NEUTRON DIFFRACTION AND SMALL-ANGLE SCATTERING STUDIES OF GRAPHITE–NICKEL CHLORIDE INTERCALATION COMPOUNDS

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Summary

Intercalation of graphite with metal chlorides leads to compounds for which chemical analyses give non-integer stoichiometric coefficients. In particular, an excess of chlorine is observed with respect to free metal chlorides. For $NiCl_2$ intercalated graphite, the composition of the second-stage compound corresponds to the formula: $C_{11.3}NiCl_{2.13}$. This chlorine excess was accounted for by assuming the existence of small islands of intercalated chloride. As $NiCl_2$–graphite compounds are known to undergo a magnetic phase transition at about 20 K, neutron scattering and diffraction experiments were carried out in order to provide evidence for the islands and to specify the magnetic ordering at low temperature.

From the small-angle scattering data collected below and above the magnetic transition, the first experimental evidence for the presence of intercalated islands has been obtained. The mean size of the islands is about 150 Å, as previously assumed. From diffraction experiments, it has been shown that the spins of Ni^{2+} ions in the magnetic phase are aligned ferromagnetically within the intercalant layer.

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1. Introduction

Although intercalation of metal chlorides into graphite has been known for several decades, our understanding of it is still very incomplete. One of the main problems is the role of chlorine gas, generally needed for the reac-

tion to occur. Chemical analyses give an excess of chlorine in the compounds with respect to free metal chlorides, which shows that chlorine is an essential member of the intercalation reaction. Moreover, it has been shown [1] from a bond length analysis that the charge transfer from graphite to metal chloride is determined by the chlorine excess.

It has been assumed that graphite is oxidized by chlorine before intercalation of metal chlorides. However, chlorine is known to intercalate graphite only below room temperature and not at temperatures where intercalation of metal chlorides occurs (300 - 600 °C). Dzurus and Hennig [2] have proposed that chlorine is present in the form of Cl^- ions, whereas according to Stumpp and Rüdorff [3] complex ions such as $AlCl_4^-$ or $FeCl_4^-$ would be formed. However no experimental evidence has been given for the presence of these ions. Another proposition, which cannot be ruled out, has been made by Hérold [4], namely, the existence of metal ion vacancies: the intercalant species would be a non-stoichiometric chloride (*e.g.*,: $Fe_{1-\epsilon}Cl_3$).

A few years ago, while studying the intercalation of nickel chloride, we proposed that the chlorine excess results from the existence of small islands (only ~ 100 Å in diameter) of $NiCl_2$ [5]. This model has been recently shown to be suitable for manganese chloride [1] and probably also for other metal chlorides. It is based on the following experimental facts: chemical analyses gave the limit composition $C_{11.3}NiCl_{2.13}$ for the second stage compound, whereas from the unit cell parameters of the graphite and $NiCl_2$ sublattice a composition of C_8NiCl_2 should be observed. Thus, the $NiCl_2$ layers are far from being complete. It must be noted that this conclusion is valid even with Hérold's assumption of metal vacancies: the ratios C/Ni = 11.3 and Cl/Ni = 2.13, given by chemical analyses, would correspond to a composition $C_{10.6}Ni_{0.94}Cl_2$ accepting this assumption. Moreover, analysis of diffuse diffraction lines due to nickel chloride showed that the coherence length in the $NiCl_2$ layers is about 100 Å. Thus, the simplest way to account for an incomplete filling of the layers is to assume them to be made up of $NiCl_2$ islands of diameter 100 Å. Such small islands allow an explanation for the chlorine excess as being due to chlorine atoms at the periphery of these islands. As an $NiCl_2$ layer consists of chlorine octahedra placed side by side with the nickel at their centers, a ratio Cl/Ni strictly equal to 2 is obtained only for an infinite layer. A straightforward calculation shows that for circular islands, a ratio Cl/Ni: 2.13 would correspond to an island diameter of 95 Å.

It is the purpose of this paper to provide direct experimental evidence for the existence of $NiCl_2$ islands, by means of small-angle neutron scattering. The main advantage of neutrons over X-rays, in this case, lies in the fact that $C_{11.3}NiCl_{2.13}$ exhibits a magnetic phase transition at about 20 K [6]. As this compound can be obtained in suitable quantity only in the form of polycrystalline powder, neutron diffraction experiments performed above and below the phase transition make it possible to distinguish between scattering due to islands or due to the powder particles themselves. Finally, neutron diffraction data have also been acquired in order to obtain information on the magnetic structure at low temperature.

2. Small-angle scattering study

(i) Experimental

The $NiCl_2$ compound was prepared from Madagascar natural graphite (100 - 1000 μm powder) and anhydrous nickel chloride from Merck. The mixture of powders was heated at about 600 °C for several days in a chlorine atmosphere. After reaction the products were washed with diluted HCl to remove the excess metal chloride. For analysis, the samples were oxidized in a Parr bomb, then chlorine and nickel were determined by titration. The amount of nickel was also obtained by gravimetry from the weight of NiO after burning the samples in air. Finally, the stage of the compounds was verified by examining the (00l) reflections obtained using a conventional X-ray diffractometer.

Small-angle scattering data were collected on the D17 neutron diffraction apparatus at the ILL, Grenoble. The wave-length was 9.36 Å and the sample-to-detector distance 2.82 m. Powdered samples were placed in a parallelepipedic container and counts were accumulated over a period of 90 min at each temperature. Measurements were made out to θ = 6.77° (Q = $4\pi \sin \theta /\lambda$ = 0.16 Å^{-1}). The temperature could be monitored from 4 to 300 K and an external magnetic field of about 9 kG could be applied in order to align the spins.

(ii) Results

Data were collected mainly at 100 K and 5 K, i.e., well above and below the magnetic transition. Figures 1 and 2 show typical isointensity contours obtained at these temperatures. It is seen that the scattering has an elliptical symmetry. Clearly, most of the small-angle scattering comes from the powder particles themselves. This is not radially symmetrical because of texture effects, i.e., the flat particles tend to pack with a certain orientation, resulting in elliptical scattering.
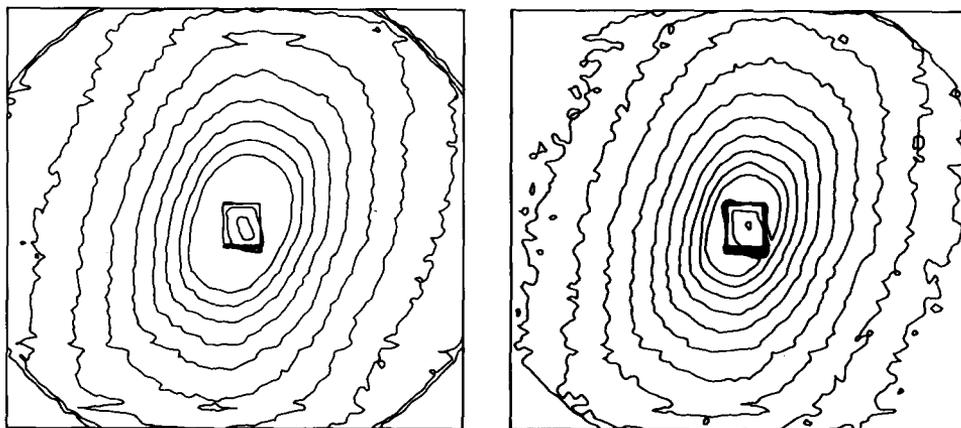

Fig. 1. Neutron small-angle scattering of $C_{11.3}NiCl_{2.13}$ at 100 K (isointensity contours).

Fig. 2. Neutron small-angle scattering of $C_{11.3}NiCl_{2.13}$ at 5 K (isointensity contours).
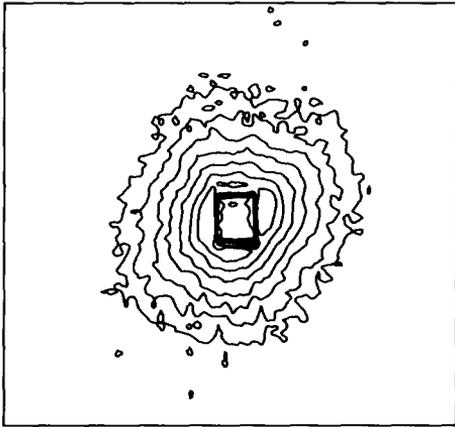
Fig. 3. Neutron small-angle scattering of $C_{11.3}NiCl_{2.13}$: difference plot (100 K)—(5 K).
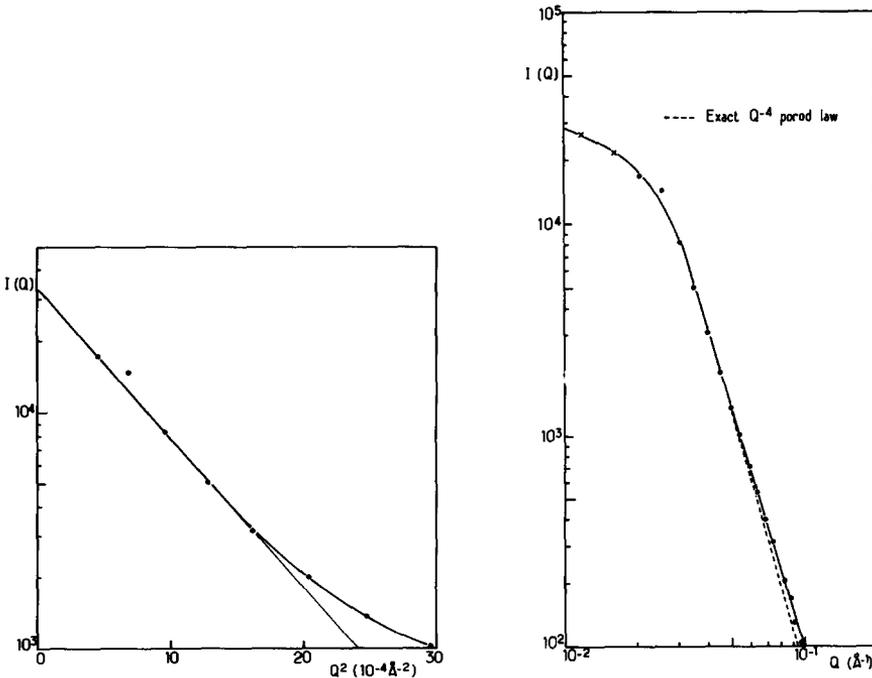

Fig. 4(a). Guinier plot of small angle scattering. (b) Porod plot of small angle scattering.

The difference plot (Fig. 3) does show radially symmetric scattering (circles), however. This is to be expected since the difference represents the magnetic small-angle scattering only, which can be attributed to $NiCl_2$ islands. The circularly averaged intensity derived from Fig. 3 is plotted in Fig. 4(a) and (b). Figure 4(a) shows that the Guinier approximation [7], $I(Q) \sim$ exp-$(-Q^2 R_g^2/3)$, is obeyed for this material to $Q \sim 0.04$ Å^{-1}, and from the slope of this straight line, $R_g \sim 66$ Å. Here R_g is the radius of gyration of the

islands, a dimension analogous to that of classical mechanics of rigid bodies wherein mass is replaced by atom density. Depending upon the exact shape of the islands the diameter is calculated to range from 130 to about 170 Å.

This is the order of magnitude expected from chemical analyses and X-ray diffraction experiments [5]. Thus, the neutron difference scattering has made it possible to separate the contribution of the $NiCl_2$ islands from the (much larger) remainder, whereas with only X-ray small-angle scattering, incorrect results would have been obtained.

If the graphite host and $NiCl_2$ intercalated islands both have uniform electron densities and the interface between each is sharp, the Porod law will be verified [8]. A graph with ordinate and abscissa as in Fig. 4(b) will have a negative slope, *i.e.*, for $Q \to \infty, I(Q) \sim Q^{-4}$. The departure from the exact Q^{-4} dependence indicates the presence of density fluctuations in the intercalated material. This will be discussed in detail in a separate publication.

3. Neutron diffraction study

Much attention has been paid to pristine nickel chloride because it belongs to that special class of materials known as "meta-magnets", which exhibits an antiferromagnetic state which can be ferromagnetically saturated in relatively weak magnetic fields. Its crystal structure is of the $CdCl_2$ type and the magnetic structure [9] consists of strongly-coupled ferromagnetic sheets of spins with successive planes weakly coupled antiferromagnetically (Fig. 5). However, to our knowledge, the spin direction in the hexagonal plane has not been determined as yet.

As the $NiCl_2$ layer intercalated into graphite has a structure very close to that of the parent material [5], it is expected that the in-plane ferromagnetic interaction is unchanged, whereas the antiferromagnetic coupling between successive layers is strongly decreased by the introduction of two carbon layers in-between (second-stage compound). Indeed, the magnetic behavior of pristine and intercalated materials, although similar at high temperature, is quite different at low temperature ($T < 100$ K). In the vicinity of the Néel temperature of pristine $NiCl_2$ ($T_N \sim 52$ K), only short range order fluctuations begin to appear in the intercalated compound [10], and a magnetic transition occurs at about 20 K, as seen by specific heat and low-field magnetic susceptibility experiments [6, 11]. The shape of low field susceptibility *vs.* temperature may suggest a spin–glass or spin–cluster–glass behavior [12]. The actual nature of the transition is not elucidated, however. Neutron diffraction should allow the precise determination of the magnetic structure below the transition and, in addition, the width of magnetic peaks should give an estimate of the island size in agreement with small-angle scattering.

(i) Experimental

Diffraction data were collected on the D1B neutron diffractometer at the ILL, Grenoble (wavelength: 2.515 Å). About 3 g of powdered sample of
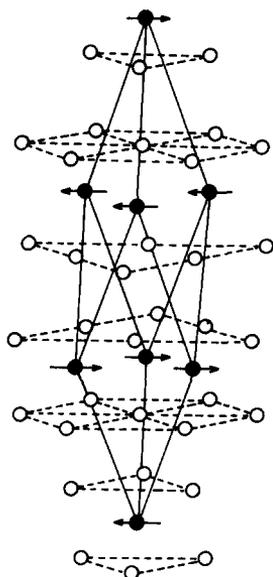
Fig. 5. Crystal and magnetic structure of pristine $NiCl_2$ (from ref. 7).
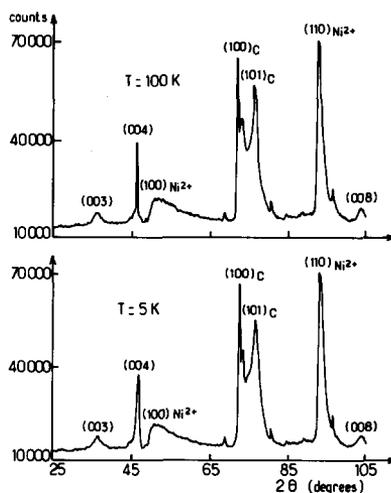
Fig. 6. Neutron diffraction of $C_{11.3}NiCl_{2.13}$: spectra at 100 K and 5 K.

the second-stage $NiCl_2$ compound were placed in a vanadium container. Spectra were obtained at 300 K, 100 K, 50 K and 5 K, with a counting period of several hours at each temperature. Spectra were obtained in the same way on a sample of pristine graphite for comparison.

(ii) Results

Figure 6 shows the spectra at 100 K and 5 K for the intercalation compound. Recalling the unit cell parameters obtained by X-ray diffraction [5] ($C = 12.65$ Å, $a_{graphite} = 2.461$ Å and $a_{NiCl_2} = 3.48$ Å), the peaks can be indexed as given in Fig. 6.

At first view the spectra above and below the magnetic transition appear very similar. However, the difference (5 - 100 K) diagram (Fig. 7) reveals two clear magnetic peaks at $d = 2.99$ Å and $d = 1.73$ Å. These peaks can be indexed as (100) and (110) reflections of the $NiCl_2$ lattice. This means that the nickel atoms have their spins aligned ferromagnetically within the Ni planes, as in $NiCl_2$. Moreover, within the accuracy, there is no extra peak at 5 K corresponding to a superstructure along the C-axis. This indicates that alternate layers are not ordered antiferromagnetically, unlike $NiCl_2$: introduction of two carbon layers between magnetic planes seems to suppress the magnetic coupling between these planes. This result is consistent with the disorder observed by X-ray diffraction and with magnetic measurements on several metal chloride—graphite compounds: no significant stage dependence for the transition temperature was found from second-stage to higher-stage compounds [13].
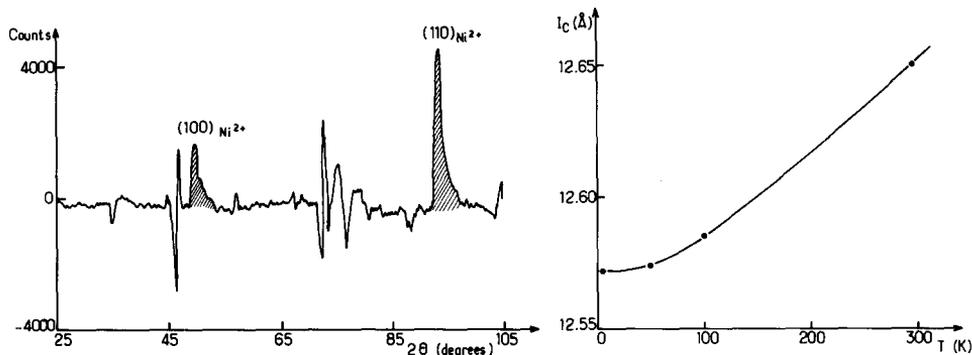
Fig. 7. Neutron diffraction of $C_{11.3}NiCl_{2.13}$: difference diagram $(5\ K) - (100\ K)$. The magnetic peaks are hatched.

Fig. 8. Temperature dependence of the C-axis repeat distance I_c of $C_{11.3}NiCl_{2.13}$.

From the width of the (100) and (110) $NiCl_2$ magnetic peaks, it is possible to obtain an estimate of the size of $NiCl_2$ entities. For both peaks the Scherrer formula gives about 200 Å, which is of the same order of magnitude as the value obtained for $NiCl_2$ islands from small-angle scattering.

Finally, Fig. 7 shows that the other peaks of the spectra are shifted due to the thermal contraction. Examination of the $(00l)$ reflections gives the temperature dependence of the C-axis lattice constant I_c, as shown in Fig. 8. An expansion of I_c by 0.078 Å is observed when the temperature is raised from 5 K to room temperature. This expansion is comparable with that obtained recently [14] for a stage 1 graphite–$FeCl_3$ sample between 4.2 and 298 K (0.071 Å). Figure 8 indicates that most of the change occurs above 100 K. The room temperature value of the thermal expansion coefficient is found to be about $4 \times 10^{-5}/K$, which is the expected order of magnitude.

4. Conclusion

Neutron small-angle scattering experiments, corroborated by a neutron diffraction study, have shown that nickel chloride intercalates graphite in the form of small islands. This is the first experimental evidence for the presence of intercalated islands of metal chloride. Recent electron microscopy experiments also give evidence for the existence of islands [15]. In addition, neutron diffraction indicates that the spins of Ni^{2+} ions in the magnetic phase are aligned ferromagnetically within the intercalant layer.

The existence of such small islands allows an explanation of the excess chlorine and the non-integer stoichiometric coefficients given by chemical analyses. It also provides novel ideas on the essential role of a chlorine atmosphere and finally on the mechanism of intercalation itself. In addition, such two-dimensional arrays of about 1000 magnetic ions should be at the root of the particular magnetic behavior of these materials, which is not understood as yet.

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