There is a definite tendency for distortion planes to pair. For the purposes of Table 5, the distances between distortion planes have been measured between the positions that oxygen atoms would have occupied in the fully-oxygenated or (non-existent) ideal structures. Thus distortion planes pair at distance between 6 and 8 ångström units. In addition to these pairs single distortion planes are distributed fairly evenly between the doublets. These can be seen in Fig. 3.

The structural consequences of thermal annealing are as follows:

1. When a member of the series Ta_2O_5–$11Ta_2O_5$.$4WO_3$ is first formed its structure is made up of a sequence of herring-boned chains of fused pentagons. The linear portions of any chain may contain 4, 6, 8, ..., $2n$ edge-shared pentagons which result in 5, 8, 11, ..., $(3n/2)-1$ basic subcell blocks. Initially, a large number of distortion planes are distributed evenly and mostly in pairs.

2. As (heat) energy is supplied to the system the lengths of the straight portions of the chains are decreased, the number of distortion planes is decreased and the number of pairs of distortion planes is decreased. These features are all interrelated and reflect changes in structure.

Table 5 and Fig. 3 both illustrate that as the oxygen: metal ratio decreases, the concentration of distortion planes increases and therefore the distances between the planes decreases. The planes are distributed mainly in pairs with occasional single planes distributed evenly between the pairs. As the concentration of distortion planes increases, i.e. at the high tantala end

of the Ta_2O_5–WO_3 system, it is possible to reverse the annealing process and, by slow cooling, increase the number of larger subcell blocks. The region over which this reversal applies in the Ta_2O_5–Al_2O_3 system is slightly larger since this latter system contains higher concentrations of distortion planes than the corresponding regions in the Ta_2O_5–WO_3 system. It appears, therefore, that when distortion planes occur frequently it is possible to pair the odd distortion plane with one introduced by an overall lengthening of the distances between the pairs.

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X-ray Study of the Structural and Ionic Configuration of the CoMnCrO₄ Spinel

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A new spinel $CoMnCrO_4$ has been synthesized. Its crystal structure has been determined by the powder method. It is found that this compound is cubic with lattice constant $a = 8\cdot34 \pm 0\cdot02$ Å. The oxygen ion parameter u in the spinel has been calculated from the intensities of various lines in the powder patterns and is found to be $0\cdot386 \pm 0\cdot002$. The K-absorption edges of cobalt, manganese and chromium have been recorded photographically in this spinel, using a bent crystal X-ray spectrograph. The positions of these edges have been compared with those in some well-known compounds. The comparison shows that the oxidation states of the manganese, chromium and cobalt ions in this spinel are two, three and three respectively. Combining the structural properties and the X-ray spectroscopic results, the charge and site distribution in the spinel is found to be $Mn^{2+}[Co^{3+}Cr^{3+}]O_4^{2-}$.

Introduction

The manganite spinels have attracted much attention in recent years because of their wide use in industry.

These oxidic spinels have given rise to much discussion (Kshirsagar & Biswas, 1967) as to their valency states and distribution of the cations in the lattice. Precise information about the charge and site distribution is

important since the electrical and magnetic properties depend upon them. During the course of X-ray spectroscopic studies of spinels in this laboratory (Mande, Kulkarni & Chetal, 1969; Kulkarni & Mande, 1970) we have been able to synthesize a new manganite spinel $CoMnCrO_4$. In this paper we report the structure of this compound as determined by the powder method. The valence state of the cations has been determined by X-ray absorption spectroscopy.

Experimental

The compound was prepared by first intimately mixing together under acetone a few grams of CoO, Mn_2O_3 and Cr_2O_3 in the molar ratio $2:1:1$. The mixture was then dried in air. It was mixed with borax and was heated in a silica crucible in a furnace for about 120 hours at $850\,°C$. The compound was purified using hot water. The X-ray patterns of the powdered sample were obtained on a Debye–Scherrer camera of diameter $11·46$ cm. using Cu $K\alpha$ radiation filtered through a nickel foil, and on a powder camera of $5·73$ cm. diameter using Fe $K\alpha$ radiation filtered by a manganese filter. It was found that the latter arrangement gave a much larger number of lines on the patterns than was obtained with the former set up. However, the patterns obtained on the latter camera are more useful for accurate measurements.

A Machlett sealed X-ray tube with a copper target was employed as a source of white radiation for X-ray absorption spectroscopy. A Cauchois type bent-crystal X-ray spectrograph of 40 cm diameter, equipped with a mica crystal was used in this investigation to photograph the spectra. Although all the three edges of the cations in this spinel could be recorded on a single films, the spectrograph was adjusted separately for each element under study for sharp focusing of the absorption edges and for accurate measurements. The

Table 1. *Results of the X-ray diffraction study of CoMnCrO₄*

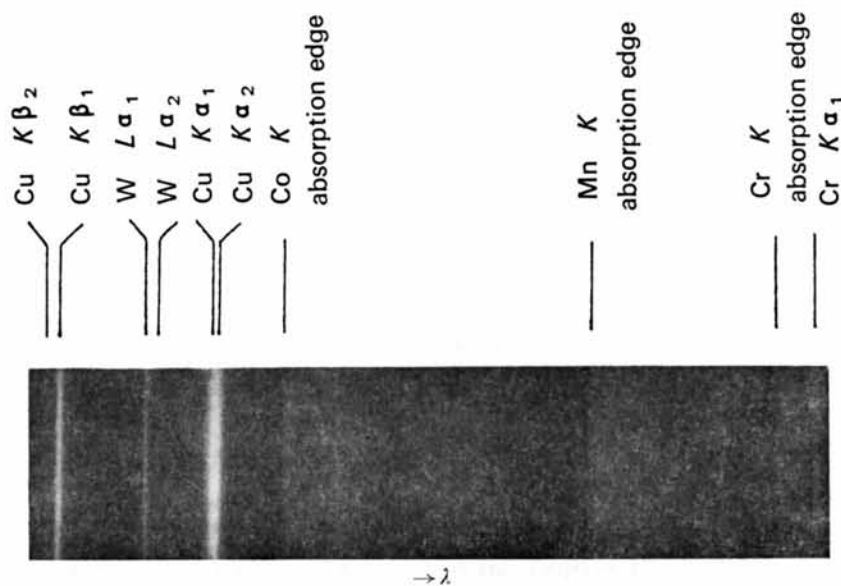| Serial number	d Observed	d Calculated	Intensity Observed	Intensity Calculated	hkl
1	4·817 Å	4·816 Å	10	9·6	111
2	2·947	2·945	45	48·4	220
3	2·515	2·515	100	100·0	311
4	2·057	2·086	40	34·0	400
5	1·704	1·702	20	19·4	422
6	1·604	1·605	65	66·2 ⎫ 8·6 ⎭	511 ⎫ 333 ⎭
7	1·476	1·474	65	60·6	440
8	1·277	1·269	30	25·0	533
9	1·203	1·203	10	16·3	444
10	1·123	1·114	15	13·2	642
11	1·094	1·089	25	24·6 ⎫ 29·4 ⎭	731 ⎫ 553 ⎭
12	1·047	1·043	5	2·5	800

Fig. 1. *K*-absorption edges in the CoMnCrO₄ spinel.

exposure times varied from about 6 to 10 hours. The experimental technique has been described in detail in an earlier paper (Mande & Chetal, 1965).

Results and discussion

A number of measurements were made on the patterns obtained on both the cameras. The observed d values for the different atomic planes obtained from the average values of the measurements are given in Table 1. In this Table are also included the intensities of the corresponding lines along with the planes responsible for their reflexion. From the average a value obtained from the observed d values, the d values were recalculated and are also included in this Table. These data show that this compound has a spinel structure with lattice constant $a = 8\cdot34 \pm 0\cdot02$ Å. The space group is O_h^7 or $Fd3m$. The possible cation distributions for the spinel are

(a) $Co^{2+}[Mn^{3+}Cr^{3+}]O_4^{2-}$
(b) $Co^{2+}[Mn^{4+}Cr^{2+}]O_4^{2-}$
(c) $Cr^{2+}[Mn^{3+}Co^{3+}]O_4^{2-}$
(d) $Mn^{2+}[Co^{3+}Cr^{3+}]O_4^{2-}$.

The intensities of the various reflexions were calculated theoretically for these distributions by using the

formula (Henry, Lipson & Wooster, 1961)

$$I_{hkl} \propto |F|^2 \cdot P \cdot \frac{1 + \cos^2 2\theta}{\cos\theta \sin^2\theta} , \qquad (1)$$

where the notations have their usual meaning. For each plane $|F|$ was calculated by taking the scattering powers of the different ions as given by Umanskogo (1961). The 311 reflexion was found to be the strongest and was assigned an intensity 100. The intensities of all the other reflexions were calculated with this reflexion as a standard. It was found that the intensities calculated theoretically for the distribution $Mn^{2+}[Co^{3+}Cr^{3+}]O_4^{2-}$ were closest to the observed intensities given in Table 1.

The oxygen ion parameter u was determined by calculating the intensity of the 111 reflexion for $u = 0\cdot375$ to $u = 0\cdot392$ in steps of $0\cdot003$. The plane (111) was chosen because it is most sensitive to changes in the u value. It was found that the value $u = 0\cdot386 \pm 0\cdot002$ suits best for the observed intensities given in Table 1. The intensities calculated with this u value for the ion configuration $Mn^{2+}[Co^{3+}Cr^{3+}]O_4^{2-}$ are also included in Table 1 for comparison.

One of the spectrograms obtained in this work is shown in Fig. 1, in which all the three edges of cobalt, manganese and chromium in the spinel were recorded

Table 2. *Wavelengths of the K-absorption edges*

K-absorption edge of	Absorber	Valency	Wavelength (X.U.)	Δλ (X.U.)
	Mn metal (Cauchois & Hulubei, 1947)	–	1892·54	—
	Mn metal (Present work)	–	1892·55	—
Mn	MnCl₂.4H₂O	2	1890·96	1·59
	MnSO₄	2	1890·76	1·79
	MnCO₃	2	1891·16	1·39
	Mn₂O₃	3	1888·96	3·59
	Mn₂(SO₄)₃	3	1889·20	3·35
	MnO(OH)	3	1889·16	3·39
	MnO₂	4	1887·56	4·99
	CoMnCrO₄ spinel		1890·56	1·99
	Co metal (Cauchois & Hulubei, 1947)	–	1604·87	—
	Co metal (Present work)	–	1604·92	—
Co	CoCl₂	2	1602·5	2·42
	CoSO₄	2	1602·67	2·25
	CoO	2	1602·8	2·12
	Co₂O₃	3	1601·24	3·68
	Co[(NH)₅Cl₂]NO₃	3	1601·36	3·56
	CoMnCrO₄ spinel		1601·54	3·38
	Cr metal (Cauchois & Hulubei, 1947)	–	2065·95	—
	Cr metal Present work)	–	2065·85	—
Cr	CrCO₃	2	2064·7	1·15
	Cr(CH₃COO)₂	2	2064·6	1·25
	Cr₂(SO₄)₃	3	2063·4	2·45
	Cr(NO₃)₃.9H₂O	3	2063·1	2·75
	Cr₂O₃	3	2063·5	2·35
	CoMnCrO₄ spinel		2063·4	2·45

simultaneously. We have also measured the positions of the K-absorption edges of cobalt, manganese and chromium in several compounds in which the valencies are well established. Table 2 shows our measurements of the K-absorption edges in the pure metals, in certain compounds and in the spinel. In this Table, the wavelengths of the K-absorption edges of the metals as given by Cauchois & Hulubei (1947) are also included for comparison.

It is well known that the position of the K absorption limit in a compound depends upon the valence state of the absorbing ion (Kunzl, 1932). From the magnitudes of the shifts for the cations in this spinel, it is seen that the manganese ion is divalent while the remaining ions are trivalent.

The structural properties, such as crystal symmetry, lattice constant and u parameter also give some indication about the ion configuration. The cubic symmetry shows that the spinel does not contain any distortive ion (Orgel & Dunitz, 1957) such as Mn^{+3} or Cr^{+2}. The calculated value of the lattice parameter $a = 8 \cdot 30$ Å. determined by Mikheev's (1955) method for this configuration, taking the values of the ionic radii as given by Sanderson (1966), agrees very well with the observed lattice constant $a = 8 \cdot 34 \pm 0 \cdot 02$ Å. Thus from our X-ray crystallographic and spectroscopic studies it can be concluded that this spinel has the structure $Mn^{2+}[Co^{3+}Cr]^{3+}O_4^{2-}$.

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The Crystal and Molecular Structure of Denudatine*

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The alkaloid denudatine, $C_{22}H_{33}NO_2$, crystallizes in space group $P2_1$ with two molecules per unit cell of dimensions: $a = 14 \cdot 229$ (12), $b = 7 \cdot 296$ (10), $c = 9 \cdot 552(7)$ Å and $\beta = 107 \cdot 64$ (4), measured at 20°C. The observed and calculated densities are $1 \cdot 194$ and $1 \cdot 207$ g.cm^{-3} respectively. The intensity measurements were made by the moving-crystal moving-counter technique. The structure was solved by the symbolic addition procedure for non-centrosymmetric crystals. Anisotropic least-squares refinement was concluded with a final R value of $0 \cdot 036$ for 2084 observed reflexions. None of the bond distances or angles differ significantly from the expected values, except for one long carbon–carbon bond of $1 \cdot 576$ Å. The molecules of denudatine are held, through hydrogen bonds, in chains parallel to the b axis.

Introduction

Denudatine is an alkaloid which was first isolated by Singh, Singh & Malik (1961) from *Delphinium denudatum.* They found that it had the molecular formula

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$C_{21}H_{33}NO_2$, and assigned to it structure (I) (Fig. 1). Recently Götz & Wiesner (1969) repeated the isolation of denudatine and established its molecular formula as $C_{22}H_{33}NO_2$. Investigating its structure by chemical methods they concluded that it could be either (II) or (III), where C(20) could be connected to C(14) or C(7). At this stage it was decided to determine the structure of denudatine by X-ray diffraction. This investigation, first reported in a preliminary communication (Brisse, 1969), revealed that denudatine has structure (IV).