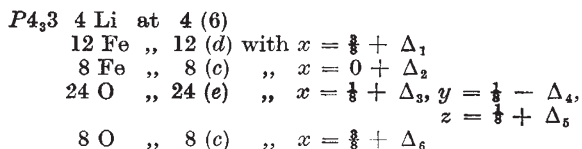## A Superstructure in Spinels

In 1935, E. Kordes[1] recognized that $LiAl_5O_8$ has nearly a spinel structure, but he observed a large number of extra lines, which he could not explain. A. Hoffman[2] prepared the corresponding compound $LiFe_5O_8$, which again was recognized as having nearly spinel structure. We found[3] that the powder diagrams of $LiFe_5O_8$ correspond with a primitive cubic lattice with a lattice constant of 8·33 A. The space group was found to be very probably $P4_33$ (or $P4_13$) and the positions of the atoms (in the notation of the International Tables, 1935) are :

$P4_33$ 4 Li at 4 (6)
  12 Fe ,, 12 (d) with $x = \frac{1}{8} + \Delta_1$
  8 Fe ,, 8 (c) ,, $x = 0 + \Delta_2$
  24 O ,, 24 (e) ,, $x = \frac{1}{8} + \Delta_3, y = \frac{1}{8} - \Delta_4,$
      $z = \frac{1}{8} + \Delta_5$
  8 O ,, 8 (c) ,, $x = \frac{3}{8} + \Delta_6$

with Δ_3, Δ_4, Δ_5 and Δ_6 approximately 0·007 and Δ_1 and Δ_2 still smaller.

For all Δ's equal to 0, this would mean an ideal spinel lattice with an ordered arrangement of lithium and iron ions in the ratio 1 : 3 over the octahedral sites. The type of the order is best described by considering only the sixteen octahedral interstices. These are occupied by four lithium and twelve iron ions in such a way that each lithium ion is surrounded by six iron ions in an octahedron elongated along a trigonal axis and each iron ion by four iron and two lithium ions.

Single crystals of $LiFe_5O_8$ have been grown and investigated and the above deductions are fully confirmed.

Below 735° C. the four lithium ions are distributed in this ordered way over the sixteen octahedral interstices. The long-range order decreases only very slowly up to this temperature. Above 755° C. the long-range order has completely disappeared and the four lithium ions are distributed over the sixteen octahedral interstices only. Up to at least 1,000° C. they do not enter to an appreciable extent into the tetrahedral interstices.

Between 735° and 755° there exists a transition region where the equilibrium long-range order vanishes within a temperature-range of a few degrees. The transition velocity above 755° C. and below 735° C. (down to 450° C.) is very high (transition within a few seconds to a minute). Between 735° and 755° there exists a region where the transition to the equilibrium is extremely slow. By rapid quenching from 950° C. we obtained the disordered phase at room temperature.

$LiAl_5O_8$ shows the same type of superstructure, but the order–disorder transition takes place at much higher temperature. We obtained the disordered phase by quenching from 1,350° C.

Some specimens of γFe_2O_3, prepared by E. W. Gorter of this laboratory, gave very nearly the same diagrams as $LiFe_5O_8$. They proved to contain some water molecules. In these γFe_2O_3 specimens the type of ordered structure described for $LiFe_5O_8$ is present, which in the ideal case would require a ratio of 1 : 3 for the ordering elements. In the description of γFe_2O_3 as a spinel with vacancies[4], $Fe_8(Fe_{13^1/_3}\Delta_{2^2/_3})O_{32}$, the ratio of vacancies to iron ions at the octahedral interstices would be at most 1 : 5. The ratio ideal for ordering would be reached by incorporating water molecules, approaching the formula HFe_5O_8 as a limiting formula.

Recently, Houben[5] has shown by absorption measurements that the compound HAl_5O_8 also exists under certain conditions. As shown by Ervin[6], the transition from boehmite to αAl_2O_3 and goethite to αFe_2O_3 through the γ oxides can be regarded as a gradual rearrangement of the aluminium and iron ions in the cubic close-packed oxygen framework. Since the products of the first transition steps are only nearly anhydrous, the very mobile protons might be expected to play an important part in these transformations. In special cases such as the γFe_2O_3 preparations mentioned, they can even give rise to a highly ordered superstructure in the γFe_2O_3 phase, thus showing that they are not merely present as absorbed water.

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Crystal Distortion of Graphite in Cast Irons

Recently, Debye–Scherrer line-breadths, the parameters of unit cells and the proportions of α- and β-modification of graphite present in cast irons, have been published by W. S. Owen and B. G. Street[1]. In connexion with this and other work, I have investigated the variation of disordered structure within a graphite grain by removing, step by step, outer layers of the grains by an oxidizing agent, since the variation seems to exist if we consider the crystal growth of irons.

The graphite samples used were a coarse flake graphite in a commercial grey cast iron, and a temper graphite in a commercial black-heart malleable cast iron of pipe fittings. The graphites were extracted from the cast irons by dissolving with hot dilute hydrochloric acid and washing with hydrofluoric acid. Then the outer layer of the grains was dissolved by wet oxidization. Many examples are known[2] of penetration of foreign atoms between the layer planes of the graphite crystal by the action of liquid agents ; this results in the increase of the lattice parameter normal to the layer planes. In the present treatment it is necessary that the oxidizing agent should attack gently and uniformly over the grain surface without destroying inner structure. For this purpose, the samples were boiled in an 8 per cent solution of potassium dichromate mixed with sulphuric acid (sp. gr., 1·29) in a flask fitted with a reflux condenser. The grain size of the powder gradually decreased as the boiling continued ; after 12 hr. in the case of the flake graphite, most of the grains became hexagonal in shape or fragments of hexagons, although the initial shape was irregular and only in rare cases were hexagonal figures observed on the grain surface.

The Debye–Scherrer patterns of these specimens were obtained by using copper $K\alpha$ rays and a camera