

## On the Ultrastructure and Morphology of Colloidal Cobalt Ferrite

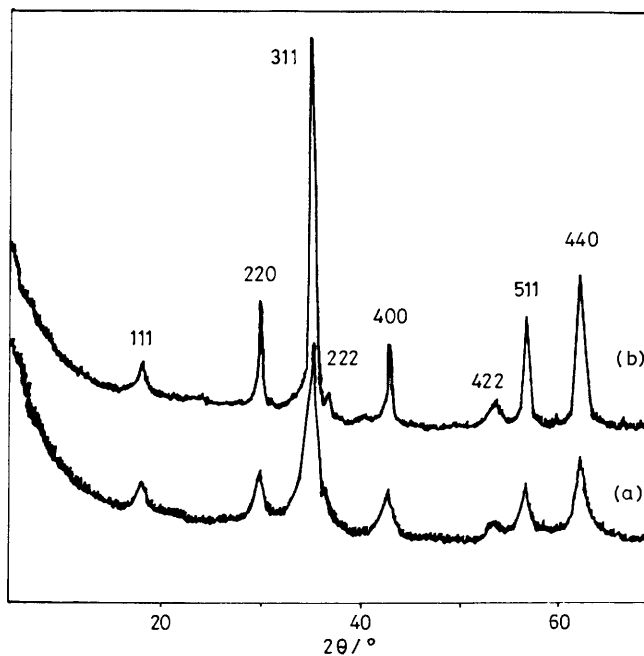
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Electron-optical and related techniques show that both unannealed and annealed samples of  $\text{Co}_{0.73}\text{Fe}_{2.27}\text{O}_4$  of colloidal dimensions are highly crystalline and of well-defined morphology: samples annealed at 600 °C have particles of mean diameter *ca.* 220 Å, with <332> preferred zones and {022} and {311} preferred faces.

Ever since stable lyophobic sols were first prepared,<sup>1</sup> over 140 years ago, there has been speculation concerning their structure. When the diameters of aggregates of metals or simple binary and ternary compounds fall in the range 10–100 Å, questions arise as to whether crystallographic order is maintained within the bulk and whether the surfaces have a specifiable crystallographic identity. Of late, such questions have taken on fresh physicochemical significance, since many remarkable electronic, photo-physical, photochemical, and other properties have come to light concerning ultrafine particles.<sup>2–8</sup> Thus, the electronic band-gap of minute (e.g. 20 Å) clusters of binary chalcogenides can exceed that of the corresponding bulk material by more than 1 eV. Such finely divided solids therefore have considerable promise photoelectrochemically and in photocatalysis. Moreover, ultrafine metal and oxide systems are promising heterogeneous catalysts,<sup>9</sup> a fact highlighted in the early work of Rideal.<sup>10</sup> Furthermore, when the finely divided materials are magnetic and dispersed as ferrofluids many extra practical applications are possible.<sup>11</sup> As there is a pressing need to elucidate the structural properties of these materials, we have, to this end, extended<sup>12</sup> our earlier use of high-resolution electron microscopy and associated techniques. Internal and surface structure is established by direct, real-space imaging; the composition is determined by electron-induced X-ray emission microscopy; and optical and electron diffraction,



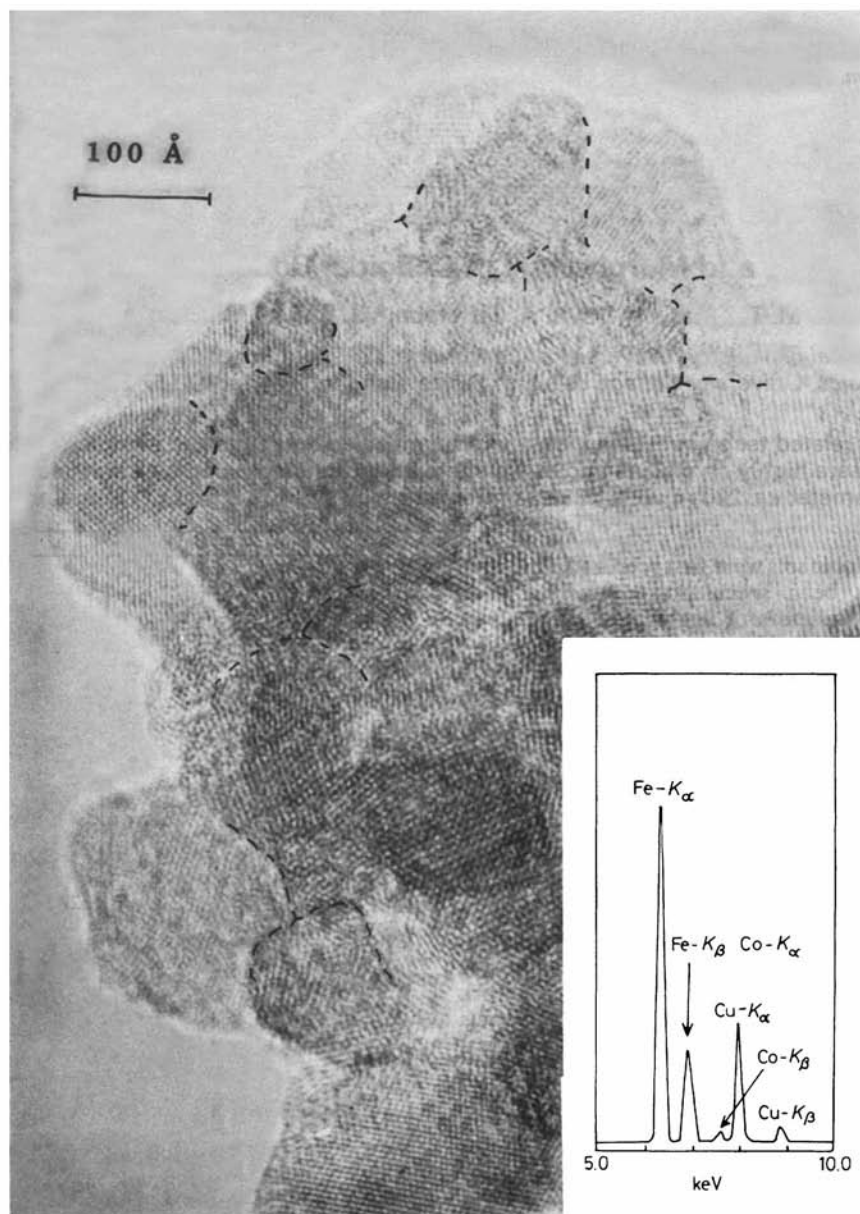
**Figure 1.** X-Ray powder patterns (Cu- $K_{\alpha}$  radiation, Fe filter) for the (a) as-prepared and (b) annealed (at 600 °C) samples of finely divided ferrite. (The peak profiles recorded for a ferrite sample annealed at 900 °C provided the instrumental profiles used to determine the particle sizes listed in Table 1.)

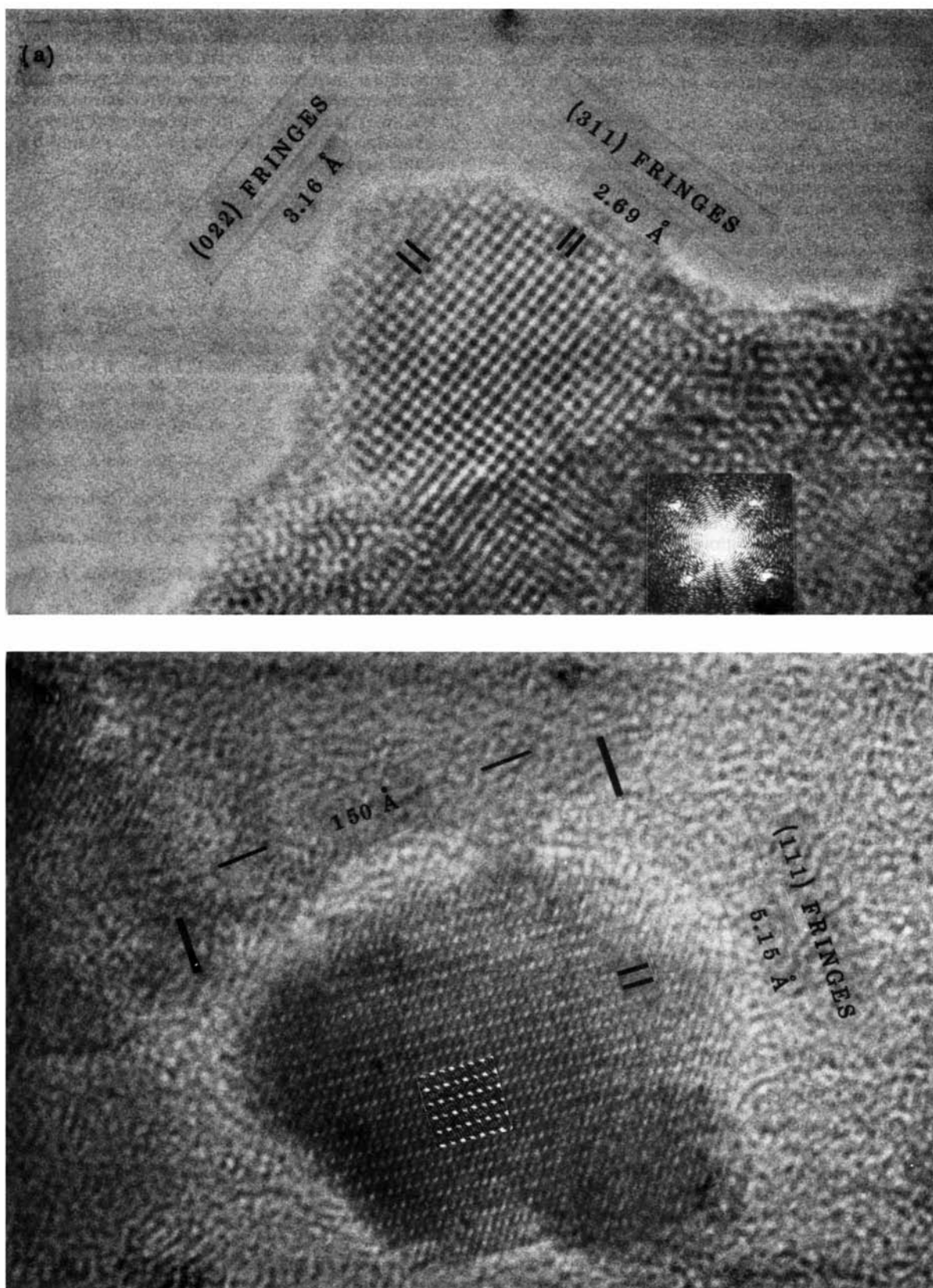
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**Table 1.** Summary of particle sizes of  $\text{Co}_{0.73}\text{Fe}_{2.27}\text{O}_4$  determined by X-ray and direct imaging by electron microscopy.

Sample	X-Ray				Electron microscopy: mean particle size/Å
	311 reflexion		440 reflexion		
	$2\omega/\beta$	$\epsilon/\text{Å}$	$2\omega/\beta$	$\epsilon/\text{Å}$	
As-prepared	0.65	77	0.67	110	80
Annealed (300 °C)	0.65	165	0.65	172	165
Annealed (600 °C)	0.65	211	0.66	204	235

<sup>a</sup>  $2\omega$  and  $\beta$  are, respectively, the full width at half-maximum and integral breadth of the X-ray reflexion.  $\epsilon$  is the volume-averaged particle size deduced from the Scherrer equation. Since the ratio  $2\omega/\beta$  was always close to the value expected for a Cauchy profile (0.637), it is safely concluded that line broadening is attributable exclusively to crystallite size and not to strain. <sup>b</sup> Read-off from atomically resolved images.

**Figure 2.** A typical electron micrograph and corresponding electron-stimulated X-ray emission spectrum for as-prepared samples of the ferrite. Note domain boundaries (dotted lines).



**Figure 3.** High-resolution micrographs of (a) as-prepared, and (b) annealed (at 300°C) samples of the ferrite. Note high degree of structural order and well defined morphology. Optical diffractograms, such as that shown in (a), are used to determine the zone axis which is  $\langle 332 \rangle$  in (a) and  $\langle 110 \rangle$  in (b). A computed image, based on the idealized  $\text{Fe}_3\text{O}_4$  structure and included in (b), confirms the identification of the structure.

image simulation, and *X*-ray powder diffractometry are used as supplementary tools. With our recently developed<sup>12</sup> electron-optical lens pole-piece and specimen stage, information relating to distances of less than 1.8 Å is retrievable.

The material described here, cobalt ferrite of nominal composition  $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$ , is used in transducers because of its high magnetostriction.<sup>13</sup> It was prepared in aqueous solution from stoichiometric amounts of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  to which was added NaOH solution so as to reach a pH of 12. The sol was matured at 80 °C for 8 h. The annealed samples were prepared after drying and heating the product to the temperatures listed in Table 1.

Both the as-prepared and annealed ferrite yield good *X*-ray powder diffraction patterns, which are indexable, as expected, on the basis of an inverse spinel structure (Figure 1). The cubic unit cell repeat is 8.395 Å, intermediate between the corresponding values for magnetite and stoichiometric  $\text{CoFe}_2\text{O}_4$ . The absence of extra reflexions signifies that there is no regular ordering of the cations even upon annealing to 600 °C.<sup>14</sup> The line profiles (Table 1) of the 311 and 440 reflexions yield estimates of particle size in reasonable agreement with those determined directly by electron microscopy (Figures 2 and 3). The *X*-ray emission spectra (calibrated *via* the  $\text{Fe-}K_\beta$ : $\text{Co-}K_\alpha$  intensity ratio for a 70:30 Fe-Co alloy) yielded a composition, which was remarkably uniform from particle to particle, of  $\text{Co}^{\text{II}}_{0.73}\text{Fe}^{\text{II}}_{0.27}\text{Fe}^{\text{III}}_2\text{O}_4$  (Figure 2). These results show that in the ultrafine ferrite particles, as in the bulk, the Co ions are statistically distributed in the B sites of the spinel structure.

Whereas the as-prepared particles showed a variety of crystallographic orientations, the  $\langle 332 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  poles being prominent, those annealed at 600 °C almost invariably took up an orientation which yielded only the  $\langle 332 \rangle$  zone, there being a tendency for  $\{022\}$  and  $\{311\}$  planes to dominate over others. Aggregation of the fine particles, leading to the formation of domain boundaries, tends to occur, even at room temperature, but is much more pronounced after treatment at 300 and 600 °C. Of considerable interest is the fact that, within the single crystal domains of both as-prepared and heated samples, there is little evidence of structural imperfection. We have seen none of the

twin boundaries recently identified<sup>12</sup> as a feature of aggregates of Pt and Au of colloidal dimension. It is of interest to note that rather larger single-crystal domains of magnetite in the intracellular inclusions of magnetotactic bacteria have also been characterised by high-resolution electron microscopy.<sup>15</sup>

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