° not observed. Down to the lowest temp. studied, namely 12°K, there is a continual diminution of χ (from 84 $\times 10^{-6}$ at 117°K to 59 $\times 10^{-6}$ at 12°.

Crystal structure of Manganite MnO(OH).

Buerger Z. Kr. A 95, 163 (1936)

monocl. $a = 8.86$
$b = 5.24$ $Z = 8$.
$c = 5.70$
$\beta = 90°$

"Mn is in square coordination ~~with~~ between 2(OH) and 2(O) in the same (010) sheet, with one more (OH) and one more O above and below the centre of the sq., and in adjacent sheets in such a way as to approach octahedral coordination ~~between~~ for the Mn"

See also Strukturbericht. 4 pp 28 + 141 (193

The structure corresponds to that of arsenopyrite

See Zs. Kr. 95 (1936) 83–113. also American Mineralogist. 21 (1936) 203.

In FeAsS and probably also in FeS_2, the Fe, according to Buerger, is trivalent!

In FeAsS Fe is taken by Buerger (see Zs Kr. 95 bez. it) to be trivalent. See his explanation.

2 4 2 2

Naphthalene
Anthracene
Phenanthrene

Diphenyl —
Terphenyl —
Quaterphenyl —

Chrysene
Fluorene
Pyrene
Triphenylene

Hexamethyl benzene
Hexaethyl benzene
Durene
Benzoquinone
quinhydrone
p-Hydroquinol
m. Resorcinol
Catechol.

1,2:5 6 dibenzanthracene
Phloroglucinol.
1,2,3 5 triphenylbenzene

Cyanuric Compds

Polyenes =

Naphthacene

CONFIDENTIAL.

INDIAN SCIENCE CONGRESS ASSOCIATION.

92, Upper Circular Road,
CALCUTTA. AUG 1 2 1940

A meeting of the Finance Committee of the Indian Science Congress Association was held at 4 P.M. on Friday, August 2nd, 1940 at the University College of Science and Technology, 92, Upper Circular Road, Calcutta.

Present - Prof. J. N. Mukherjee, Treasurer, in the chair,
Prof. S. P. Agharkar,
Prof. S. K. Mitra, General Secretary.

1. Considered the question of payment of the outstanding Bills Nos.2865, 2866, 2952 to 2956 and 3089 from the Baptist Mission Press amounting to Rs.607-15-0.

Resolved that the amount of Rs.607-15-0 be paid to the Baptist Mission Press in full payment of their Bills Nos.2865, 2866, 2952 to 2956 and 3089.

2. Considered the question of transferring Rs.150/- (one Life Membership subscription received this year) to the Reserve Fund of the Association.

Resolved that the amount of Rs.150/- be transferred to the Reserve Fund of the Association.

The Committee further resolved recommending to the Executive Committee of the Indian Science Congress Association that in future all payments on account of Life Membership subscriptions be credited to the Reserve Fund of the Association and a provision be made accordingly in the Regulations under Section 'III. Financial'.

S. K. MITRA

General Secretary,
Indian Science Congress Association.

RD.

$(MnO_4)^-$

$KMnO_4$ at 21°C has a susceptibility of

$0.175 \times 158.03 \times 10^{-6} = 27.7 \times 10^{-6}$ per gm. molecule

whereas $Ba(MnO_4)_2$ at 20° has the susc.

$10.1 \times 375.2 \times 10^{-6} = 2 \times 190 \times 10^{-6}$ per gm. molec.

See I.C.T. VI p. 360.

i.e. per MnO_4 ion, the latter salt has nearly 7 times the susc. of the former!

$Mn(CN)_6^{4-}$ ion, according to Freed and Kaspe J. A. C. S. 52 1012 (1930) has a susceptibility of 1650×10^{-6} per gm ion, as compared with 1700×10^{-6} for the $Fe(CN)_6^{3-}$ ion.

Ferrous chelate $K_4 Mn(CN)_6$ has a large anisotropy like $K_3 Fe(CN)_6$.

Zircon

$(ZrO_2 \cdot SiO_2)$
$ZrSiO_4$ according to Voigt and Kinoshita, has the susceptibilities

$$R_{\parallel} = +0.732 \times 10^{-6} \text{ per gm. along the tetrag. ax}$$
$$R_{\perp} = -0.170 \times 10^{-6} \quad \text{"} \quad \perp^{r} \text{ to the ax.}$$

Try with a good specimen. whether the para & diamagnetism for the two directions are verified.

Crystal Structure of $Fe(CO)_6$

Rudorff + Hoffmann, Zs. P. Ch. B 28 351 (1935)

$Fe_2(CO)_9$

Brill, Zs Kr. 65 89 (1927).

Powell + Evans J.C.S. 1939 p. 286.

Paramagnetism(?) of Ce^{4+} ion

According to Foex (C. R. 208, 738, 1939) the

gm. mol. suscep. of $Ce(SO_4)_2 \cdot 4H_2O$ is -97×10^{-6}

Taking the contribution for $2 \times SO_4$ = -67

" " $4 H_2O$ = -52

-119×10^{-6}

he concludes that χ_a for Ce^{4+} = $+22 \times 10^{-6}$

143 36·0

Contd from pp. 98-95. Sugden J.C.S. Jan 1943, 328.

χ per gm. water $-.72 \times 10^{-6}$
$CuSO_4 5H_2O + 6 \times 10^{-6}$ — more than 50×10^6 times χ_{H_2O}!

Best Swedish iron 40

(Barkworth Ph.D. thesis Lond. 1938)

$\mu_{eff} = 5.33\beta$ $Co\,Py_4\,Cl_2$ (violet) $\xrightarrow{120°}$ $Co\,Py_2\,Cl_2$ (blue) 4.62β.

By dissolving in $CHCl_3$ + adding ligroin blue form precipitated.

$Co\,2NH_3\,Cl_2$ } red + blue forms. Both forms μ_{eff} same 5.5β
" Br_2 }

$Co\,2NH_3\,I_2$ both same but 4.6β.

Barkworth suggests

Violet variety = $[Co\,Py_4]^{++}$ red $[Co\,Cl_4]^{--}$ blue $\rightleftarrows$ $2\,[Co\,Py_2\,Cl_2]$ blue.

$K_4\,Fe(CN)_6$ } both diamagn.
" Ni "

Tetrahedral sp^3 or ~~sp d~~ ?
Planar (4) $d\,sp^2$
Octahedron $sp^3 d^2$

$K_3\,Cr(CN)_6$ $s = 3/2$.

Exception to Pauli's rules regarding hybridization

Cupric compounds of β diketones : X-rays show are planar $s = 1/2$ tho no d vacant

Be compound of phthalocyanine also planar; no d.

	Al	Fe	Co
Tris acetylacetonates μ_{eff}	0	5.9	0

(1) why ferric $\neq$ $s = 1/2$?
or (2) why is Fe compound ionic + Co covalent?

(2) Can not be correct Fe not ionic ∵ (i) can be volatalized
(ii) sol in ~~not~~ nonpolar solvents ~~(iii)~~

Trisdipyridyl derivates

144

Again $[M(diPy)_3]Br_2\ 6H_2O$ $M = Fe^{++}$ or Ni^{++}

optical isomeric? Both forms resolved $M = Fe^{++}$ $\mu = 0$

Ni^{++} $s = 1$. $\mu_{eff} = 3$.

Is Fe compound covalent & Ni ionic?: Ni compound does not ionize in soln!

According to Van Vleck 2 opposing tendencies 1) energy least when S max. 2) Electron pairing.

Cambi (1935)

$Ni(Su)_2 \cdot 2H_2O$ Su = succinimide $\underbrace{\mu_{eff} = 3 \quad s = 1}_{\text{same}}$

+ 2 py.

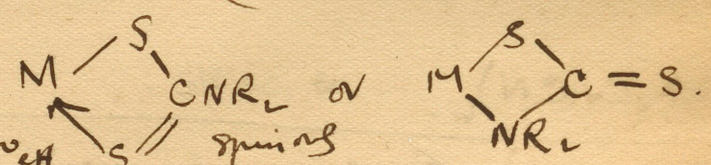
If ~~instead of~~ Py replaced by methylamine, ethyl " piperazine } $\mu \to 0$.

$K_2[Ni(Su)_4]\ 4H_2O$ ~~[illegible]~~. $\mu = 1$.

why ferrous exception!

Cambi & Cagnassi

	$Mn(Phen)_2Cl_2$	$Fe(Phen)_2Br_2$	Co	Ni
		$Fe(Phen)_3Br_2$		
μ_{eff}.	5.7	1.1	5.1	3.0
if ionic	(5.9)	5.2	(5.0)	(3.3)



Parent ion	Compound	μ_{eff}	spin only			
M: Mn^{III}	$M(S_2CNR_2)_3$	4.8–5.0	4.9			
Fe^{III}	$(S_2CNHR)_3$	5.3–6.0	5.9	$Fe(S_2CNR_2)_3$	2.5	5.9
Co^{III}	"	0.3–4.9	4.9		0.4	4.9
Ni^{II}	$(\ )_2$	0.3	2.8	$(\ )_2$	0.2	2.8

Pyrrhotite Composition Fe_7S_8 (varies actually from Fe_5S_6 to $Fe_{16}S_{17}$)

Apparently hexagonal. Wyckoff gives it as hexagonal. According to Miers (Mineralogy p. 371) "the etch figures, prism cleavages, curve of thermal conductivity and magnetic properties point to its hexag. symmetry, though there is no evidence of polarity of vert. ax. On the other hand thermoelectric properties suggest it is pseudo-hexagonal."

For magnetic data see I.C.T VI p. 413

also Weiss, J. de Physique 4, 469, 829 (1905)

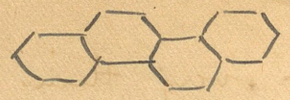
W + Plener, " 7, 5 (1908)

W & Foex Arch Genev. 31, 39 (1911).

see also (Haraldsen + Neuber) / Naturwiss. 24 280 (1936)

Magnetite

Discontinuity in its magnetic properties at about -160° C [corresponding to a discontinuity in sp. heat observed previously by Millar J.A.C.S. 51 215 (1929)] has been noted by Li [Phys. Rev. 40, 1002 (1932)].

Chrysene 

According to Sundararajan's measurements the principal refractive index data for the crystal.

λ in Å	μ for vibrations along 'a' axis	'b' axis	Diffce.
5461	1.615	1.787	.172
4358	1.648	1.849	.201

measurements were made with a crystal flake — ⊥ to c(001) plane — ~~and about~~

With very thin films of KNO_3 or $NaNO_3$ crystals verify whether beyond 200 mμ the birefringence changes sign and becomes +ve.

In Wood's optics there is mention of a special microtome designed by Czerney for cutting thin films of crystals.

Find whether it is possible to prepare thin films by evaporation or between two quartz plates. or to prepare colloidal solutions of the nitrates in suitable media transparent in the region, and orient them with a magnetic field.

Tomlinson writing in Mechanics Magazine for Sep. 8 1838 (quoted in Nature Sep. 3, 1938, p. 446) writes:

"When a drop of balsam of Peru is allowed to fall upon the surface of water we instantly get a magnificent display of colored rings. ...

A magnet seems to have an action upon the film, the N pole tending to repel it, and the South pole to attract it."

Some Copper salts suitable for magnetic measurements.

$K_2CuCl_4 \cdot 2H_2O$ (D. P. Mellor Zs Kr. 101, 160) "is essentially an assemblage of sq. coordinated $CuCl_2 \cdot 2H_2O$ molecules, potass. ions and chloride ions".

brilliant yellow prism. } Cs_2CuCl_4 for preparation see Wells, Am. J. Sc. 47 94 (1894); Godeffroy Ber. 8, 9 (1875)

orthorhombic bipyramidal

$a : b : c = \cdot 7835 : 1 : \cdot 6141$
$9.69 : 12.33 : 7.58$ A

(Mellor + Quodling, Zs. Kr. 95 315 (1936))
(X ray exam: Mellor " 101, 160, 1939)

~~Cs~~ When Cs is replaced by tetramethyl ammonium the resulting crystal has similar axial ratios Topsoe Zs. Kr. 8 (1884) 246,

$\cdot 7973 : 1 = 0.5963$
$12.11 : 15.5 : 9.05$

The corresponding Co ~~Cs~~ tetraethyl ammonium salt has similar axial dimensions, but it is not certain whether it is isomorphous with the Cu tetraethyl ammonium salt,

$KCuBr_3$: Sol- of mix of aqueous solutions of $KBr + CuBr_2$, with excess of latter.

Black metallic. in colour.

Hygroscopic.

Monoclinic $a = 4.28$

$b = 14.43$

$\rho = 3.92$ $c = 9.68$ 9.71.

$Z = 4$. $\beta = 108°23' \pm 10'$

Sp. Gr. $C_{2h}^2 - P2_1/m$

see A. Silberstein C. R. 209, 540 (no. 14) 1939.

In the rotational method of determining the magnetic anisotropy of a crystal, let α_c be the observed critical angle of rotation of the torsional head, i.e. the angle by which it has to be rotated from the position for which the torsion on the crystal when it has taken up its equilibrium direction in the magnetic field is zero, in order to bring the crystal just to its unstable position.

Then evidently, denoting by λ the quantity

$$\frac{1}{2}\,\frac{mH^2}{Mc}\cdot\Delta\chi$$

where m is the mass of the crystal, M its mol. wt., $\Delta\chi$ is the anisotropy in the horizontal plane per gram molec. M., c is the torsional const. of the fibre and H is the magn. field, we have

$$\lambda = \frac{\alpha_c - \pi/4 - \tau}{\cos 2\tau}$$

whence $\sin 2\tau = 1/(2\lambda)$

When α_c is large evidently $\lambda = \alpha_c - \pi/4$. If $\alpha_c - \pi/4$ is the observed critical angle, λ should obviously be smaller than $\alpha_c - \pi/4$ by only a small angle, which we shall call the correction.

The following table gives the corrections for various values of $\alpha_c - \pi/4$.

log $\frac{180}{\pi}$ = 1·7582

$\alpha_c - \pi/4$ both in degrees.	Correction
106	4·0
116	3·6
144·5	2·9
157	2·7

$\alpha_c - \pi/4$ both in degrees	Correction
200·5	2·0
220	1·8
238	1·8
240	1·7
246	1·7
2	
266	1·6
272	1·5
275	1·9
282·5	1·6
289	1·4
298	1·4
305	1·4
313	1·2
391·5	1·1

Paramagnetic Crystals already studied
for their anisotropy at room temperature

I Iron group

Structure of salts & electrolytes

See Stewart, J. ch. Phys. 10, 869 (1939).

Bernal & Fowler, ibid 1, 515 (1933).

On the colors of dyes

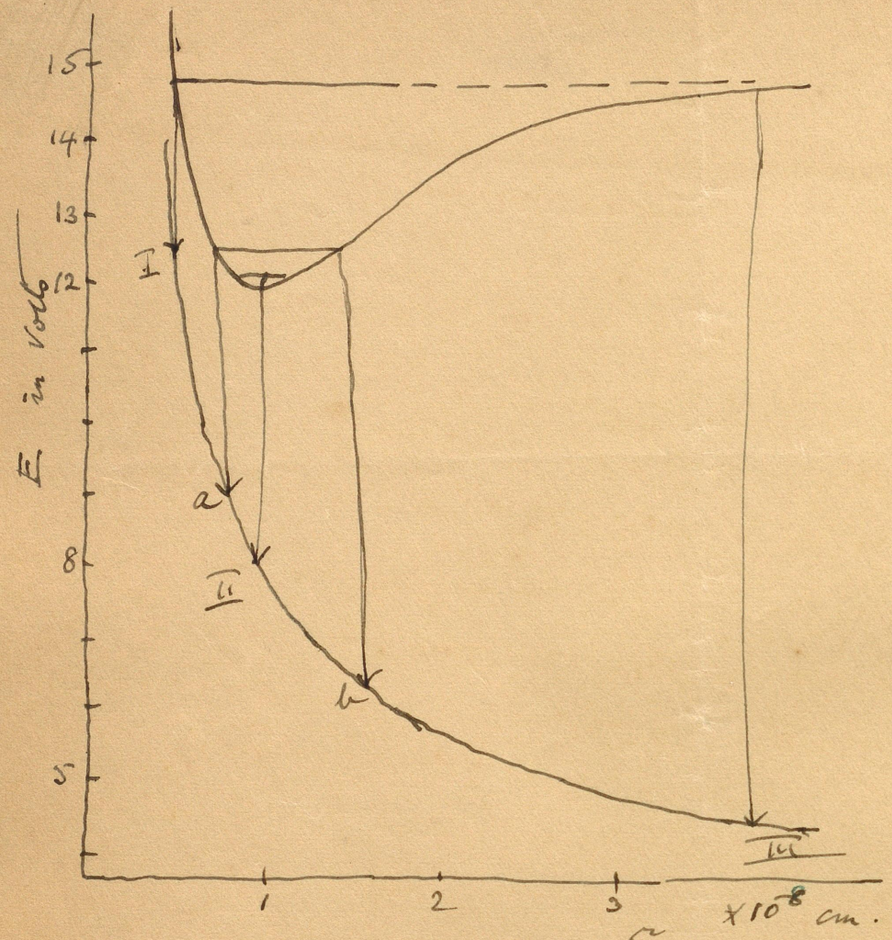
Linus Pauling, Proc. Nat. Acad. Washington, 25 577, 1939.

Some estimates of intensities of short-electromagnetic waves

from a magnetron tube

λ in cms	8	2·8	1·5	·75	·49
I in watt	$7{\cdot}5\times10^{-1}$	$2{\cdot}5\times10^{-2}$	$1{\cdot}4\times10^{-5}$	3×10^{-6}	3×10^{-7}

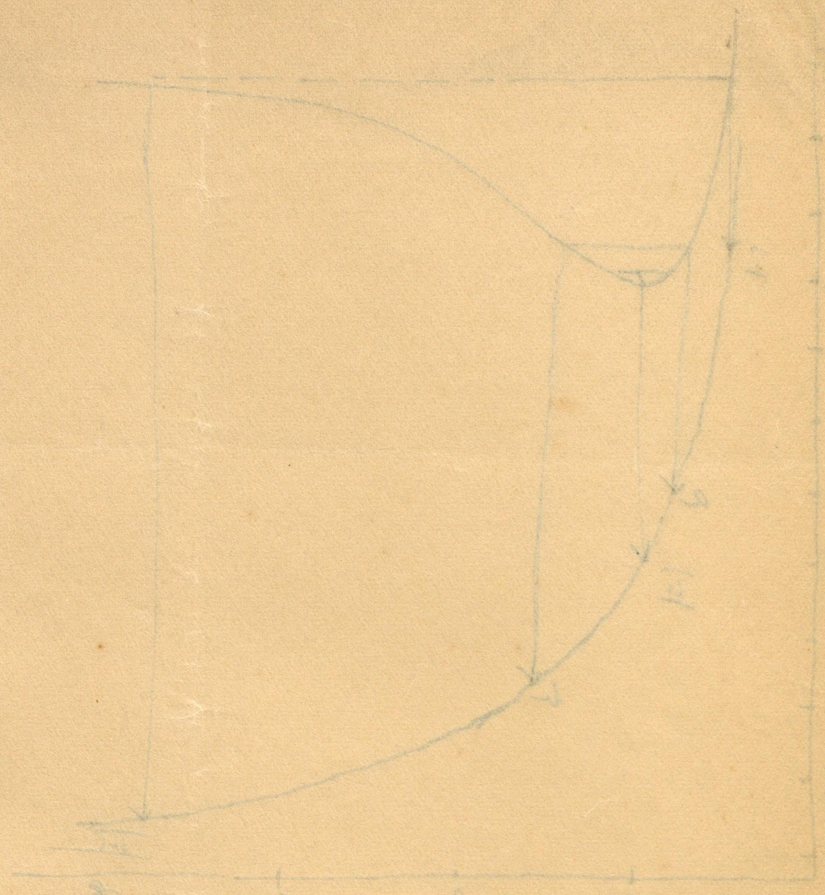
quoted in Zs. Phys. 115, 323 (1940).



Benares
27/3/48

Dear Professor Krishnan,

I am very sorry I was not definite about the details of the famous hydrogen Continuum when I spoke last week. I have looked into the Curves & have given them above. The repulsive curve is indeed very steep at the equilibrium inter nuclear distance of the stable upper Curve so that the left turning point of the vib. levels build up an extended Continuum (e.g. a) on the long wave side of the maximum (II) which arises from transition between Zero to level & the vertically opposite point on the repulsive Curve; the right turning points contribute to the continuum towards shorter waves (e.g. b). Long wave limit is fixed by I & the short wave limit by III. I think I am now clear. I was so unclear that day.



there. If it is possible to get an opportunity of working in the N. P. L. he would like to know what he may expect for his salary, status etc. I shall be grateful if you kindly let me know what you would like him to do.

With kindest regards

Yours very sincerely

A Sundi

Absorption bands of organic Compounds

Ultra violet- absn. bands from reflection by the powdered substance studied by

1) anthracene

2) dianthracene

by Berton (C. R. 208, 1898 (1939))

Absorption & Photodissociation in Solids

P. R. S A172 299, 314. (1939) Particularly BaN_6.

Ag oxalate. $Ag_2C_2O_4 \rightarrow 2Ag + 2CO_2$.

See also Trans Farad Soc. 44, 256 (1948).

NaN_3 Hexagonal (See Wyckoff Supplt. p. 38.)

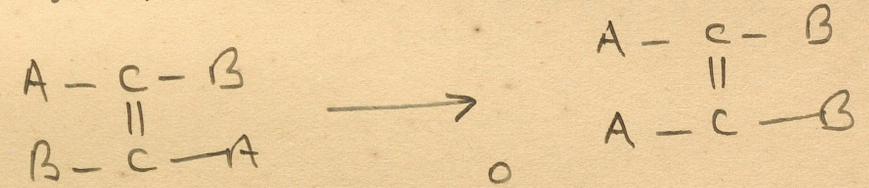
Photochemical transformation of trans to cis diparatolnyl ethylene (Martin & others, Trans R. S. Canada, 34, 35 (1940))

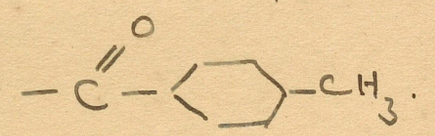
trans m.p = 148° C
cis 123° C.

both stable in crystalline state up to m.p.

Thermodynamically trans stable isomer ∴ cis converted to trans by addition of acid, iodine or other catalyst.

Trans yellow, cis ~~white~~ colourless
trans converted to cis under action of light



A = H, B = 

cis in soln transparent up to 2537 line of Hg.
trans absorbs 4358 feebly, + 4047 + shorter λ's strongly.

Ferromagnetism

Alnico the new magnetic alloy of Al, Ni, Co and Fe when permanently magnetised, can lift 1500 times its own wt. In tests a magnet ~~a pellet~~ of the material weighing 1.85 gms. has been made to lift 2750 gms.

About half the size of an eraser at the end of a pencil can lift a 5 lb flat iron with ease!

~~[illegible]~~ magnet developed by W. E. McKibben of the G. E. C. See J. App. Phys. 10, x April 1939.

(Norsk. Geol. Tids. 9, 258 (1927));

V. M. Goldschmidt, in discussing the crystallographic properties of BN, refers to

(1) the similarity between diamond and BeO (just like the one between grey Sn and hexagonal Ag I) or In Sb or Cd Te.

(2) Phosphorescence of BN containing C as impurity (according to the investigations of Tiede + Tomaschek, Zs. anorg. chem. 147 111 (1925).

(3) the metallic properties of graphite (opacity, conductivity etc.) contrasted with those of BN. [he quotes Friederich Zs. Ph. 31 813 (1925) as supplying the explanation]

Compton in his lecture before the Franklin Inst. (J. Fr. Inst. Aug. 1940 p. 151) refers to the effect of the magnetic vector of the X-ray waves on the spin moments of the electrons, and the resulting motion of the electrons and scattering of the X-rays; as also to expts by Rodgers. Look up Rodger's paper.

Why shd these scattered rays be unpolarised?

~~What~~ why is this scattering predominant only for short wave-lengths ($\lambda \sim 2 \times 10^6$ e volts) ?

Exptal verifn. of zero-pt. energy (See p. 157)

"When X-rays are scattered into changed wave-lengths they act independently of each other" — p. 156.

Short-wave-length limits of the fluorescence of some simple substances :- [taken from Franklin + Allen, J. Frank. Inst. Aug 1940, p 263]

	A.U
Benzene	2650
Naphthalene	3150
Pyrrole	3150
Quinoline	3500
Anthracene	4200
Diphenyl	3200
Triphenyl carbinol	2800
Pyridine	3150
Furane	3150
carbazole	3500
Hexane	2300
Methyl alcohol	2700
Paraffin oil	2750
Sodium bromide	2400.

Sunlight- approximates to 10,000 ft.-candles.

For ~~[illegible]~~ reading ordinary printed page 100 to 1000 ft candles best- suited.; this 50 to 100 is good enough.

Chrome alums

H. P. Klug

cryst- structure data [J. A. C. S. 62 2992 (1940)]

A $Cr(SO_4)_2 \cdot 12\,H_2O$	structure type	Lattice const- at 25° a_0 in Å.	Deviat- from x-ray data
A = NH_4	α	12.251	1.717
K	α	.175	1.826
Rb	β	.256	1.957
Cs	β	.378	2.064
Tl	β	.238	2.394
NH_3CH_3	β	.516	1.658

why are they called "the purple chrome alums"?
are there other chrome alums?

Make accurate susceptibility- measurements on the crystals corresponding to A = NH_4, K and Tl (+ any others if possible) and find the values of Dq for them: Examine in particular whether

(a) Dq for A = K, Dq = 1500 cm^{-1} as found by Schlapp + Penney (See also Van Vleck J. ch. Phys. 7 81 (1939); or whether it- is 1820 cm^{-1} as regards according to calc-

lations by Van Vleck J. Ch. Phy 8, 790 (1940) from
the Zeeman effect data for the crystal.

(b) whether Dq is very different for the
α & β types? What is the symmetry of the
field superposed on the cubic field, in the two
types? (In α Van Vleck mentions that it is
~~b~~ trigonal symmetry.)

Magnetic Anisotropy of some complex cyanides

Compound in solid state	μ/β
$K_2 Mn Fe(CN)_6$	6.05
$K_2 Co Fe(CN)_6$	4.90
$K_2 Cu Fe(CN)_6$	1.85
$K_2 Co Co(CN)_6$	5.30
$K Co Co(CN)_6 \cdot 2H_2O$	5.30
$K Ni Co(CN)_6$	3.10

(β = Bohr magneton
μ = effective magnetic moment

from Richardson and Elliott, J. Am. Ch. Soc. 62, 3182 (1940).

All the crystals cubic. For xtal structure see R + E's paper

For measurement of Elec. resistance at high temps. — the technique — see Armstrong and Dauphinee Canad. J. Research 25 357 (1947).

Skin effect with high freq. currents

Pippard : Proc. R.S. A 191 370, 383, 399 (1947)

Relaxation times

39.4

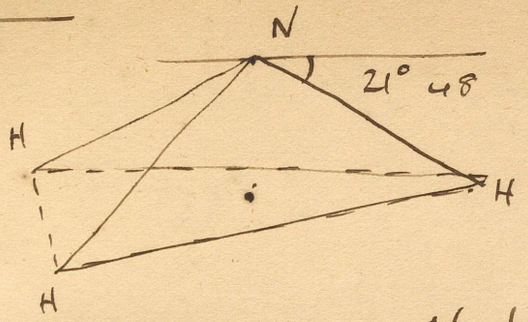
Octanol. ~~13 metres~~ $\lambda = 40$ cms $\tau = 1.33 \times 10^{-9}$ sec.

9.4×10^{-12}

Water

Mills J.C.S. 1943 p. 194 — Molecular constants

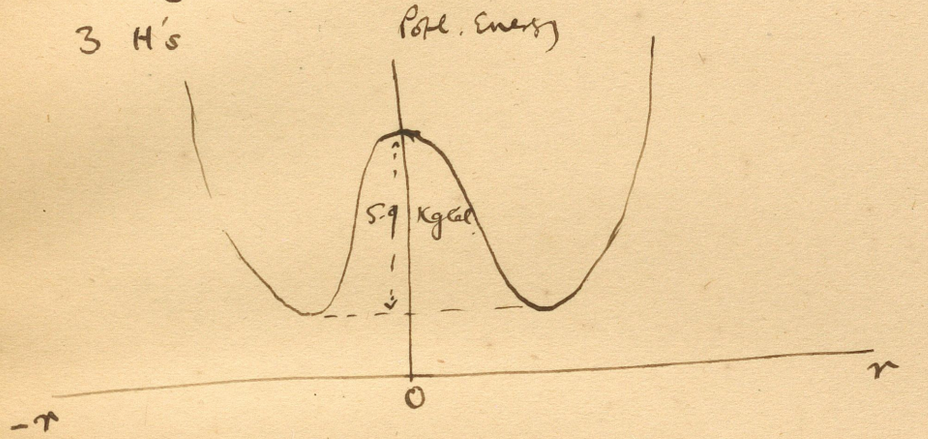
NH_3



$H\hat{N}H = 107° 3'$

Dennison Rev. Mod Physics
12, 175, 1940.

Taking r to be the dist. of N from the plane of the 3 H's



Low pote barrier
Hence Tunnel effect.

Inversion of "tropic Two" of the N nucleus

Structures of Molecules

Butadiene — Schomaker + Pauling J ACS 61 1769, '39

Piperylene — Craig J ACS 65, 1007 '43

Mods of Oscillation of C_6H_6 molec. J ACS 65, 815 '43

Elastic constants of diamond

$c_{11} = 10$

check $c_{12} = 4$

$c_{44} = 3.5$

as against $c_{11} = .52$, $c_{12} = .40$, $c_{44} = 0.41$ for Na crystal.

λ - pt

MnO_2 a hump in Sp. heat - temp curve at $92^\circ \cdot 12$ K.
He refers to other materials wh near such a hump do not ~~take~~ attain equilibrium in a short time — MnO_2 does.
Are in terms of order disorder type?

Coordination compounds

In cobalt diselenide, according to Lewis & Elliot, J Am. ch. Soc. 62 p 3180 (1540),

Co – Se = 2.43 Å (.03 Å greater than the sum of the covalent radii)

Se – Se = 2.49 (.21 Å larger)

In $NiSe_2$ Se – Se = 2.61 Å which is even greater:

With this anomaly is associated the large elec. conductivity of $CoSe_2 + NiSe_2$ (as contrasted with $MnSe_2$ which is a non conductor).

The 3 cryst. forms of TiO_2

Rutile, anatase & brookite

Rutile C_4-Type $a = 4.58$ A $\quad c = 2.95$ " $\quad u = 0.3_1$ $\quad Z = 2$

$\rho = 4.18$ $\quad$ Ti–O dist = 1.99 A

4.226 $\quad$ 1.948

4.283.

Anatase C_5 Type $a = 3.7_3$ $\quad c = 9.3_7$ $\quad u = 0.2_0$ $\quad$ Ti–O = 1.95

Deformed diamondlike structure

Brookite C_{21} Type $\quad a = 9.1_4$ $\quad b = 5.4_4$ $\quad c = 5.1_5$ $\quad \rho = 4.12_5$ $\quad Z = 8$. $\quad$ Str Per. 4, 14.

V_h

Ilmenite $Fe\,Ti\,O_3$

Rhombohedral $a =$ $Z = 2$

$\alpha = 53^\circ 47'$

CO_2 has FeS_2 (Pyrite) structure (cubic)

Str. Berich. I, 150.

and is not isomorphous into ice. The effect of ~~co~~ dry ice on precipitation of cloud is evidently due just to cooling & formation of ice.

Ag I has 3 cryst. modifns. (See Wycoff Suppl. p. 16.) 2 of which are cubic, and the 3rd hexagonal, having the dimensions

Ag I ~~CO_2~~. $a = 4.580$ $c = 7.494$ Å, as compared to the following data for H_2O, namely

H_2O $a = 4.508$ $c = 7.338$.

Their crystal types are not the same: Are they isomorphous?

Crystal structures of elements

B. needles or hexag. plates. Probably tetragonal
$a = 8.93$, $c = 5.06$ Å.
But optical exam shows symmetry can not be higher than monoclinic symmetry.
Semi metallic properties.

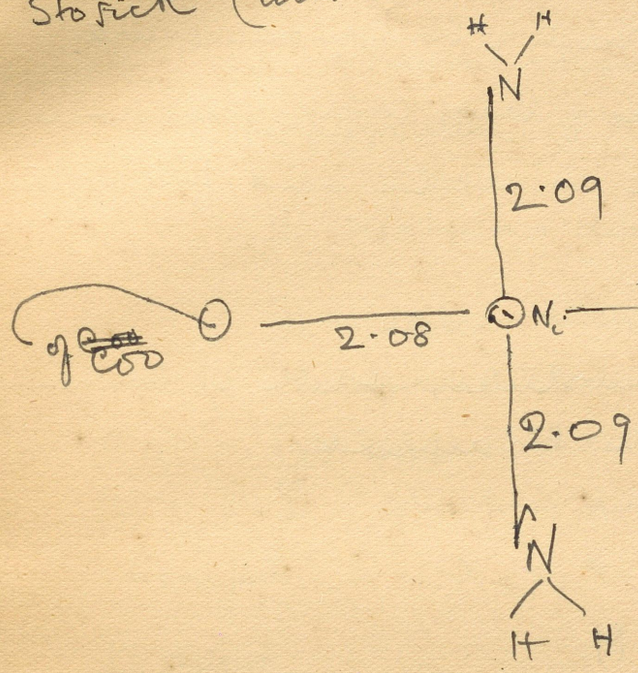
Evidently 6-coordinated

$Ni(NH_2CH_2COO)_2 \cdot 2H_2O$

Nickel glycine Dihydrate

JACS 67 365 1945

Stosick (with Linus Pauling)



The oxygens of the 2 water molecules above & below Ni respy. at 2·12 Å.

i.e. the 4 oxygens and the 2 Nitrogens form an orthorhombic ~~Oct~~ octahedron with 3 ⊥ axes (centre of Symmetry)

a = 2·08 (O)
b = 2·09 — (NH_2)
c = 2·12 — O of H_2O

Crystal monocl.

a = 7.60 Å β = 180° − 63° 25′

b = 6.60

c = 9.63 Z = 2.

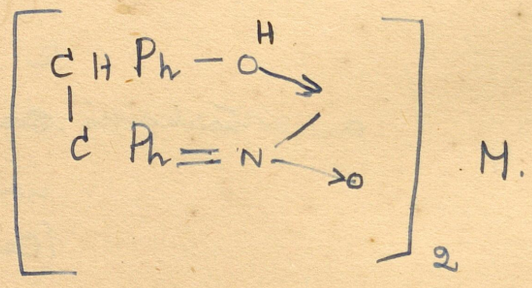
Find the relative orientations of the two sets of axes associated respectively with the 2 Ni atoms in the unit cell.

α benzoin oxime compound of Ni. J.C.S. 818, 1935.

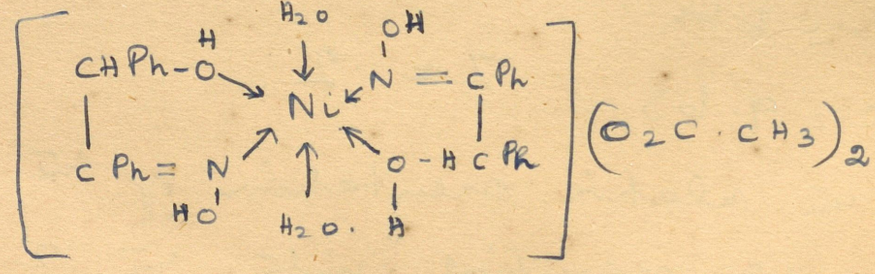
Jennings, Sharratt and Wardlaw (Birmingham)

An alcoholic solution of benzoinoxime with aqueous Ni Sulphate in presence of large Concn. of Ammonium acetate or excess of Na acetate in acetic acid forms two Compounds.

1) a buff coloured substance, soluble in benzene, chloroform, acetone and carbon tetrachloride.



2. Brilliant green salt, insoluble in all organic solvents except chloroform.



Sugden on examining these compounds, found them to be paramagnetic.

Disalicylaldehyde and disalicylaldimine complexes of divalent copper and Nickel. Tyson and Adams (Linus Pauling) J. A. C. S. 62, 1228, 1940.

I. Nickelous disalicylaldehyde probably has tetrahedral configuration.

II Nickelous disalicylamine has planar configuration

III copper disalicylaldehyde planar [like Cox's compound ie cupric complexes with β diketones X.].

IV copper disalicylaldimine planar.

V cobaltous disalicylaldehyde tetrahedral.

Compd.	$X_s \times 10^6$	$X_m \times 10^6$	Bohr magneton Exptl.	Bohr magneton calcd.
I Nious disalicylaldehyde.	11.43	3851	3.1	2.83.
II Nious. disalicylamine.	Diamagnetic			
III. Copper. disalicylaldehyde.	4.11	1256	1.9	1.73.
IV Copper disalicylamine.	4.14	1236	1.9	1.73.
V Cobaltous di-salicylaldehyde.	24.26.	8180 (?)	4.5	3.88.

I & V

A study of the Configuration of the Nickel Salt of Formyl Camphor.

French and Corbett. J.A.C.S. 62, 3219, 1940.

By a study of ~~Bi~~ ultraviolet absorption spectrum and ultraviolet rotatory dispersion of Ni formyl camphor, a tetrahedral configuration is suggested. It is found to be paramagnetic -2500×10^{-6} (?).

Isoelec. pt-

Nature 163, 485 (1949)

$Ni(CN)_2 NH_3$ M. M = C_6H_6) - - -

Nature 163, 566 (1949)

Age of the Earth

Holmes, Nature 163 453 (March 19, 1949)

Jeffreys 162 822 (1948)

α - Brass

Heat of activation 60 Kcal/gatom
75 " "

See J A P 18, 1028, 1947.

1. In age-hardening of Al-Cu (or Al-Ag) alloys intermediate stage in which metastable $CuAl_2$ grows on Al matrix (∵ one of its main faces can fit on one of the main faces of cubic Al structure)

2. Presence of foreign substance may influence crystal habit, without entering in actual crystal.

3. Cu_2O red + yellow identical except for crystallite size

Red + yellow PbO have different crystal structures.

Cu Be. all ordered. There is also a disordered body centred cube but not of equiatomic comp.

Cu Al No.

Cu Si No

Cu Zn Yes.

Cu Ga b-c cube & cp hex of same composition

Ag Mg ordered b.c.

Ag Al. disordered b.c & c.p. hex of same comp.

Ag Zn. ~~[illegible]~~ ditto but the cp hex is ordered.

Ag In Complex

Ag Cd Very interesting random b.c. cp. hex ordered b.c.

See Lonsdale Sc. Prog. Jan 1947.

order - disorder phenomena

1. In certain spinels of formula AB_2O_4 (valencies A+2B add up '58, or half of the B atoms + all A atoms randomly distributed in cation positions — $B(AB)O_4$.

2. $(KNa)Cl$. K : Na any ratio.

3. (a) $Li_2Fe_2O_4$ (rock-salt lattice) ∴ metal ions quite random.

Each cation surrounded by 6 O's

Similarly (b) Li_2TiO_3 rock salt type

~~Ca~~ (a) (b) + MgO (also of rock salt structure) can form mixed crystals.

4) $NaBiS_2$ + $KBiS_2$ Each have an averaged rock salt structure.

But $KFeS_2$ or $NaCrS_2$ have not.

∴ K + Fe, similarly Na + Cr have widely different ~~atomic~~ ionic radii

5) $Fe(CNCH_3)_6 \cdot Cl_2 \cdot 3H_2O$ In the unit cell of this cell there are 3 equiv. positions randomly occupied by 2Cl + one H_2O (i.e. $\frac{2}{3}Cl + \frac{1}{3}H_2O$)

~~Lisy~~ Powell + Bartindale J.C.S. 1945 799.

6) Even in 'random' alloys (eg Au Ag.) local order according to Guinier (Proc Phys Soc. Lond 57 310 (1945) + Wasastjerna (Soc. Sci. Fenn. Comm. Phys. Math 13 (5) 1 (1946)

which means a finite Curie temp. verify? check

7) Crystals in wh some cation or anion positions are vacant, but crystal as a whole electrically neutral. examples

I. ~~eg.~~ FeS Excess of S up to 55.5% due to ~~Corresponding no. of~~ absence of some Fe^{++} ~~sites being vacant~~ ions, and presence of a smaller no. of Fe^{+++} ions to make up Electrical balance.

Let $Fe : S = 1 : n \quad n > 1$

$n-1$ sites of Fe vacant

Out of the Fe atoms a fraction x is Fe^{++} and $(1-x)$ is Fe^{+++}, where

$$x \times 2 + (1-x) \cdot 3 = n \times 2$$

$$3 - x = 2n \qquad \underline{\underline{x = 3-2n}}$$

$\therefore$ $3-2n$ atoms Fe^{++}

$2(n-1)$ Fe^{+++}

n S

Total no of Fe atoms $= 1$

Vacant Fe sites $n-1$.

II γ Al_2O_3 $\rightarrow$ Fe_2O_3 can form spinels with 32 O ions in unit cell, and $21\frac{1}{3}$ Fe atoms to occupy 24 sites, i.e. out of 72 sites (=3 unit cells) 8 are vacant.

Hence normal spinels can take up unlimited quantities of ~~Al~~ this form of Fe_2O_3 or Al_2O_3 & form mixed crystals in which some metal sites remain vacant.

III $MgCl_2$ in LiCl $CdCl_2$ in AgCl.

Every Cd ion which goes in keeps one Ag site vacant. Hence increases enormously the electrical conductivity (ionic).

Ionic conductivity - part of existence of holes in the lattice. (See Bowen, Physical States of aggregation, Sc. Progress. 34 477 (1946))

IV Ag_2HgI_4, which is yellow, becomes cubic & red at 50° C. at low temps. In the cubic form 2 Ag + 1 Hg occupy 4 metal sites. 1 in 4 vacant.

V High temp form (α-?) of AgI also "defect" structure. I atoms form a comparatively rigid structure (body centred cubic) Ag mobile & contribute to conductivity — which is even greater than in liquid AgI

8) in NaCl type crystals metal ions more loosely bound to the lattice than the anions.

9) Flat molecules of melamine vibrate strongly in a direction ⊥r to their plane. (Hughes J ACS 63 1737 (1941): Similarly is the case with hexamethylbenzene, and the graphite

Is the compressibility ⊥r to these planes large?

Compressibility of long chain compounds along the length of the ~~[illegible]~~ chain, is small. Diffuse scattering associated with planes ⊥r to chain length takes the form of long thin streaks.

10) CN groups in NH_4CN oscillate in the diagonal planes of the tetragonal structure (Lely + Bijvoet Rec. Trav. chim Pays-Bas 63, 39, 1944)

11) NaCN, KCN, RbCN have NaCl structure
CsCN has CsCl "

Hence CN group has same symmetry as Cl^- which is probably secured by the rotation (~~[illegible]~~ which will be the final result of oscillation of greater + greater ampl.

Other ~~...~~ evidence available for onset of such an oscillation in NH_4Cl. According to Zernicke (Ned. Tijd. Natuurkund 8 66 1941) right value of entropy of this crystal obtained if the transition pt. is taken to correspond to an order-disorder change in the orientation of the revolving NH_4 groups.

According to Ferdok (Thesis Groningen 1942) ~~...~~ $C(SCH_3)_4$ has 3 modifns.

1) piezoelec. tetragl. stable below 23°.2C

2) apparently body centred centrosymm. tetrag. stable betn 23°.2 + 45°.5

3) Body centred cubic 45°.5 to mp. 65°.7.

Thinks in (2) body-centering and centrosymmetry simulated by the statistical cooperation of a large no of unit cells.

Pauling thinks in ice molec. configuration is changing all the time: cf its peculiar diffuse scattering.

12) Some types of ~~...~~ diffuse scattering not due to thermal vibration but to static periodicity e.g. Cu_4FeNi_3 during heat treatment. Lattice spacing at one stage approximately sinusoidal (Daniel + Lipson Proc. Roy Soc. A. 181, 368; 1943)

13) In hexagonal Co — mistakes in the pattern occur in an approximately regular way. cubic instead of hexag! for 2 or 3 planes in every 10 or 20.

14) In graphite from many sources 14% different modification 6% random arrangt.

15) In graphite the valency bonds are of the bond order 4/3.

16) In aliphatic long chain compounds such as paraffins or fatty acids, C-C bonds similar to those in diamond, + C atoms arranged in a plane, zigzag at nearly tetrahedral ∠le; In Polythene, besides large terminal motion ~~at~~ ⊥r to length of chain, there is large sideways spreading of electron cloud.

17. Picryl iodide (tetrag!) + hexamethylbenzene (tricl.) crystallize together to form an orthorhombic pseudo - hexagonal layer structure,

18 Fraenkel + Rudall suggest that insect-mono cuticles consist of alternating layers of protein + polysaccharide.

As little as 10^{-9} gm of U can be detected by its X-ray spectrum.

Hafnium & rhenium detected by this method (now isolated)

Natural 93 (isotope of neptunium) detected by Mlle Cauchois & her colleagues in tantalites & monazites. (awaiting confirmation by other methods)

Development of curved crystal focussing spectrographs has enormously increased the possibilities of ~~curve~~ X-ray spectroscopy.

The number of anions a cation can hold (its coordination no. n) depends mainly on the cation to anion radius ratio r

r	$> 0.73 = \sqrt{3}-1$	betn 0.41 & 0.73 $(\sqrt{2}-1)$	< 0.41
n	8 (cubic) e.g. CsCl	6 (octahedral) NaCl, MgO	4 (tetrahedral) BeO

Simly in the series AX_2, with decreasing cation size

AsX_2	CaF_2	MgF_2	BeF_2
Coordination ratio	8:4	6:3	4:2

CO_3^{2-} $PtCl_6^{2-}$ obey similar structural rules.

Both $NaPO_3$ & Na_3PO_4 can exist ∴ P^{5+} is big enough to hold 4 O^{2+} around it, but N^{5+} is not.
∴ $NaNO_3$ exists but not $NaNO_4$.

Covalent bonds may be infinite in one, two, or 3 directions eg. Te, Sb & diamond.

Rare Earth Salts

Crystal Structure

$Nd(BrO_3)_3 \cdot 9H_2O$

X-ray studies by Helmholz J.A.C.S. 61, 1544 (1939)

grows in large prisms, 4 × 4 × 10 mm in one plane
expts. Quite stable in air

Prepared from sulphate soln by adding Ba bromate; sulphate prepared from the oxalate by treating with sulphuric acid.

Hexagonal $a = 11.73$ A
$c = 6.76$

$a : c = 1.736 : 1$
$\rho = 2.79$ gm/cc. at 20°C
$Z = 2$

Sp. Gpr. $C_{6v}^4 - C6mc$.

9 H_2O molecs coordinated about the rare earth ion, 6 at the corners of a trigonal prism, and three out from the prism faces. $Nd-OH_2$ dist = 2.50 A for all the 9 water molecs.

Sym. of isolated $Nd(OH_2)_9^{+++}$ group is approximately that of D_{3h}. From the Sp. Gpr determination, the pt. groups symmetry at the Nd ion is C_{3v}.

cryst. structure of pyrrhotite : Bystrom 1945

Bnerge 1947.

The frequency of a piezo oscillator of quartz, say
in the 6 to 8 megacycle range, may be decreased
as much as 3 Kcycles by exposure to x-rays
The change is permanent. See Sc. Am Feb. 1945 p. 91.

Rare earth Salts contd

magnetic data.

Gd salts

Gd_2O_3

The gm. molecular suscept. ~~for a mass~~ of $\frac{1}{2}$ Gd_2O_3, according to Giauque and Stout, J. A. C. S. 61, 1384 (1939), can be represented by $\chi_M = \frac{7.827}{T + 15.5}$ (theor. value for ^8S.) roughly, over the range $1^\circ.4$ K to $20^\circ.3$ K, and also at liquid air temp.

At temps above 4° K χ was found to be indep. of field to within 1 or 2% up to 8,000 gauss.

Rheology of solids

Diamond

Jacobs & Chatrian in Le Diamant- 1884

of the 1000's of diamonds that passed thro' their hands more than 1/3 octahedra, & in the majority of cases into curved faces.

J.R. Sutton Diamond, a descriptive treatise: gives statistics of crystal forms of stones betw 1.5 & 10 carats from

Wesselton 19% dodecahedral (14% by wt.) Remaining octahedral & intermediate types.

Bultfontein average 7.7 cts
28.5 ~~38%~~ (23½% by wt.)

Dutoitspan ave. 10.7 cts
38% (39% by wt.)

Cube by truncating corners of the octahedron
Dodecahedron " edges.

Ref index 2.419 only surpassed by Si carbide and realgar AsS

Cuprite Cu_2O 2.85

Pyrargyrite Ag_3SbS_3 3.08, 2.88!

~~Pyr~~ Proustite Ag_3AsS_3 2.98.

greenish yellow fluorescence indicates one of the
rarer types.

Superconductivity + Superfluidity

1. In both a transport of matter takes place without friction, + in both this frictionless transport breaks down when a critical rate of flow is exceeded.
2. A remarkable degree of disorder in space persists in both up to lowest temps.
3. The appearance of a frictionless transport- when ~~cooling~~ cooling below λ or transition point, is accompanied by a large lowering of entropy (as measured from temp-spec. heat- curve) i.e. by a large increase in order [order in what?
4. Flow of liquid He II faster in tubes of smaller diameter. Is this so for superconductivity.

Electrical Resistivity Geophysical Surveys.

See Nature 161 812 (1948) and the references given there.

W. Trzebiatowski [Z. f. Phy. ch. B 24 87 (1934)] quoted by W. D. Jones "Powder metallurgy" (Arnold) pp. 104, 105.

appears as though for both Cu + Au, even at 0°C the material may be in thermodynamic equilibrium, i.e. that relaxation time associated with the (migration of atoms, i.e.) movements of atoms over distances greater than the interatomic distance, may not be large; and that at any rate at temps of 300°C for Cu + 400°C for Au, there is thermodynamic equilibrium.

J. Inst. metals 1945 : Goetzel. Cu powder compacts:

Copper-Silver Solid Solns. 0-8.8% Cu 0-8.0% Ag.

Optical Rotatory Power

1. Lowry Nature, Aug. 3 1935 p. 191
2. Born, Roy. Soc. P. A, May 1st 1935.

Specific Heats of Crystals

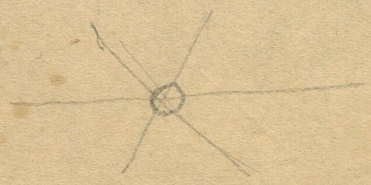
Fowler: Bakerian Lecture, Proc. Roy. Soc. A 151, 1, 1935.

Über das Leuchten von Flüssigkeiten beim
Durchgang schneller Elektronen (Tscherenkov
or Čerenkov?)

Some paramagnetic crystals suitable for anisotropy measurements

Any ionic salt of trivalent Ti which is not cubic (i.e. alums excluded)

or of Sc^{++}



Mn^{4+}

Six coordinated V^{3+} should be strongly anisotropic

inverted into reference to 2+

Four coordinated V^{3+} feebly anisotropic

4 coordinate Cr^{3+} strongly anisotropic

Co^{3+} strongly anisotropic like Fe^{2+}

V^{2+} feebly anisotropic.

Mn^{4+} feebly.

$K_4 Fe(CN)_6$

Mn

Cr.

Nal- Jan 10.

~~xix Rt- bolton Hughes~~

~~36. 37, 40 Rt-, 52~~

~~5~~

p. sinter benzene

p. intraviline

Niggli.

To read

Dielectrics

Insulation ~~p~~ Nat. 161, 23 (1948)

High permittivity values at

Cm. wave-lengths ibid p. 25

J. D. Cockroft.

Dr W. Ivor Jennings

Nature p. 50. Compton.

Nature Nov 15 p 673.

Floating thread

β. Quinol p. 53

~~59 Rt~~

~~60 Rt + Lt~~

~~61 Lt + Rt~~

Vol V Beilstein page 691.

1) $C_6H_5 \cdot (CH=CH)_3 - C_6H_5$.

Preparation Heat a mixture of 1 mole wt sodium salt of β-benzylidene propionic acid, cinnamic aldehyde & acetic anhydride 40 minutes at 140°C.

Properties Yellow plates (from acetone or $CHCl_3$) mp 194°C. Dilute solns fluoresce blue (solns in $CHCl_3$ or acetone). Refraction & dispersion in $CHCl_3$ see Smedley Soc 93, 376.

Ref. Smedley. J. Chem. Soc 93, 373.

— . x —

$C_6H_5 \cdot (CH=CH)_4 - C_6H_5$

$C_{12}H_{10}$
C_8H_8

$C_{20}H_{18}$

— x —

2) α ν diphenyl - αγεη octatetren:
$C_6H_5 \cdot (CH=CH)_4 - C_6H_5$:

a) yellow form: From cinnamic acid, sodium salt of "Bernsteinsäure" & acetic anhydride at 90°C; (Fittig, Batt Annalen der Chem 331, 160). Golden yellow leaves from ethyl acetate; Shows a green fluorescence (Stobbe Ber 42, 568) nearly insoluble in ether, alcohol & benzene: illumination causes production of the white form; if air is

excluded; Illumination in air ~~gives~~ causes oxidation & decomp. ⟶ benzaldehyde + benzoic acid. Action of alkaline $KMnO_4$ ⟶ benzaldehyde & benzoic acid.

Colourless form

1) obtained along with γ-styryl itaconic acid by condensation of "Bernsteinsäure" ester with cinnamic aldehyde in presence of sodium ethoxide. Fichter & Hirsch Ber der Deut. ~~Che~~ Chem. Ges. 34, 2189.

2) Also by illumination of yellow form. with exclusion of ~~light~~ air.

Illumination in presence of air causes oxidative decomposition ⟶ Benzaldehyde & benzoic acid. See above for alk. $KMnO_4$.

$C_6H_5 \cdot (CH=CH)_5 = C_6H_5$

$C_{20}H_{18}$

C_2H_2

$C_{22}H_{20}$.

(1) Superlattice Structures in Alloys.

Many characteristic properties that distinguish a metal from a non-metal:

1) It is a good conductor of ~~the~~ electricity = In electrostatics synonym = metallic sphere : metallic contact
2) Heat = cold as steel:
3) Metallic ring = sound = Peculiar elastic properties
4) As ductile or malleable as a metal; [Beaten into transparent thin leaves]
Beating 5) metallic lustre, metallic reflection =
6) metallic bond = (Geoid)

Free electrons that are capable of migrating = Properties Expt.

Estimate = Wireless = density of electrons in ionosphere =



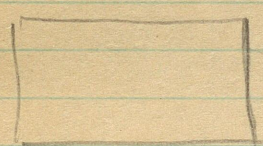
$n^2 - 1 = 4\pi N \frac{e^2}{m v^2}$

E, R, T 1 per atom

$l \sim 100$ at dist.

C. 1/100

Wave aspect is predominant. $\lambda/2$ ←——→

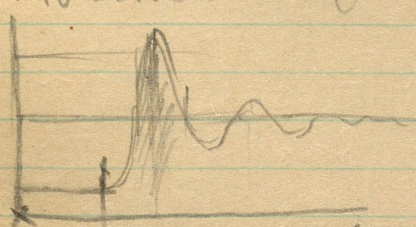


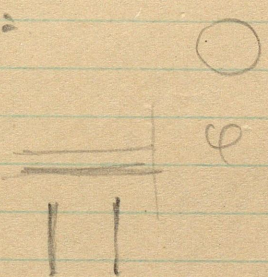
Low Rayl. Blackbody = Walls a nodal surface

Blind = Estimating = Bats:

Very short λ Energy = 40,000 °C

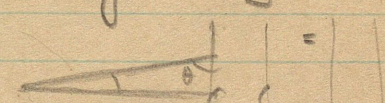
Thermal agitation:





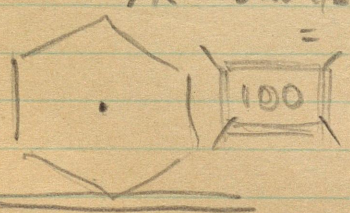
Different metals!

Hg very different



$\sin\varphi/2 / \lambda$

2ds $\frac{1}{2} d \sin\theta = \lambda$



$\boxed{\text{close packing}}$

Body Cen. FC cube (close packed)

close pack hexagon

axial ratio in charge cube tetragonal.

|| Br: Zones ||

Primary solid solns 2 Temp variation || Sharpness

Cu | Ag Au | with Zn Al Sn

α β γ

β Cu Zn 50% Zn 3/2
Cu_3Al 25% Al 6/4
Cu_5Sn 16.7% Sn 9/6

3 valency electrons to 2 atoms:

3/2

β-brass structure
B.C. Cubic

Cu Be
Cu Zn
Ag Mg
Ag Zn
Au Zn
Au Cd
Cu_3Al
Cu_3Ga
Cu_5Sn

$\frac{3+n}{2}$

Complex
Cubic β Mn structure

Ag_3Al
Au_3Al
Cu_3Si

21 : 13
γ brass str

Cu_5Zn_8
" Cd_8
Cu_9Al_4
" Ga_4
" In_4
$Cu_{31}Si_8$
Sn_8
$Na_{31}Pb_8$
×4

Formerly thought Na_4Pb

Cu Zn Al

Close packed hexag: 7 : 4

$CuZn_3$ | Ag, Au
" Cd_3 | Ag, Au
Ag Au / Cu_3Sn | " Ag_5Al_3 Au_5Al_3
" Ge
" Si

Digression Mobilities.

Cu_3Au Face-centred cubic

F.C. — corners.

Cu Au Tetrag.: Layers

$2d\sin\theta = \lambda$

Fe_3Al || Fe Al

$\frac{a\sqrt{3}}{2}$, a, $a\sqrt{2}$
8, 6, 12

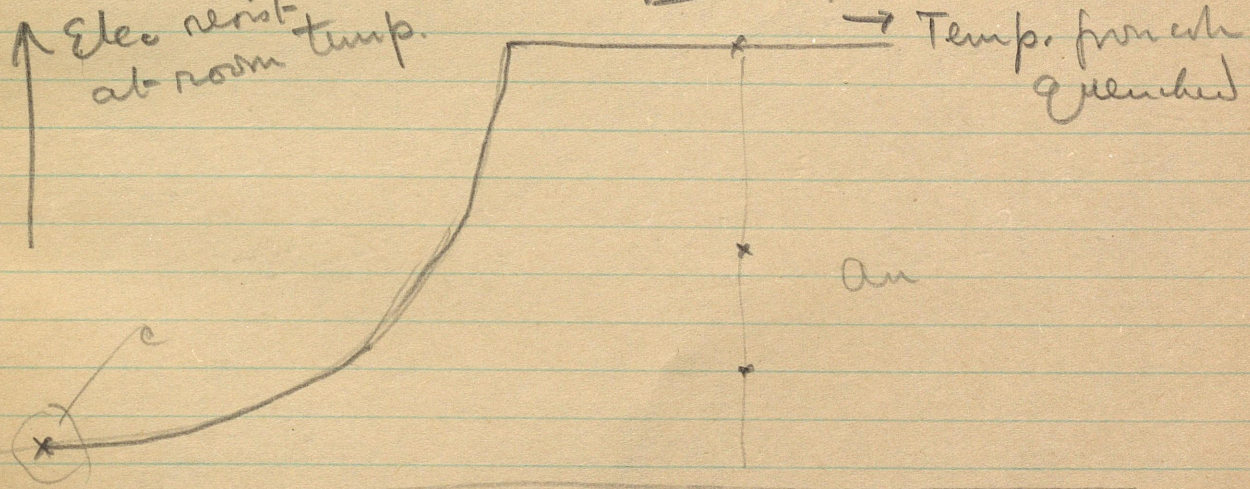
Centre Al. || no Al in 1st or 2nd || none in 1st

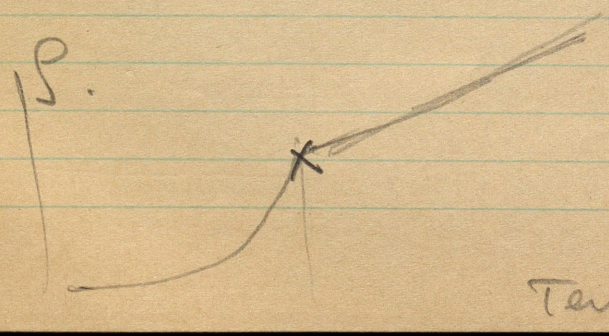
Theory or Energy =

Elec. conductivity

Tendency to avoid one ~~[illegible]~~ of its kind.

~~Short range~~





after annealing at low temp.

Short range order.

An Ag alloy -

Superlattice Structure in Alloys

Pres. Address Inst. metals Dec 19

~~Normally close packing: as tho' they were spheres:~~

1. Crystal as a perfectly regular arrangement of atoms kept in place by forces of attraction & repulsion:

2. This idealized picture is not true of course:

May keep external form without being a single crystal: Beryl for eg.

Can demonstrate by irradiation of quartz: or beryl: Laue Pattern completely disappears: Diffuse rings characteristic of amorphous quartz: which shows rearrangement possible in the solid state too.

3. Small imperfections produced artificially:

~~Can~~ With the help of microwave resonance.

Quartz: Al of a particular isotopic variety.

Diamond: 4 electron system.

One knows in some cases more about these imperfections than about bulk ~~sub~~ crystal.

4 Occur naturally ** Vacant Sites

a) FeS Excess of S up to 55%.

A smaller no of Fe^{+++} can take the place of Fe^{++}

$Fe : S = 1 : n \quad n > 1$

$$\left\{\begin{array}{ll} Fe^{++} & 3-2n \\ Fe^{+++} & 2n-2 \\ S & n \end{array}\right\} \quad \text{Total } 1+n$$

$2(3-2n) + 3(2n-2)$

Vacant Fe sites $n-1$ $\} = 2n$. as it shd be

~~4~~ 4 (b) $\gamma\, Al_2O_3$ & $\gamma\, Fe_2O_3$ can form spinels

32 O atoms in unit cell

24 sites for metal atoms

but only $21\frac{1}{3}$ can be occupied, i.e. 8 vacant sites in 3 unit cells :

~~Unlimited~~ Al : Fe any $::^n$.

4(c) $CdCl_2$ in AgCl Every Cd ion keeps one Ag site vacant.

as evidenced by increased elect. condy (ionic)

5 ~~4(d)~~ Random ~~positions~~ sites

a) Spinels AB_2O_4 [valences of A & of 2 B together $= 8$]

$B(AB)O_4$ AB randomly distributed in certain positions

i.e. All A & $\frac{1}{2}$ of B

5(b) $Li_2Fe_2O_4$

5(c) $NaBiS_2$, $KBiS_2$ have an averaged rock-salt structure.

5(d) $Fe(CNCH_3)_6Cl_2 \cdot 3H_2O$
In unit cell 3 ~~rando sites~~ equiv positions randomly occupied by 2 Cl & 1 H_2O. must rotate

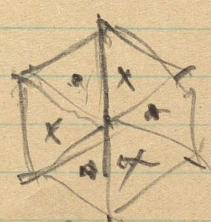
5e NaCN KCN RbCN NaCl str
CsCN CsCl.

CN and rotate.
NO_3 ion rotates =

Metals: B.C. cubic
F.C. "
close pa. Hexag.

close packing of spheres ABAB.
12 contacts with neighbours.

1:1.633



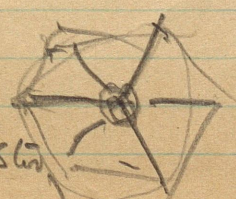
Rhombic dodecahedron.

12 faces.
14 corners.

Bee hive: Bee wiser than matter.
slip plane & direction.

Another exactly same. Rotate by 60°

Co High temp c -
1 low h - AB some c's too



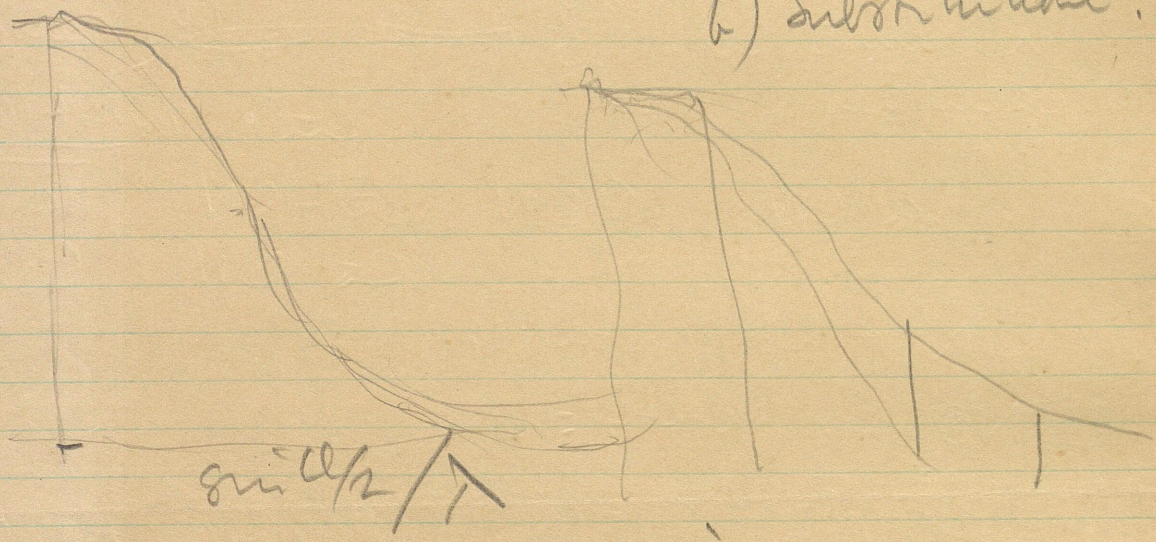
Face centred cube
close packed cube

Slip plane (111)

Slip direction [110]

B.C. cube open structure =
No slip plane Slip direction [111].

Primary solid soln = a) interstitial H, B, C, N.
b) Substitutional, tolerance lt.



Temp variation
Does not affect Sherpness
Hut does higher order in [illegible]

Mg Cd =

— Rare gas: Vander Walls:

what

VII group I_2 — It is possible to recognize the diantomic molecules. # I_2 in the crystal

VI S Se Te

Te shows spiral chains:

V S_8 As_4 | As, Sb, Bi

IV Diamond, Si Ge Grey tin

Diamond Structure.

III B, II B I B. # Transition elements

A Sub Group

one of 3 B.C Cubic

F.C. Cubic

close packed: hexagon

3000

Among the transition elements except —

Mn, Ur, Wolf, complicated

2

Zn Cd Elongated hexagon-

Six close neighbours

Other 3 + 3 at greater dist-

Hg 3+3 rhombic.

Ga In. F.C. tetragonal structure

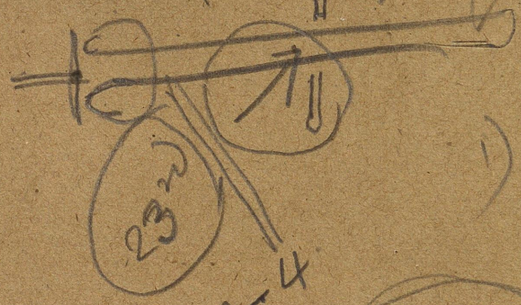
but c/a ~ 1

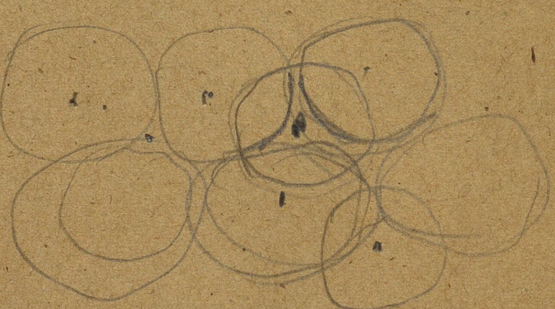
∴ close approximation to



24 Cube

Weak close packing of Spheres







Hexagonal close packed

