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Intercalation compounds of cadmium chloride in graphite: formation, structural data and electrical resistivity

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The progressive intercalation of $CdCl_2$ in natural graphite and pyrocarbon, as well as its desorption, has been studied. The evolution of the products obtained has been followed by X-ray diffraction. The characteristics of the saturated product are given. The electrical resistivity $\rho_{\parallel}$ of the products has been studied as a function of temperature for a product with a high proportion of $CdCl_2$ and as a function of halogenide content for various other compositions. The value of $\rho_{\parallel}$ is compared to that of various other products.

1. Introduction

Significant modifications in the properties of graphite occur by intercalation of compounds between graphitic planes; particularly, the electrical resistivity $\rho_{\parallel}$ parallel to the planes and the magnetic anisotropy are smaller. We have pointed out that the decrease in $\rho_{\parallel}$ with increasing amount of $FeCl_3$ is less than with bromine or $GaCl_3$ [1]. Formerly, Rudorff *et al.* had reported that X-ray diffraction patterns of $FeCl_3$– or $CdCl_2$–graphite and those of bromine or $GaCl_3$ graphite are different in that additional diffraction lines appear on the former. These lines were interpreted as being due to a possible array of the reactant [2]. It seemed to us that detailed studies of well-oriented graphite–$CdCl_2$ would allow previous data to be completed.

2. Experimental

Natural graphites (Madagascar, Graphoil in flakes or powder) and pyrocarbon H.T.T. 3000°C have been used. Pyrocarbon is a step in the synthesis of graphite. Although it does not reach the crystalline perfection of the best natural graphites, it is available in large pieces. The required size of samples can thus be obtained for electrical and kinetic measurements. Immediately prior to use, cadmium chloride is melted under a stream of chlorine. The best results are obtained when the graphite samples are immersed in molten cadmium chloride at 575°C in the presence of a stream of chlorine (5 ml min^{-1}). After treatment, the surface of the sample is "cleaned" by heating to steady weight at 540°C under a mixed chlorine–$CdCl_2$ vapour stream. With $CdCl_2$ vapour at 535°C, intercalation is slower than with the molten salt. Non-saturated compounds are obtained by desorption of higher concentration compounds above 535°C rather than by stopping intercalation at a given level. The crystallographic *c*–axis (perpendicular to the planes) is easily identified in intercalation compounds from natural graphites and, to a lesser extent, from pyrocarbon. X-ray diffraction patterns were therefore obtained with a simplified "rotating crystal" method and CuK_{α} radiation; the X-ray beam is filtered, though in special cases, it is used as it is. At sample scale, a $1 \times 1 \times 0.2$ mm^3 sample is adequate to gauge the sample homogeneity. The resistivity $\rho_{\parallel}$ of samples is determined by a contactless method [3, 4] which also yields the magnetic anisotropy $\Delta\chi = \chi_{\perp} - \chi_{\parallel}$. The samples are cylindrical ($\phi = 5$ mm, thickness a fraction of a millimeter before intercalation). The cylinder axis is parallel to the *c*-axis of the graphite, which is a pyrocarbon H.T.T. 3000°C such that before intercalation $\rho_{\parallel} = 42.0$ μΩ cm, a value close to that of the best natural graphites. The determination of thickness for the intercalation compounds is made under adequate pressure; the thickness decreases first when pressure is applied but then reaches a steady value which is maintained.

3. Results and discussion

3.1. Composition of compounds, intercalation and desorption kinetics

In Fig. 1, macroscopic expansion e/e_0 (e_0 = original thickness) is shown as a function of total $CdCl_2$ content for samples during progressive intercalation or desorption. As in the case for bromine [5], maximum expansion is reached before the final composition. The action of molten $CdCl_2$ on graphite leads to the clearest phenomena. By direct determination of weight, saturation seems to be reached for $\Delta m/m_0 \approx 2.30$ (m_0 = weight of graphite). Although it does not pass through the origin ($e/e_0 = 1$), the desorption curve follows the "ideal" relation for which the expansion e/e_0 would be a linear function of the concentration. This curve reaches the value $e/e_0 = 2.85$ (corresponding to a first stage as determined by X-ray diffraction) for $\Delta m/m_0 = 2.26$, the value which we accept for saturation.

In Fig. 2, the intercalation kinetics for $CdCl_2$ vapour at two different temperatures is shown. At 560°C, the rate of reaction is greater than at 535°C but the ultimate concentration at 560°C is lower. Intercalation rarely occurs after 570°C while $\Delta m/m_0$ reaches the value 2.26 at 535°C. It thus seems that the vapour pressure of high-concentration compounds ($\Delta m/m_0 > 1$) shows an important increase (as compared to pure $CdCl_2$) close to the melting point of the chloride. We have also observed that a saturated compound obtained at 560°C ($\Delta m/m_0 = 0.95$) brought to 535°C continues its intercalation although it had only been treated at 535°C. On the other hand, a compound with $\Delta m/m_0 = 1.53$, heat-treated from 535 to 560°C, is decomposed until its content becomes constant and $\Delta m/m_0 = 1.22$. This value is greater than that observed during direct intercalation. X-ray diffraction studies have given an explanation of these facts by revealing differences in homogeneity between the two compounds in spite of long-time annealings.

3.2. X-ray diffraction studies

The X-ray diffraction pattern given by a saturated compound obtained from natural graphite (motionless sample with the c-axis parallel to the X-ray polychromatic beam) shows near its centre six sets of spots symmetrically spaced along six radii separated by angles of 60° and thus indicating a six-fold symmetry about the c-axis. With a filtered beam the pattern is the same (except for the absence of the $K\beta$ spots). The persistence of these spots seems to indicate that the intercalation com-

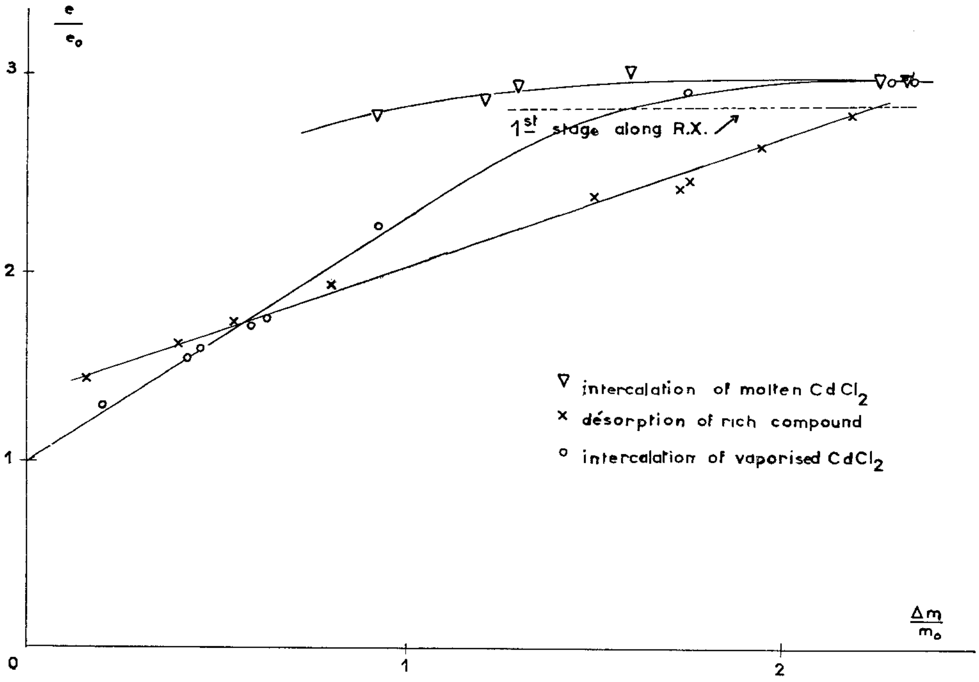

Figure 1 Macroscopic sample-expansion along the c-axis as a function of intercalated compound content.

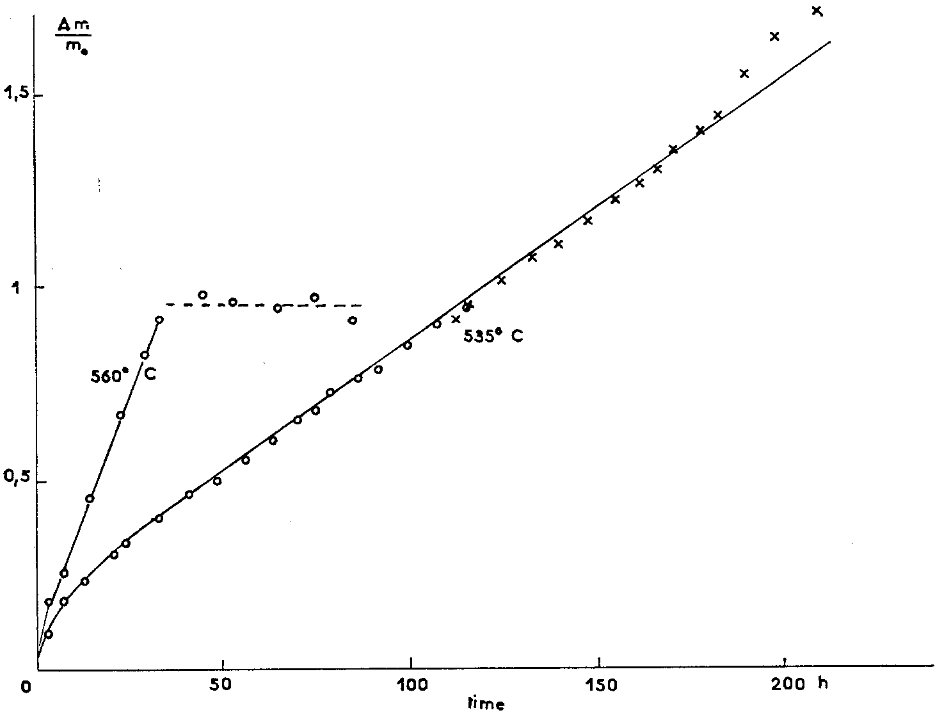

Figure 2 Rate of intercalation as a function of time for two temperatures.

pound is not as monocrystalline as was (or nearly was) the original graphite, and that it is made up of crystallites with their *c*-axis included within a cone. What we previously called the *c*-axis actually corresponds to the axis of the cone. The half angle at the apex of the cone is about 12° as calculated from the position of the most intense spots if one adopts this interpretation. If the same sample is set with its *c*-axis parallel to the axis of rotation and perpendicular to the X-ray beam, the diffraction pattern includes spots elongated perpendicularly to the equatorial line. With respect to the centre, the corresponding angle is close to 12°, confirming the previous interpretation. The elongation of the spots and their scarcity however make it difficult to accurately evaluate the identity period along the *c*-axis that this type of X-ray picture should normally provide. The spots closest to the equatorial line corresponds roughly to 26 Å, so that one can be sure that the identity period I_c is greater than 26 Å. Finally, if the sample is set with "*c*-axis" rotating in the plane perpendicular to the axis of rotation and containing the filtered beam, the diffraction pattern is quite different from that of graphite but includes well-defined spots which roughly correspond to those expected from the basis of the pure $CdCl_2$ lattice ($a = 3.84_4$ Å) close to the $00l$ (and perhaps hkl) spots on the equatorial line. It is hardly possible to accept that the $CdCl_2$ molecules in the intercalated layer could be in the same position as in the pure product since the maximum content would then be much greater than the 2.26 value which has been determined. It is therefore likely that the chlorine atoms, ionized or not, are placed partially at the spots where $CdCl_2$ molecules should be. On the basis of a regular 2 $CdCl_2$, 1 Cl pattern instead of 3 $CdCl_2$, the value $\Delta m/m_0 = 2.29$ is calculated close to the value measured. X-ray patterns give little information when obtained from saturated pyrocarbon samples, except when the sample is placed with its *c*-axis in the plane of the beam; in this case, narrow and well-defined spots which lie on the equatorial line can be indexed as being $00l$, as shown in the following table:

Observed d values in Å units	Relative intensitives
4.818	Strong
2.409	Strong
1.924	Weak
1.609	Strong
1.377	Weak
1.203	Strong

These distances are sub-multiples of 9.63_5 Å which is close to the sum of the thickness of a $CdCl_2$ layer (5.84 Å) and a graphite interlayer distance (3.35 Å). Along with Rudorff [6], we think that we are dealing with a first stage compound whose identity period I_c is a multiple of 9.63_5 Å. When the halide content of the compound is lower than in the saturated compound, a new set of lines appears (along with those pertaining to the first stage) which we have attributed to a second stage with $I_c = 12.9$ Å or a multiple thereof. With still lower contents, a third stage seems to occur with $I_c = 16.4$ Å or a multiple thereof. Finally, the graphite spectrum reappears.

In brief, the $CdCl_2$ intercalated layers seem to be organized in a fashion similar to that of the pure product. This behaviour is different to that shown by graphite in KC_8, for instance, since the carbon layers do not seem to impose their organization upon the intercalated species, at least as regards short distance effects. The crystallographic lattice is most probably hexagonal with large parameters.

These results have all been used to study the homogeneity of the samples used in the electrical measurements to make sure the latter have a physical meaning. After the electrical measurements were performed, samples were taken both from the periphery and the heart of the blocks and were oriented so that the $00l$ spots would show on the diffraction pictures. Except for the case of the saturated compound, the samples show an important lack of homogeneity which, in extreme cases, goes as far as the presence of first and second stage areas at the periphery and unaltered graphite at the heart in spite of the lengthy annealing to which the block was submitted. As a general rule, the lack of homogeneity increases with the dilution of the halide especially when $\Delta m/m_0 < 1.13$. Lastly, samples obtained by desorption of richer compounds are, for a given content, more homogeneous than those obtained by direct intercalation.

The presence of inhomogeneity seems to be due to a number of causes. On one hand, first and second stage compounds seem to be the only stable ones between 535 and 650°C. On the other hand, the vapour pressure of $CdCl_2$ at about 550°C is low, being merely 3 mm Hg at 722°C [7], which may explain the very slow diffusion of the halide. The intercalated product will meet and even perhaps increase pre-existing defects of the carbon lattice; it must necessarily proceed between the carbon layers. Should a product be formed at the periphery of a sample, the part of the graphite which has not yet been altered will only be subjected to the vapour pressure p_2 of the compound which has been formed, with $p_2 < p_1$ where p_1 is the vapour pressure of pure $CdCl_2$; p_2 may be such that at a given temperature, local intercalation equilibrium conditions are not met or are "below" the intercalation threshold. Similar processes may occur during desorption so that the part rich in $CdCl_2$ may be practically blocked.

3.3. Electrical resistivity as a function of content and temperature coefficient of the saturated compound

Fig. 3 shows only the $\rho_{\parallel}$ values for graphite-$CdCl_2$ compounds with $\Delta m/m_0 > 1.13$. Below this value, the samples were not sufficiently homogeneous in spite of the annealing. The dispersion in $\rho_{\parallel}$ values is in accordance with the X-ray data and confirms the fact that the chloride is localized within the sample. In the figure, contents are given in $\Delta m/m_0$ values but also as a function of the ratio X/C of intercalated moles per atom of carbon. This latter means of presentation is not as rigorous as the previous one since it does not take into account the slight excess of chlorine but it does nevertheless suggest an interesting comparison with the result obtained from other compounds. The $\rho_{\parallel}$ curves obtained from the $FeCl_3$ and $CdCl_2$ compounds are very close and are both clearly different from those obtained with the bromine-$GaCl_3$ group [1]. The similarity between the $FeCl_3$ and $CdCl_2$ compounds is not immediately evident because of the difference in properties of the cations, neither is it evident if one supposes that the excess chlorine which is present in both cases in the ionic form is the only species responsible for the decrease in $\rho_{\parallel}$, since the role of $GaCl_3$ can then no longer be understood. We feel rather that the reason lies in the persistence of a two- or three-dimensional crystalline lattice for the intercalated species.

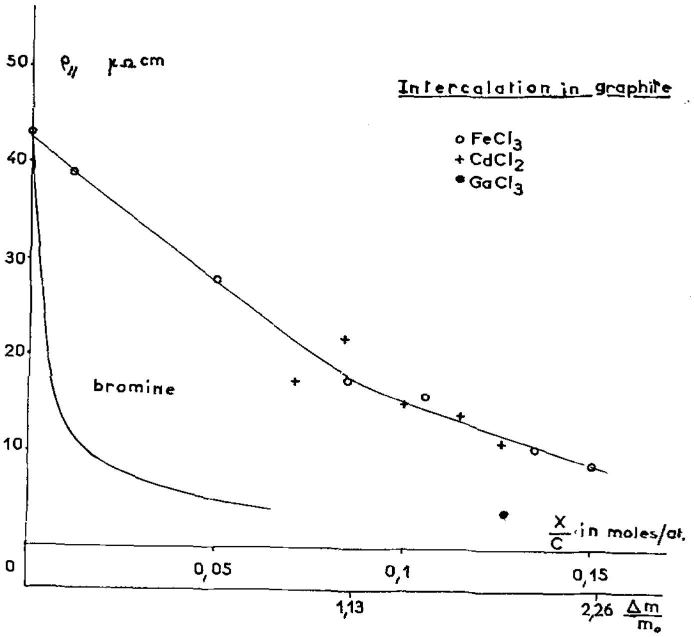

Figure 3 Change in $\rho_{\parallel}$ with content for compounds of $CdCl_2$, $FeCl_3$, bromine, $GaCl_3$ with graphite.

The temperature coefficient of $\rho_{\parallel}$ for a nearly saturated compound chosen for its homogeneity and with $\Delta m/m_0 = 1.95$ is nearly constant between 77 and 298 K.

$$\frac{\Delta\rho_{\parallel}\,{}_{77\mathrm{K}}{}^{298\mathrm{K}}}{\rho_{\parallel\;298\mathrm{K}}} = 0.73$$

with $\rho_{\parallel\;298\mathrm{K}} = 10.8 \times 10^{-6}$ Ωcm.

4. Conclusion

Our results show that, among all the graphite-$CdCl_2$ which were studied, the saturated compound obtained from natural graphite is the best defined. In the case of this compound, the intercalated cadmium chloride lies in a way which is reminiscent of that of free cadmium chloride; the graphite does not seem to impose the organization of the carbon planes, as is the case in KC_8. When the content is lower than in the second stage compound, we were unable to obtain products sufficiently homogeneous, even after long annealing periods, as shown by X-ray diffraction. The $\rho_{\parallel}$ versus halide content curves are practically identical in the case graphite-$CdCl_2$ and graphite-$FeCl_3$ compounds, and are clearly different from those obtained with graphite-bromine or graphite-$GaCl_3$. The temperature coefficient of $\rho_{\parallel}$ in saturated graphite-$CdCl_2$ indicates a metallic character.

References

1. J. F. BOISSONNEAU and G. COLIN, *Carbon* **11** (1973) 567.
2. W. RUDORFF and R. ZELLER, *A. Anorg. u. Allgem. Chem.* **279** (1955) 182.
3. G. COLIN and C. MAZIERES, *J. Chim. Phys.* **67** (1970) 323.
4. G. COLIN and R. SETTON, **64** (1967) 287.
5. G. A. SAUNDERS, A. R. UBBELOHDE and D. A. YOUNG, *Proc. Roy. Soc.* **271A** (1963) 499.
6. W. RUDORFF and H. SCHULZ, *Z. Anorg. u. Allgem. Chem.* **245** (1940) 121.
7. TARASSENKOFF and KOJMIAKOFF, *J. Chim. Gen.* **5** (1935) 830.

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