Letters

Iron–graphite lamellar compounds prepared by chemical reduction of $FeCl_3$ with potassium–graphite in tetrahydrofuran

In two papers D. Braga *et al.*[1,2] described the reaction of $FeCl_3$ and C_8K in tetrahydrofuran (thf) to form an iron(0)–graphite compound. The *X*-ray diffraction pattern of the product was interpreted on the basis of a lamellar compound of graphite involving different insertion stages (stages 2, 3, and 5) but indicated too the presence of several solid phases including graphite. Only for the different stages of the iron(0)–graphite product were *d* values given (Table). The big differences in the filled carbon–carbon interlayer distances of different stages (stage 2 = 0.560, stage 3 = 0.578, and stage 5 = 0.556 nm) are quite unusual in graphite intercalation chemistry. We have indexed these *d* values in terms of a mixture of several heterogeneous phases possibly present under the conditions of preparation (Table).

d Values from ref. 2, indexed by a mixture of heterogeneous phases *

d/nm	Phases	ASTM ref. no.
0.621	γ-FeO(OH)	8—98
0.316	KCl	4—0587
0.298	Fe_3O_4	19—629
0.248	γ-FeO(OH)–Fe_3O_4	8—98/19—629
0.237	γ-FeO(OH)	8—98
0.224	KCl	4—0587
0.213	Graphite–Fe_3O_4	23—64/19—629

* For particle-size distributions down to the sub-*X*-ray region, reliable quantitative intensities from *X*-ray diffraction measurements cannot be made (H. Krischner, Einführung in die Röntgen-Feinstrukturanalyse, Vieweg-Volag Braunschweig, 1980, pp. 92–100) because of texture effects, preferred orientations on the carbon surface, particle disordering, porosity, surface roughness, *etc.* However, the new diffraction patterns of a stage-4 iron(0)–graphite compound presented by Braga and co-workers[3] in their reply are also in agreement with the identity period, Ic, of a stage-4 $C_{48}K$ residue compound reported by Rüdorff and Schulze.[4] Furthermore, as for the other postulated metal–graphite compounds, Braga and co-workers do not take into account that ordered (001) reflections may be derived from $C_{8n}K(thf)_m$ compounds, which are also formed when the metal content of the initial C_8K crystals is reduced by decalation of the potassium (F. Beguin, R. Setton, A. Hamwi, and P. Touzain, *Mater. Sci. Eng.*, 1979, **40**, 167; L. Facchini, M. F. Quinton, A. P. Legrand, F. Beguin, and R. Setton, *Physica*, 1980, **B99**, 525; L. Facchini, F. Beguin, M. F. Quinton, R. Setton, and A. P. Legrand, Carbon 80, 3rd International Carbon Conference, Baden-Baden, 1980, Preprint, p. 100; I. B. Rashkov, J. M. Panayotov, and V. C. Sháhkova, *Carbon*, 1979, **17**, 479).

The procedure for the preparation of $C_{8n}Fe$ ($n = 2$, 3, or 5) included washing the products with 0.5% HCl, H_2O, MeOH, diethyl ether, and drying *in vacuo* at 0.01 Torr [1 Torr = (101 325/760)Pa] and 100 °C for 10 h in the presence of P_2O_5.

The reduction corresponding to the equation was

$$3\ C_8K + FeCl_3 \xrightarrow{thf} C_{24}Fe + 3\ KCl$$

carried out with a 'brown' thf solution of $FeCl_3$. Because anhydrous $FeCl_3$–thf solutions have a green colour, we believe that the $FeCl_3$ used was contaminated with moisture, and the possibility cannot be excluded that some C_8K reacted to give hydroxide ions. Considering that anhydrous $FeCl_3$ is an extremely hygroscopic compound, the reported[1-3] yellow-brown solution, typical for $FeCl_3 \cdot 6H_2O$ in thf, may be due to the purchased $FeCl_3$ sample absorbing water prior to use in the experiment. Furthermore, the stoicheiometry of the products was obviously estimated only from the carbon content of the samples. The stability of the potassium–graphite residue was not considered.[4,5] The alkaline contents, specifically the KCl phases were always present in the residue samples, even after boiling the compounds several times with water, with acid[4] or after aqueous Soxhlet extraction for 120 h.[5]

By means of *X*-ray and Mössbauer methods we have reinvestigated the products obtained by reduction of iron(III) chloride according to ref. 1 and found no evidence whatsoever for an ordered compound containing monolayers of iron atoms between the carbon layers.

We find that the method described by Braga *et al.*[1] yields bulk graphite and iron particles on the surface of graphite and amorphous carbon phases instead of the lamellar iron–graphite claimed. During the reaction of bronze-coloured C_8K (40 mmol) (synthesized from the host component: Feinpudergraphit, Messrs. Kropfmühl, crystal size *ca.* 20 μm) under argon in anhydrous thf (20 cm³) with a green solution of anhydrous $FeCl_3$ (13 mmol) in thf (100 cm³), the potassium decalated and the reaction solution darkened immediately.

The *X*-ray diffraction patterns show, apart from two very weak diffuse lines at *ca.* 0.347 and 0.247 nm (probably belonging to a graphite residue or the iron oxide compound γ-FeOOH), only the strong lines of KCl and graphite and, in addition, weak lines of an α-iron phase.

The Mössbauer spectrum of a sample which was obtained in this manner after a reaction time of 2 h, having been filtered, dried, and examined without any washing procedure and exposed to the air for 2 min, shows, besides the six lines of α-Fe (*ca.* 50% of the total absorption area), a doublet component [chemical shift, $\delta = 0.38$ mm s^{-1}, quadrupole splitting = 0.86_5 mm s^{-1}, relative to α-iron. (The spectra were fitted by the program MOESFIT, version TR 440, adopted by R. Skorczyk, Rechenzentrum Universität Konstanz)]. In the spectrum measured at 4 K this doublet had disappeared and only the magnetically ordered six-line systems of α-iron and iron oxides [γ-FeO(OH) and Fe_3O_4, $H_{\text{int.}}$ *ca.* 513 kOe (1 Oe = 1 $\text{cm}^{-\frac{1}{2}}$ $\text{g}^{\frac{1}{2}}$ s^{-1}), the lines are not resolved] were still present.[6]

It must therefore be concluded that the size of the particles of the iron present in the sample exceeds 3.0 nm. The distribution of the range of the iron-particle sizes is random, so that uniformity in the interlayer distances of the ferromagnetic and superparamagnetic iron particles and the graphite layers cannot be expected. After washing the sample several times with hydrochloric acid, the iron contents of the residue had been reduced to 3%.

We hope to have shown that the location and chemical composition of the iron particles in the system under discussion cannot be derived by *X*-ray diffraction only. Additional methods such as Mössbauer or *X*-ray photoelectron spectroscopy [7] are required.

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[0/807 *Received, 28th May,* 1980]

[1] D. Braga, A. Ripamonti, D. Savoia, C. Trombini, and A. A. Umani-Ronchi, *J.C.S. Chem. Comm.*, 1978, 927.

[2] D. Braga, A. Ripamonti, D. Savoia, C. Trombini, and A. Umani-Ronchi, *J.C.S. Dalton*, 1979, 2026.

[3] D. Braga, A. Ripamonti, D. Savoia, C. Trombini, and A. Umani-Ronchi, following reply.

[4] W. Rüdorff and E. Schulze, *Z. anorg. Chem.*, 1954, **277**, 156.

[5] R. Diebold and A. Herold, *Compt. rend.*, 1961, **252**, 1328.

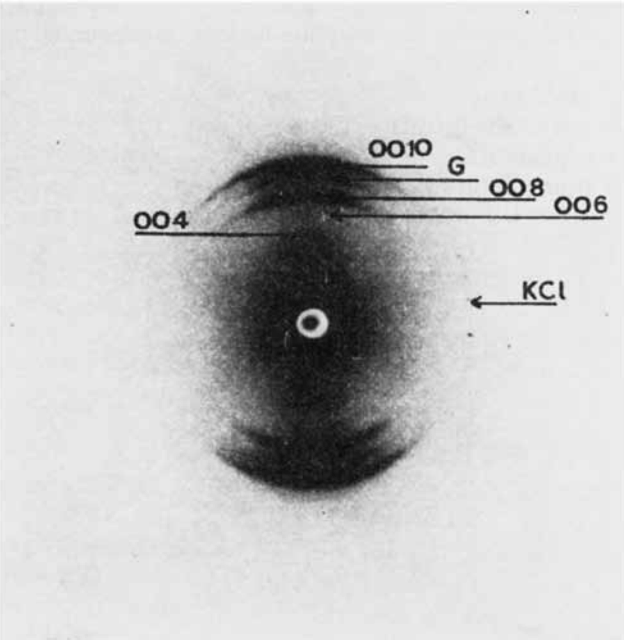
[6] S. M. Aharoni and A. H. Litt, *J. Appl. Phys.*, 1971, **42**, 352.

[7] R. M. Fischer, D. J. Smith, L. A. Freeman, S. J. Pennycook, and A. Howie, 14th Carbon Conference, Pennsylvania, 1979; *Carbon*, 1980, **18**, 54.

Braga *et al.* reply. Schäfer-Stahl states that the product obtained by reaction of potassium–graphite with $FeCl_3$ dissolved in tetrahydrofuran (thf), which we identified as graphite lamellar compounds of different stages,[1,2] is on the contrary a mixture of several heterogeneous phases such as KCl, Fe_3O_4, and γ-FeO(OH).[3]

However Schäfer-Stahl neglects that: (*a*) KCl cannot be present because our product was washed with water. On the other hand, we detected KCl Debye–Scherrer lines in unwashed oriented samples. These lines, which disappear after washing, are easily recognizable by their discrete nature. (*b*) If the γ-FeO(OH) phase is present, a Debye–Scherrer line at 0.329 nm should also be observed, together with the reported line at 0.621 nm, the intensity of the two lines being in the ratio 90 : 100. (*c*) The strongest line of Fe_3O_4 is at 0.253 nm and therefore should be clearly distinct from the line at 0.248 nm under our experimental conditions (Debye–Scherrer camera, diameter 114.6 mm, Fe-K_α radiation).

Furthermore, Schäfer-Stahl does not take into account that our indexing has been based mainly on the *X*-ray diffraction pattern of transition-metal lamellar compounds of graphite prepared from oriented pyrolytic graphite.[2] A typical *X*-ray diffraction pattern obtained from oriented iron intercalated pyrolytic graphite is shown in the Figure. As can be seen, oriented reflections corresponding to planes parallel to the carbon layers, together with the (001) reflections of graphite, are present. These reflections, which unambiguously indicate the formation of an intercalate compound, can be indexed as (001) reflections of stage 4 of iron–graphite lamellar compounds.



X-Ray diffraction pattern of unwashed oriented iron pyrolytic graphite recorded with a flat camera (sample-to-film distance 50 mm) using Cu-K_α radiation. The *c* axis of graphite is along the vertical and is perpendicular to the *X*-ray beam. Indexes of the reflections corresponding to the basal plane of stage-4 iron–graphite lamellar compounds (*c* = 3.15 nm) are given. G indicates the graphite reflections. Spots corresponding to the reflection at 0.315 nm of KCl are discernible

It must be noted that graphite powder (Roth) and oriented pyrolytic graphite (La Carbone Lorraine, Paris) give rise to products which differ somewhat in the ratio graphite : intercalate phase and in the relative proportions of different stages. These differences can be explained by considering the role that the nature of graphite (crystallinity, particle size, amorphous content *etc.*) plays in the chemistry of carbon intercalation compounds.[4]

Moreover, we observed that, even starting from the same graphite powder, we sometimes obtained irreproducible results since mixtures of intercalation compounds, iron oxide particles, and highly dispersed iron were observed. In fact the nature of the products is strongly dependent not only on the graphite, but also on several other factors such as salt and solvent dryness and reaction temperature. Best results were obtained by slowly pouring the deep brownish yellow solution of $FeCl_3$ (anhydrous salt purchased from Merck or Carlo Erba, used without further drying) into thf (distilled from sodium benzophenone ketyl) over a slurry of C_8K in thf, externally cooled with an ice-bath.

In conclusion, it is our opinion that the critical conditions of reaction may explain the failure of Schäfer-Stahl to prepare iron–graphite lamellar compounds.

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[1] D. Braga, A. Ripamonti, D. Savoia, C. Trombini, and A. Umani-Ronchi, *J.C.S. Chem. Comm.*, 1978, 927.

[2] D. Braga, A. Ripamonti, D. Savoia, C. Trombini, and A. Umani-Ronchi, *J.C.S. Dalton*, 1979, 2026.

[3] H. Schäfer-Stahl, preceding letter.

[4] A. Hérold, in ' Intercalation Layered Materials,' ed. F. A. Lévy, D. Reidel Publishing Co., 1979, vol. 6, p. 323.