On 'seeing' the Stacking Sequence in Graphite–Iron(III) Chloride Intercalates by High-resolution Electron Microscopy

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Lattice images of iron(III) chloride intercalate residue compounds, when recorded with their layer planes parallel to the electron beam, reveal the occurrence of coherent intergrowths of the so-called first-, second-, fifth-, and sixth-stage intercalates in which a sheet of $FeCl_3$ is inserted between, respectively, all, every second, every fifth, and every sixth individual sheet of carbon.

WHEN graphite and iron(III) chloride are heated together in chlorine vapour in a sealed tube, two-dimensionally extended sandwich compounds (intercalates) are formed, the stoicheiometry of which is governed by the precise conditions of the preparation.[1-5] Previously published X-ray and electron-diffraction studies have confirmed that in the so-called first-stage intercalate (C_7FeCl_3)

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[1] W. Rudorff, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 224.

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[3] A. R. Ubbelohde and F. A. Lewis, 'Graphite and its Crystal Compounds,' Oxford University Press, 1960.

[4] R. C. Croft, *Quart. Rev.*, 1960, **14**, 1.

[5] J. G. Hooley, in 'Chemistry and Physics of Carbon,' ed. P. L. Walker, jun., Marcel Dekker, New York, 1969, vol. 5, p. 321.

each interlamellar space in the parent graphitic structure accommodates an extended sheet of $FeCl_3$ such that the iron atoms are octahedrally co-ordinated to the chlorine atoms. In the second-stage intercalate (more dilute with respect to $FeCl_3$), $C_{12}FeCl_3$, only alternate interlamellar spaces are occupied by sheets of unit thickness of $FeCl_3$. In third, fourth, and higher stages, sheets of $FeCl_3$ octahedra occur every third, fourth, *etc.*, interlamellar space respectively. In all the various stages of the graphite–iron(III) chloride intercalates so far studied, the lattices of the host graphite and guest $FeCl_3$ are not in exact registry.

These are the structural patterns that emerge from X-ray diffraction analyses, which yield results spatially averaged over a total of, generally, not less than some 10^{18} unit cells. It is of interest to assess the structural homogeneity of such intercalates, and in this paper we analyse the ultrastructural inhomogeneities that occur in samples of graphite which originally extend to no more than 10^2 unit-cell repeat distances in the c direction (*i.e.* in slabs of graphite less than *ca.* 60 nm thick). Such analyses may be carried out [6] by means of direct imaging using high-resolution electron microscopy (h.r.e.m.). When intercalates of graphite are exposed to high vacuum, most, but not all, of the intercalated material is desorbed. The retained material is generally dispersed in a non-uniform manner throughout the so-named residue compound.

Contrast features in images recorded by h.r.e.m. may be optimized by selecting the appropriate defocus condition of the objective lens, which itself has to possess a low coefficient of spherical aberration.[7-11] Ideally, a series of through-focus images should be taken so as to assist in the correct interpretation of the projected charge-density present in the object under investigation. (Further details of the reliability and usefulness of this technique are discussed elsewhere.[10,11]) In the results reported here, instrumental defocus settings were chosen so as to provide optimal evidence of intercalation. The approach is akin to that which has been successful for other systems, notably non-stoicheiometric oxides and certain minerals.[6,9,12,13]

Figure 1 represents the distribution of the layer-averaged potential of a 0.5-nm thick slice of first-stage iron(III) chloride-intercalated graphite projected on to the c axis. The potential map was calculated from data provided elsewhere,[6,14] but because the $FeCl_3$ and graphite lattices do not match up exactly an approximation was necessary. We chose as our unit cell the central unit shown in Figure 3c of ref. 6, of dimensions $a = 0.606$, $b = 0.606$, and $c = 0.920$ nm and angles $\alpha = 90$, $\beta = 90$, and $\gamma = 120°$, giving a composition C_5FeCl_3. A crystal one unit-cell thick in the a and b directions and of effectively infinite extent in the c direction was constructed and the (001) structure factors calculated, $l = \pm 40$. A one-dimensional Fourier transformation was then used to yield a layer-averaged potential distribution for one unit cell projected on to the c axis.

An acceptable image of this structure should demonstrate the essential features apparent in Figure 1, *i.e.* fringes separated by 0.92 nm, representing graphite layers, with broader intervening fringes corresponding to the sheets of $FeCl_3$. It is unlikely that the individual chloride and iron peaks of the potential distribution (seen as three discrete peaks in Figure 1) would be resolved using standard high-resolution methods, at least with the limitations imposed by currently available instruments.

The intercalated samples examined were prepared initially as first-stage compounds, but in the electron microscope decomposition occurs and the residue compound [5] is formed. Not unexpectedly, images exhibiting extended regions of first-stage intercalates were rarely observed. Nevertheless, the lattice-fringe image of Plate 1 shows that the essential features of the potential map of Figure 1 are indeed reproduced in the electron-microscopic images. We identify fringes A and C (separation 0.92 nm) and E and G (also separated by 0.92 nm) with carbon and B and F with $FeCl_3$. Fringe D is probably also carbon. The remainder of the crystal showed fringes of separation 0.34 nm corresponding to carbon layers in the graphitic structure. Such an interpretation of Plate 1 is dimensionally correct but it is necessary to ascribe the relatively high contrast of

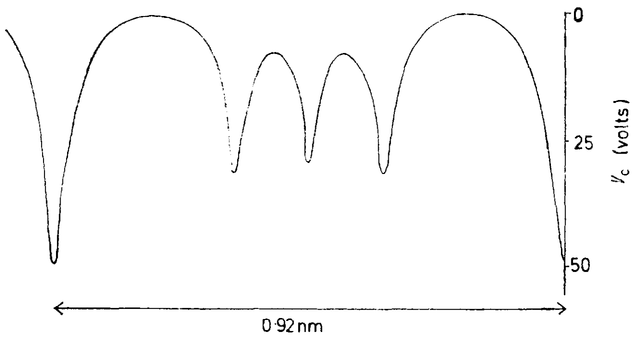

FIGURE 1 Calculated distribution of potential (projected on to the c axis) of a sheet of iron(III) chloride octahedra inserted between two sheets of carbon. The specimen thickness is 0.5 nm

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[13] D. A. Jefferson and J. M. Thomas, *Materials Res. Bull.*, 1975, **10**, 761.

[14] J. M. Cowley and J. A. Ibers, *Acta Cryst.*, 1956, **9**, 421.

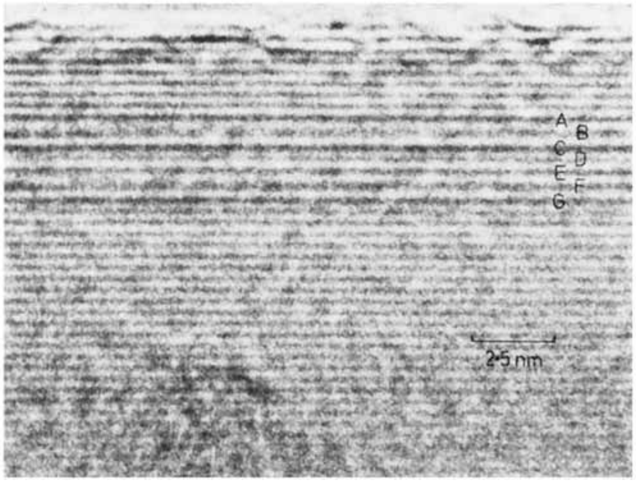

Plate 1 Bright-field lattice image indicating the presence of two strips of first-stage graphite–iron(III) chloride intercalate (spacing 0.92 nm) in coherent contact with and separated by graphite (spacing 0.68 nm, see text)

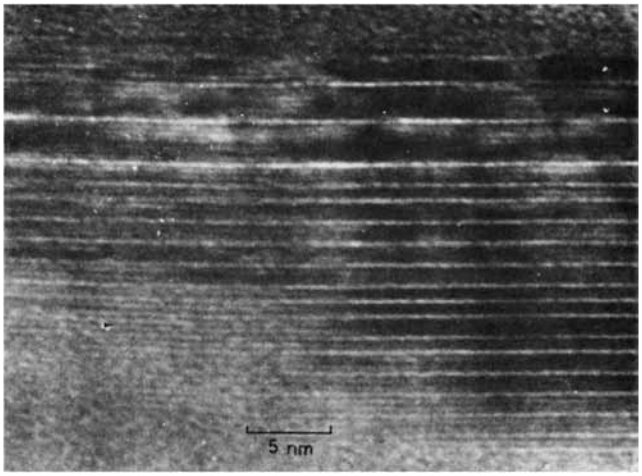

Plate 2 Bright-field lattice image of a 21-nm thick slab of graphite–iron(III) chloride intercalate with average composition $C_{12}FeCl_3$, corresponding to a second-stage intercalate. The light striations on the right of the micrograph delineate the sheets of $FeCl_3$ octahedra, and from their separation and the simple formula given in the text the particular stage (*i.e.* whether sixth or first) of the various intercalates, which are coherently intergrown, may be readily identified

fringes A, C, E, and F to modulations of the image intensity imposed by image-forming processes.

The electron micrograph shown in Plate 2 was obtained under less favourable imaging conditions but it, too, exhibits interesting features. If the light striations in these micrographs are taken to coincide with sheets of $FeCl_3$ and the less pronounced striations between them with the graphite layer planes, the specific identification of several distinct *n*th stages of the graphite–iron(III) chloride intercalates becomes possible. The *c* direction repeat unit in trigonal $FeCl_3$ $R\bar{3}$ ($a_0 = 0.606$ nm, $c_0 = 1.740$ nm), consists of three layers of $FeCl_3$ octahedra and the *c* direction repeat of 0.671 nm in graphite consists of two layers of carbon. Thus the *c* direction repeat distance in any *n*th stage graphite–iron(III) chloride intercalate is given by $(0.671n/2) + (1.740/3)$ nm so that first-, second-, third-, fourth-, fifth-, and sixth-stage intercalates should possess repeat distances of 0.92, 1.25, 1.59, 1.92, 2.26, and 2.59 nm respectively. Figure 2 summarizes the sequence of the various stages of intercalation proposed from the evidence of Plate 2. The measured repeat distances in Plate 2 were 0.92 ± 0.10, 1.26 ± 0.10, 2.30 ± 0.10, and 2.60 ± 0.10 nm, corresponding to the first, second, fifth, and sixth stages, respectively. The micrograph, therefore, is readily interpretable on a dimensional basis. As in the case of Plate 1, however, it is necessary to invoke modulation of image contrast by instrumental transfer properties, or, possibly, differences in thickness of the two samples, in order to reconcile the actual relative contrast of the image fringes. In this respect the reversal of contrast, a not infrequent occurrence in h.r.e.m., of the striations from those shown in Plate 1, should be noted. It is of interest to note that the higher (*i.e.* fifth and sixth) stages of intercalation, of which there is scant description in the literature, seem readily identifiable by h.r.e.m.

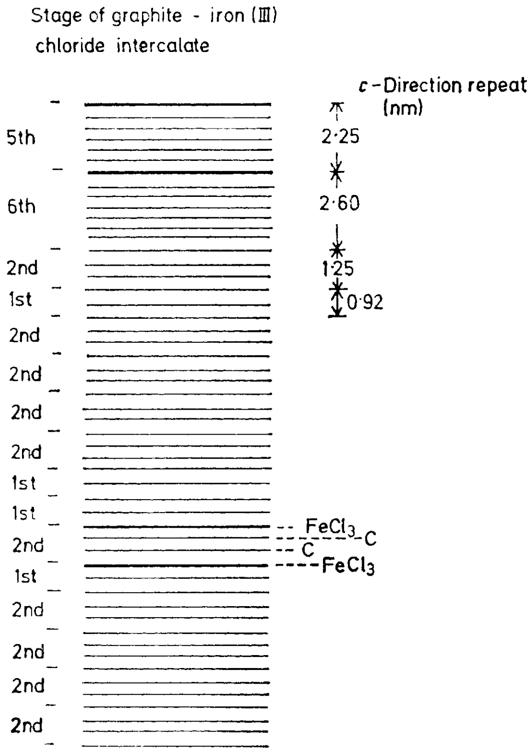

FIGURE 2 Schematic diagram illustrating the interpretation of Plate 2 in terms of various stages of coherently grown graphite–iron(III) chloride intercalates

Unfortunately it is, at present, difficult to study iron(III) chloride and other intercalates (*e.g.* potassium or bromine[15] which have been described briefly elsewhere [6]) by h.r.e.m. under dynamic conditions of interconversion from one stage to another. Such studies should elucidate the mechanism of formation of intercalates generally.

EXPERIMENTAL

Samples of the iron(III) chloride intercalates C_7FeCl_3 were prepared using Hooley's procedure [5] from specially thinned (see ref. 6) samples of purified [16] Ticonderoga graphite. Only those flakes with curled-up edges and so oriented as to have their layer planes parallel to the electron beam were examined. Only *ca.* 1% of the specimens prepared were in this orientation, and of these only a small fraction were thin enough (in a direction parallel to the layer planes) to yield satisfactorily interpretable micrographs. With the Philips EM300 microscope, the resolution attainable with the double-tilt goniometer stage was inadequate to distinguish the individual layer planes in the parent graphite. The high-resolution stage, which affords much less scope for orienting the specimens, was therefore used.

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