Charge Transfer and Diamagnetism of Halogen Residue Compounds of Pyrocarbons and Their Hysteretic Behavior at High Temperatures

André Marchand and Patrick Espelette
Centre de Recherche Paul Pascal (CNRS)
Université de Bordeaux I
Domaine Universitaire - 33405 Talence, France

The diamagnetic susceptibilities and Hall coefficient of bromine and iodine chloride residue compounds of pyrolytic carbons (P.C.) deposited at 2100°C ("Le Carbone-Lorraine") were measured at room temperature, at liquid nitrogen temperature, and also during heating-cooling cycles between 300 and 850 K. Some pyrocarbons had been doped during their deposition with various amounts of boron (400 and 1000 ppm). Samples of the same carbons have been used in a previous study of sodium intercalation[1].

Intercalation resulted from the direct action of ICl vapor or liquid Br_2 on the carbons, and the STABLE residue compounds were obtained from subsequent exposure of several days or weeks to ambient air at room or higher temperature, up to 850 K. The presence of boron does not seem to have any influence on the amount of intercalate that P.C. are able to retain in these conditions.

Hall effect studies were made at 77 and 300 K (with magnetic field perpendicular to the carbon plane of deposition), and usually no change in the Hall coefficient was observed between these temperatures: it then was assumed that charge carriers of a single type were responsible for the electrical conduction, and their concentration N was computed from the Hall coefficient values.

Results

The charge transfer parameter f for boron is the ratio of the hole concentration N per carbon atom to the boron content of the pyrolytic carbon. We found an average value f = 0.5 slightly smaller than the 0.7 value given by previous authors for both graphite[2] and pyrocarbons[3]. But figure 1, where the diamagnetic anisotropy is plotted vs. the hole concentration N, shows clearly that the diamagnetic anisotropy of boronated P.C. is smaller by at least a factor of 2.5 than that measured[2] for boron-graphite with the same hole concentration. It may then be concluded that, although the boron doping efficiency is about the same (0.5-0.7 hole per boron atom), its effect on the diamagnetism is much stronger in pyrolytic carbons than in graphite.

For Br_2 and ICl, the charge transfer factor f (number of holes donated to the π valence band by each intercalate molecule) can be computed from the total hole concentration N and from the boron and intercalate contents of the samples. With atomic Br_2/C ratios ranging from 0.011 to 0.028, we found f

values between 0.02 and 0.07 electronic charge per Br_2 molecule, with a most probable value about 0.05. Results for ICl-compounds (ICl/C = 0.009) give a charge transfer coefficient of 0.07 per ICl molecule, quite close to that of Br_2.

Figure 1 also presents the diamagnetic anisotropy $\chi_c - \chi_a$ of all these P.C.-Br_2 and P.C.-ICl compounds as a function of their hole concentration deduced from the Hall effect. It shows as well the behavior of graphite-ICl compounds computed from the experimental results published by Okura and coworkers[3], with the assumed f = 0.07 value. Unfortunately there are no reliable values of the diamagnetic anisotropy of GRAPHITE-bromine intercalation compounds. Examination of figure 1 allows us to state the following facts.

1. Boron doped graphite and graphite-ICl behave very similarly.

2. P.C.-Br_2 and P.C.-ICl also behave very similarly, with nearly the same values of the charge transfer per intercalate molecule.

3. But boron doped pyrolytic carbons behave very differently from P.C.-Br_2 and P.C.-ICl, and those P.C.-Halogen compounds also behave very differently from their graphite-ICl homologs.

4. Generally speaking, for a given hole concentration, the magnitude of the diamagnetic anisotropy of P.C.-Halogens is larger than that of boronated P.C. and smaller than that of doped or intercalated graphite. It tends to behave like B-P.C. at high hole concentrations and to reach the B-graphite or graphite-ICl level at low hole concentrations.

The reasons for such different behaviors undoubtedly lie in the quasi-two-dimensional structure of pyrocarbons, as opposed to the three-dimensional ordering of graphite.

Temperature cycles

It had already been noticed (5,6,7,8,9) that bromine residue compounds, and to a lesser extent also ICl compounds, show a remarkable hysteresis of their dimensional changes and mechanical and electronic properties (diamagnetism, resistivity,... etc.) when submitted to heating and cooling cycles above room temperature. We investigated further this phenomenon by measuring the Hall coefficient of some samples during such cycles up to 850 K.
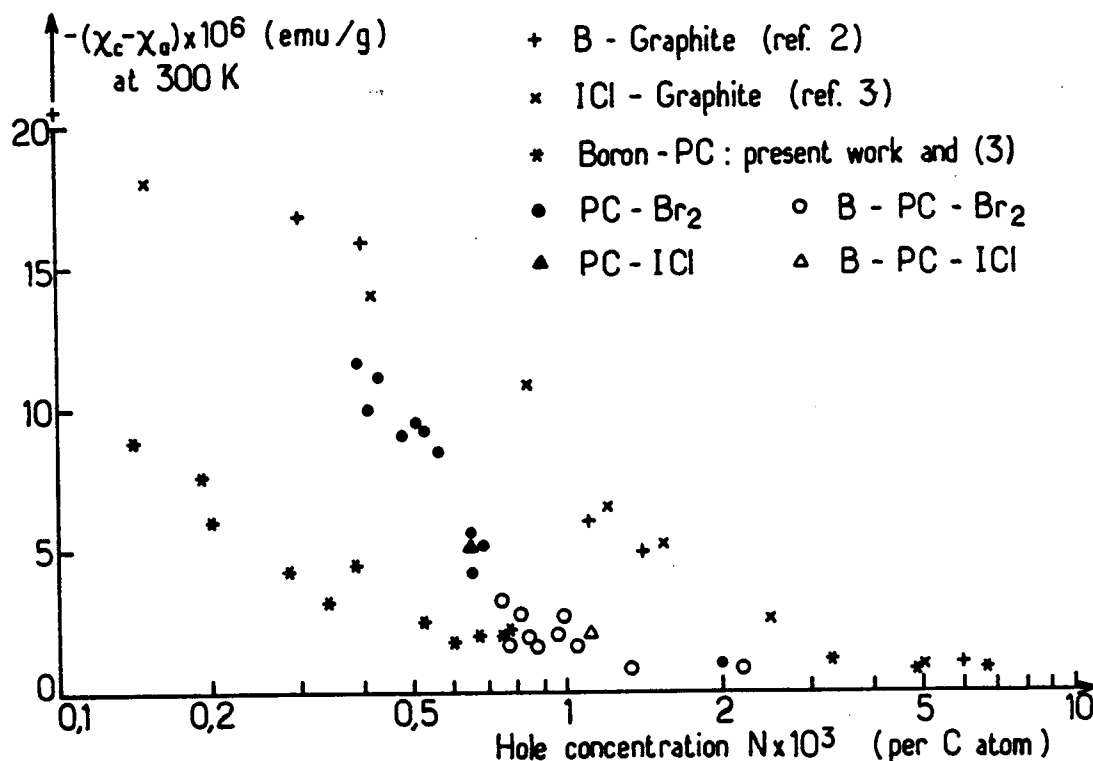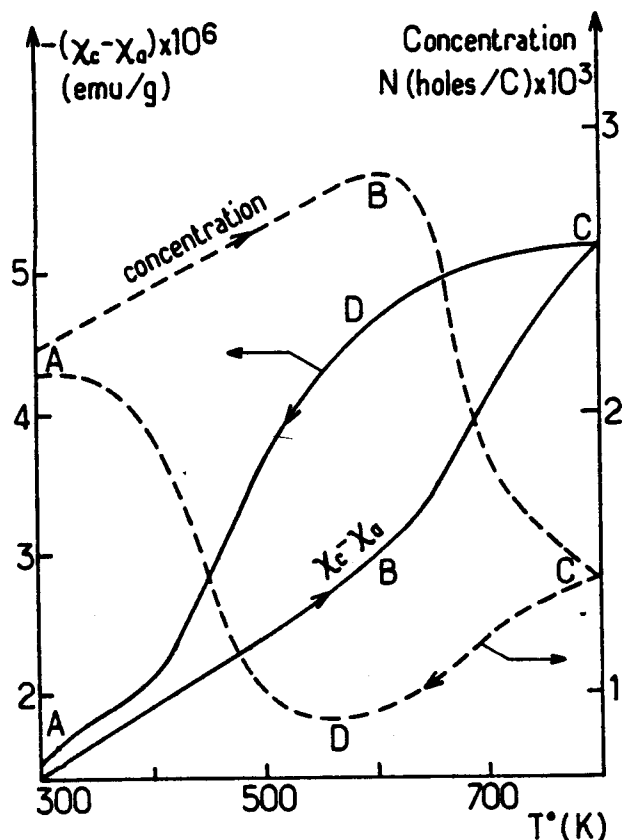
Figure 1

Figure 2. Samples of bromine residue compounds of P.C. doped with 400 ppm of boron (0.04 Br_2 molecule per C atom): variations of the diamagnetic anisotropy (full line) and of the hole concentration (dashed line) during heating from 300 to 800 K and subsequent cooling down.

The Hall effect of bromine residue compounds exhibits large hysteresis loops, which are an evidence of the corresponding changes of the hole concentration: figure 2 shows an exemple of the simultaneous variations of the hole concentration N and of the diamagnetic anisotropy $X_c - X_a$ with heating and subsequent cooling. Smaller loops may also be observed with ICl compounds.

We suggested in 1972 a model [8], which explained the ABCDA cycle of the diamagnetic anisotropy (figure 2) by a succession of intercalations (AB and DA) and de-intercalations (BCD) of bromine. The increases (AB, DA) and decreases (BC, CD) of the hole concentration in figure 2 are an excellent confirmation of these hypotheses.

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