CHEMISTRY

Cation Distribution in Ulvöspinel Fe_2TiO_4

RECENTLY we have considered it of interest to examine several spinel oxides containing iron, using the Mössbauer effect in the isotope iron-57, in order to determine the cationic oxidation state and site distribution¹. A case in which such information might be valuable is the oxide Fe_2TiO_4 . Since the original X-ray intensity investigation of Barth and Posnjak² this spinel has been considered to possess the inverse arrangement $\text{Fe}[\text{TiFe}]_2\text{O}_4$. However, the determination of cation distribution for an oxide with cations of such similar scattering coefficients is not easy. In addition the calculated intensity value for the 135 reflexion given by those authors for the normal arrangement is in error by several orders of magnitude. The inverse arrangement is favoured for a 2-2-4 spinel on the basis of electrostatic considerations³, and the known ferrimagnetic properties of Fe_2TiO_4 (Curie point 120° K (ref. 4)). The normal arrangement $\text{Ti}[\text{FeFe}]_2\text{O}_4$ requires Ti^{4+} ions on tetrahedral *A* sites. This is uncommon, but has been observed by Gorter⁵ in the material:

on the basis of saturation magnetization and *g*-factor determinations.

A sample of Fe_2TiO_4 was prepared by calcining a TiO_2 - Fe_2O_3 mixture in a CO-CO_2 atmosphere as used by Kunmann *et al.*⁶. The lattice parameter was determined as 8.529 ± 0.003 Å in good agreement with the figure of 8.53 Å given by Akimoto⁴. The X-ray diagram also indicated the presence of ~1 per cent ilmenite which, by the formation of a proportionate amount of Fe_3O_4 , could account for the sample possessing an overall ferromagnetism. (We are grateful to Dr. T. I. Barry for the magnetic measurements.) The room-temperature Mössbauer spectrum of this sample obtained with equipment described elsewhere¹, and using a source of cobalt-57 in stainless steel, is shown in Fig. 1. The derived isomer shift and quadrupole splitting values are 1.08 ± 0.06 mm sec⁻¹ and 1.65 ± 0.06 mm sec⁻¹ respectively. Within the limits of error these values are identical to those obtained earlier for FeAl_2O_4 with Fe^{2+} on tetrahedral *A* sites¹. Since the inverse arrangement is favoured for Fe_2TiO_4 (possibly with some of the Ti^{4+} ions on *A* sites), this result indicates that *A*- and *B*-site Fe^{2+} in Fe_2TiO_4 gives rise to identical isomer shifts and quadrupole splittings which may limit the use of the effect in similar situations. The presence of Fe^{2+} quadrupole interaction in Fe_2TiO_4 and FeAl_2O_4 but not in FeV_2O_4 and FeCr_2O_4 indicates that

Fig. 1. Room temperature Mössbauer absorption spectrum for Fe_2TiO_4 .

the electric field gradient at a nucleus at a given site in a spinel is dependent on the magnetic nature of the cations at neighbouring sites.

M. J. ROSSITER

Isotope Applications Unit,
Wantage Research Laboratory,
Wantage, Berkshire.

P. T. CLARKE

National Physical Laboratory,
Teddington, Middlesex.

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Superficial Ion-exchange Chromatography

RECENTLY the techniques of gas chromatography have been applied to chromatography in the liquid phase to separate small quantities of mixtures very rapidly. Techniques have been described for adsorption chromatography¹, partition chromatography², and ion-exchange chromatography³ where the inner surface of a capillary tube was coated with a liquid ion-exchanger.

In this laboratory, beads of cross-linked polystyrene which bear ion-exchange groups only in a shallow 'surface' layer have been used for superficial ion-exchange chromatography. The ion-exchange groups are not limited to amino-groups, and resins with superficial sulphonic acid groups and with superficial quaternary ammonium groups have been used successfully. The resins are expected to be as stable as the normal polystyrene resins, and columns packed with them should last indefinitely.

In normal ion-exchange chromatography the best results are obtained with very small particles and very low flow rates⁴, partly because the diffusion of ions into and out of the particles is slow. In superficial ion-exchange chromatography the distance the ions have to diffuse into the particles is greatly reduced, and rapid flow rates may be used with beads of convenient size. The beads used to obtain the elution curves shown in Fig. 1 had a mean diameter of 0.24 mm, and were surface-sulphonated to a capacity of 5.3 µequiv./ml. They were packed in a 45-in. column, 6 mm internal diameter, and eluant was pumped through at a rate of 6 ml./min. Molar solutions of metals or 1 per cent solutions of dyes were injected in quantities of 1-10 µl. Curve A shows the elution with 0.3 N hydrochloric acid of a mixture of copper and iron, and the tailing of the iron which occurs in this system. The tailing was reduced by gradient elution (curve B), and the separation was complete in 14 min. These curves should be compared with those obtained for the same metals on 'AG 50X8' by elution with more concentrated acid⁵. Curve A was not appreciably altered by faster or slower flow rates, and the tailing was not improved when a 15-in. column packed with beads of diameter 0.08 mm was used.

In practice, most ion-exchange separations depend less on the efficiency of the column than on the choice of a suitable eluant, which is often a complexing agent⁶. For the separation of metals it should be possible to prepare resins with superficial chelating groups and elute different metals with eluants of different pH. In this way the main drawback of chelating resins, which is the slow diffusion within the particles, could be avoided. However, the chief application of superficial ion-exchange chromatography is likely to be the rapid separation and characterization of organic acids and bases. Curve C shows the separation of two basic dyes, methylene blue (the first peak) and Janus green (the second peak). These dyes could not be eluted with the same eluant (5 N