

$\pm 0.01 \text{ \AA}$ or less and individual standard deviations of $\pm 0.006 \text{ \AA}$ or less. This distance is in good agreement with the results of Palenik (1964) who found an average Co-N distance from five Co-N distances of 1.968 with a spread of $\pm 0.008 \text{ \AA}$ and an individual standard error of $\pm 0.007 \text{ \AA}$ in azidopentamminecobalt(III) azide, $[\text{N}_3\text{Co}(\text{NH}_3)_5][\text{N}_3]_2$. In contrast to the results of Shigeta, Komiyama & Kuroya (1963), we do not observe a significant 'trans' effect due to the chlorine substituent.

Stanko & Paul (1967) have also determined the geometry of the molecular ion $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ in $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}[\text{SiF}_6]^{2-}$ but their standard errors were three to five times larger than ours. However, there is general agreement within the larger standard deviations. There might be some Co-N bond elongation in $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}[\text{SiF}_6]^{2-}$ due to the presence of the highly electronegative fluorine atoms.

The cobalt-chlorine distance of $2.281 \pm 0.004 \text{ \AA}$ is only slightly longer, but nevertheless significantly longer, than the 2.21 \AA expected from the sum of the covalent radii (Pauling, 1960).

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Weak Reflexions in the X-ray Diffraction Pattern of Magnetite, Fe_3O_4

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Synthetic polycrystalline specimens of magnetite, Fe_3O_4 , were studied by X-ray diffraction. Several weak reflexions were observed which have not hitherto been reported for magnetite. These reflexions can be indexed on the spinel (f.c.c.) structure as 531, 551-711, 662 and 753. Addition of Ti^{4+} ions to the lattice results in a systematic shift of these reflexions with composition, showing that they are not simply due to a second phase. Structure-factor calculations confirm the presence of the four extra lines.

Introduction

A number of X-ray diffraction studies have been made on both natural and synthetic samples of magnetite. Basta (1957) has made an accurate determination of the cell size of natural magnetite and Rooksby (1961)

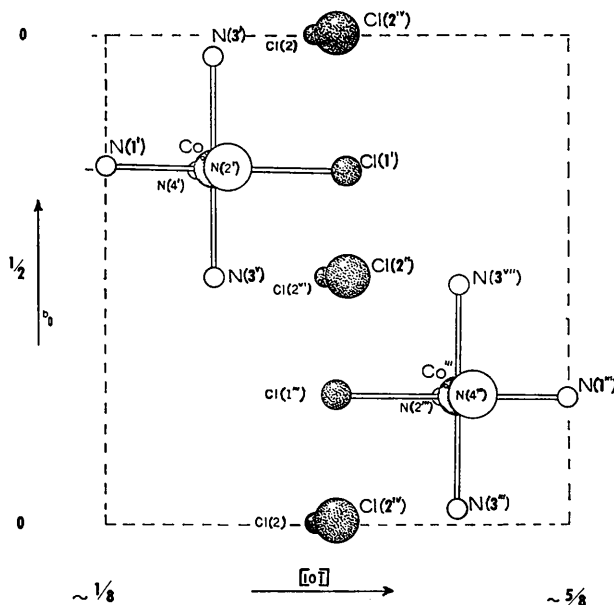


Fig. 2. View of the structure of $\text{Co}(\text{NH}_3)_5\text{Cl}_2 + 2\text{Cl}^-$ in the $[110]$ direction to show the reversed Co-Cl directions in adjacent molecules.

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has studied synthetic material. The *X-ray Powder Data File* card number 7-322 is based on Rooksby's work. Both authors publish a list of d values.

In the course of an investigation of the magnetic properties of the magnetite-ulvöspinel solid-solution series, X-ray powder pictures were made of synthetic

magnetite and magnetite with various degrees of titanium doping. Comparison of the results with the accepted patterns for both natural and synthetic material revealed the presence of an extra four reflexions in the powder picture. These could be indexed on the spinel (f.c.c.) structure as 531, 551-711, 662 and 753. A search in the literature showed that Clark, Ally & Badger (1931) reported a very faint reflexion for 551-711, for Fe_3O_4 , and a weak reflexion for 531, but no 662 or 753 reflexions.

In view of the discrepancy between the present results and the accepted patterns for magnetite in both natural and synthetic forms, intensity measurements were made on the hitherto unrecorded reflexions and the

shift of the d spacings of these reflexions measured as a function of titanium substitution. Calculations were also made for the intensities of these reflexions to see if they should be vanishingly small.

Experimental results

Accurately weighed quantities of Fe, Fe_2O_3 and (in the case of Ti doped samples) TiO_2 powder were ground together thoroughly under acetone, pressed into pellets and sealed in quartz tubes at a pressure of 10^{-5} torr. The samples were fired at 1150°C for six hours and quenched. The pellets were then ground and sieved to less than 44μ size. X-ray analysis of the synthetic titanomagnetites was then made by the powder method with a 36-cm circumference camera and Fe filtered Co radiation. A microdensitometer was used to measure the intensities of the lines on the film. The observed intensities are shown in Table 1 together with those of Rooksby (1961) and with ASTM card 7-322 which is also attributed to Rooksby. The present measurements in general lie in between the two published sets of data which differ considerably especially for high angle reflexions. The three sets are shown together rather to draw attention to the disparity between the published data than to make any meaningful comparison with the present measurements. No intensities are published for lines indexed as 531, 551-711 662 and 753. Although the intensities are low ($\leq 3\%$) the lines are easily visible on the powder picture. The cell edge was found to be 8.396\AA in agreement with Basta (8.396\AA) and Rooksby

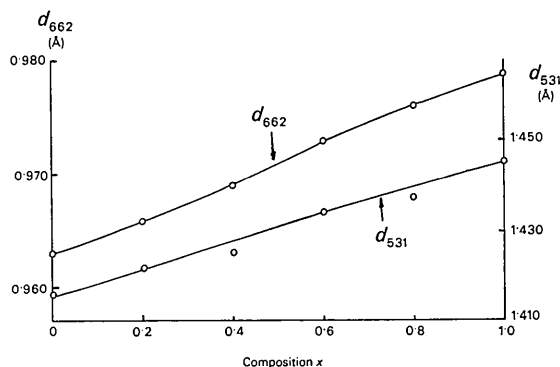


Fig. 1. Variation of d spacings (\AA) of the 531 and 662 reflexions with composition (x) in the solid solution $(1-x)\text{Fe}_3\text{O}_4-x\text{Fe}_2\text{TiO}_4$.

Table 1. X-ray diffraction pattern of magnetite Fe_3O_4 , Co $K\alpha$ radiation

Comparison of intensities of reflexions of Rooksby (1961) and ASTM card No. 7-322 with present measurements and calculated structure factors.

h	k	l	I/I_{311} (Rooksby, 1961)	I/I_{311} (ASTM card 7-322)	I/I_{311} (Present measurements)	F_{OBS}	F_{CALC}
1	1	1	10	30	17	150	68
2	2	0	30	60	39	214	155
3	1	1	100	100	100	260	245
2	2	2	8	10	8	130	126
4	0	0	20	50	17	233	270
4	2	2	15	40	19	131	110
3	3	3	25	60	46	158	162
5	1	1				188	192
4	4	0	35	70	63	352	367
5	3	1	6	10	8	31	31
6	2	0				88	82
5	3	3	10	30	20	138	134
6	2	2	3	10	5	69	90
4	4	4	4	20	10	163	130
5	5	1	15	50	37	26	32
7	1	1				12	15
6	4	2	4	20	12	67	64
5	5	3	15	50	37	100	110
7	3	1				87	95
8	0	0	4	20	17	195	211
6	6	0	3	10	10	51	52
8	2	2				50	50
5	5	5	8	40	40	83	92
7	5	1				73	80
6	6	2	4	30	27	3	58
8	4	0				77	77
7	5	3			3	15	9

(8.394 Å). That these lines are not due to a second phase is established by plotting the variation of d spacing as a function of titanium substitution. The systematic change of d_{531} and d_{662} is shown in Fig. 1. Maximum titanium substitution results in the compound ulvöspinel, Fe_2TiO_4 , and the pattern obtained differs from that of Forster & Hall (1965) in that they do not record the four weak reflexions. In the present investigation the spacings of all four reflexions varied systematically with composition x in the solid solution $(1-x)\text{Fe}_3\text{O}_4-x\text{Fe}_2\text{TiO}_4$. For values of x greater than 0.4, the 664 reflexion also became visible on the film. For $x < 0.4$ this reflexion occurs at too high an angle to appear on the film (for $\text{CoK}\alpha$). This may provide mineralogists with a method of detecting ulvöspinel in magnetite.

Structure factor calculations

The observed structure factors F_{OBS} , were calculated from the experimental intensities, which were corrected in the usual way for multiplicity, absorption and by the Lorentz-polarization factor. F_{OBS} was put on an approximately absolute scale by making the maximum value equal to one-third of the total electrons in the unit cell. A Glasgow structure-factor least-squares computer program was used to calculate theoretical structure factors F_{CALC} and match them to F_{OBS} taking the oxygen parameter, u , as the variable. Initially F_{OBS} for individual members of the five combined reflexions were obtained by splitting the observed intensities into two equal parts. In later cycles of computation these were recalculated by splitting the observed intensities into the ratios required by the ratios of

F_{CALC} . The deviation of the u parameter from the ideal value of 0.375 is a measure of the anion sublattice distortion from cubic close packing. The results of the calculation are shown in Table 1. Good agreement was obtained except for the two lowest angle lines 111 and 220. An overall fit of 13% was obtained for a u parameter of 0.381 in reasonable agreement with the value of 0.379 reported by Abrahams & Calhoun (1953).

Good agreement was found for 531 and 551–711. The calculated structure factors for 662 and 753 were also in reasonable agreement and all four lines should be expected to be found experimentally. Whether or not they are observed in practice presumably depends on the background being at a suitably low level. It is also possible that the lines may be dismissed as due to a second phase, unless the investigation being undertaken is a study of the effect of the addition of impurities (in this case titanium).

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Crystal and Molecular Structure of $[\text{RuBr}_2(\text{CO})_3]_2$

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A three-dimensional structural analysis of a new bromocarbonyl compound of Ru^{II} shows that the compound is to be assigned the formula $[\text{RuBr}_2(\text{CO})_3]_2$. It crystallizes in space group $C2/m$, with unit-cell dimensions $a = 10.74$, $b = 7.44$, $c = 9.42$ Å, $\beta = 106^\circ 32'$. Least-squares refinement led to a final agreement factor for the observed reflexions $R = 0.103$. The molecule possesses molecular point group symmetry $2/m (C_{2h})$; the Ru atoms are not bonded to each other directly but by means of two bromine bridges. The observed lengthening of non-bridging metal halide bond has been tentatively interpreted as due to the *trans* effect of the carbonyl ligand.

Introduction

Very recently Braca, Sbrana, Pino & Benedetti (1967) reported the preparation of a bromine carbonyl com-

pound of Ru^{II} . We have carried out a structure analysis on a sample of the compound, obtained in minute yellow crystals, particularly suitable for single-crystal diffraction examination. The compound was proved to