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Carbon Vol. 23, No. 5, pp. 493–500, 1985
Printed in the U.S.A.

0008-6223/85 $3.00 + .00

DOPED CARBON BLACK CATALYST SUPPORTS: I. CHARACTERIZATION BY MAGNETIC SUSCEPTIBILITY AND ESR SPECTROSCOPY

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(*Received* 27 *August* 1984; *in revised form* 13 *November* 1984)

Abstract—As-received Monarch carbon blacks (MC) from Cabot, graphitized carbons (GMC), desulfurized Carbolac-2, and CSX-203 were characterized by magnetic susceptibility and ESR spectroscopy at room temperature and those in the cryogenic range. The MC samples showed normal Langevin-type diamagnetism, whereas the GMC showed a temperature-dependent Landau diamagnetism. From this, the degeneracy temperature, the effective electron mass of the delocalized electrons, and the Fermi level (E_F) were estimated, assuming the approximations of a "two-dimensional electron gas" model for graphite. The GMC was doped with boron at the ppm level at heat treatment temperatures (HTT) of 2073 and 2773 K. Boronation at low HTT indicated that boron atoms could enter the interstitial or defect sites, in addition to the substitutional (sp^2) sites, whereas boronation at the higher HTT showed that all boron atoms entered at the substitutional sites. ESR studies indicated a lowering of g-values, and half-line widths, and a ten-fold decrease in the spin concentration as a result of boron doping. A transition from Landau to almost Langevin type diamagnetic behavior was observed; a decrease in diamagnetic susceptibility corresponded to a lowering in the E_F level of the carbons. Shifts in the E_F have been estimated as a function of boron doping. In a sequel to this paper, the preparation of Fe catalysts on the above carbon supports are presented along with their magnetic, Mössbauer, and CO-hydrogenation studies. A rationale for changing the electronic properties of the substrate by boron doping is given, in relation to changing the properties of supported metal (M_1) by "alloying" it with another metal (M_2) to form the so-called "bimetallic" clusters.

Key Words—Carbon black, magnetic susceptibility, ESR, boron.

1. INTRODUCTION

In recent years, Walker, Vannice and their coworkers have shown that commercially available carbons and graphitic carbons can be used as inexpensive supports not only for precious metals such as Pt[1], but also for abundant metals such as Fe[2]. Additional studies by Jung *et al.*[3] as well as by Mulay *et al.*[4] have further shown that small Fe particles can indeed be produced by the impregnation of $Fe(NO_3)_3$ on carbons[3] and that the Fe/carbons can be used as hydrogenation catalysts[2–4].

Carbon with a electronic configuration of $1s^22s^2sp^2$ forms an sp^2 hybridization in graphite, wherein each carbon is bonded to three others by σ-bonding while the π-electrons form a delocalized (itinerant) electron cloud above and below a given plane. Boron, with one electron less than carbon and with a similar hybridization, can enter substitutionally into a graphite lattice, and hence alter its Fermi level. Thus, boron has been known to be a good electron acceptor. The present work was undertaken to explore whether or not a change in the Fermi level of the as-received (or "amorphous") and graphitized commercial carbons could be altered by successive doping with boron. In recent years several workers have used bimetallic clusters to see if catalytic activity can be changed by this procedure. In the present case, we have attempted to see if any changes can be brought about by modifying the carbon substrate with boron. Magnetic susceptibility and ESR spectroscopy were chosen as probes for elucidating the electronic properties and deriving the band parameters for various carbons. In this paper such aspects of characterization are reported.

2. EXPERIMENTAL

2.1 *Description of samples*

The various carbon blacks used in this study as catalyst supports were Monarch 700 carbon black (MC), Carbolac-2 (C-2), and CSX 203 (CSX), which were supplied by Cabot Corporation. The Monarch 700 carbon black was graphitized by Airco Speer Carbon. As-received (AR) carbon blacks showed significant amounts of sulfur impurities; hence they were treated at ~1273 K for 12 hr under flowing H_2. This desulfurization (DS) treatment reduced the sulfur content by a significant amount, as seen in Table 1. The boron-doped samples were prepared as described below. A requisite amount of boric acid (H_3BO_3) was weighed and dissolved in 15 ml of distilled water, to which a weighed amount of graphitized Mon-

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arch 700 carbon black was slowly added with gentle stirring so as to obtain a homogeneous slurry. This mixture was then dried in an oven at 393 K for 12 hr. The sample was placed in a graphite container and heated in a graphite tube furnace under a 0.1 MPa of flowing Ar atmosphere at either 2073 or 2773 K treatment temperature (HTT). Boron loadings, the HTT (Heat Treatment Temperature) employed, the duration of the HTT, and a brief description of various samples are also shown in Table 1. The boron content in carbons was determined by leaching with HHO_3. A known aliquot of the solution was then analyzed by emission spectroscopy using a H_3BO_3 standard. Magnetic susceptibility (χ) measurements were carried out by the Faraday method using a modified Cahn RG 100 electrobalance equipped for in situ reduction with H_2 and CO, as described by Mulay[5]. The ESR spectra were obtained with a Varian E-12 series spectrometer, which was operated at a frequency of 9 GHz, with modulation amplitude of 8 G and a power level of ~125 mW. The physisorbed oxygen, which initially gave very broad lines (up to 250 G), was outgassed by heating at ~600 K for 16 hr in flowing H_2, followed by evacuation of the ESR thin-wall 5 mm quartz tubes (Wilmad Co.) to $\sim 10^{-4}$ Pa. The carbon samples in these tubes were then sealed while under vacuum. A reference compound, DPPH (1,1-diphenyl-2-picryl hydrazyl), was used which gave a signal at $g = 2.0037$; line positions of all the samples were obtained with respect to the signal from DPPH. The peak intensitives (I) were obtained by using the approximate relation, given by Poole[6]:

$$I = (\text{peak amplitude})^2 \times \delta H, \qquad (1)$$

where δH is the peak-to-peak line width observed in the first derivative signals. The spin concentration in selected samples was measured relative to a "pitch" standard supplied by Varian Associates. Measurements were obtained at room temperature (~300 K) and at a cryogenic temperature of ~100 K. The latter was obtained using a special Varian Dewar containing liquid N_2. This arrangement gave weak signals in several instances since the sample could not be "coupled" to the central mode of the ESR cavity. This was probably due to the high dielectric loss caused by the insertion of the Dewar, and the relatively high electrical conductivity of the carbon samples. This situation was circumvented by blowing cold vapors of liquid N_2 on to the sample using the Varian cryogenic accessory.

3. RESULTS AND DISCUSSION

3.1 *Characterization of carbons by magnetic susceptibility*

Mulay and Mulay[7] and Mulay and Boudreaux[8] have reviewed the magnetic properties of selected carbons and the latter[8] have succinctly described the Langevin and Landau diamagnetism of localized and itinerant (conduction) electrons. Magnetic susceptibility of doped and undoped carbons has indeed proved to be a useful probe for characterizing "amorphous" and graphitic carbons and for estimating band parameters in appropriate cases[8]. Mulay (cf. 8) has discussed in detail the "Gaussian-cgs/emu" units for magnetic parameters and their conversion to the "S.I. mks" units. Since most of the magnetic and catalysis literature continues to use the "Gaussian" system, familiar to most researchers, we have retained these units throughout this paper. Conversion factors for quick reference are given recently by Mulay and Mulay[9].

Diamagnetic susceptibilities were measured for MC, C-2, and CSX at room temperature on AR and DS samples. As expected, all AR samples showed a linear dependence of χ on the applied field, indicating the presence of trace quantities of ferromagnetic impurities. The estimated amounts of such impurities in each case were found to be in the range from 20 to 60 ppm, while the true susceptibilities were in the range from $-(0.6 \text{ to } 1.5) \times 10^{-6}$ emu/g. (These quantities multiplied by 12.56×10^{-3} give S.I. values in units of m^3kg^{-1}).

Typical plots of χ vs 1/H for MC (AR and DS) and CSX (AR and DS) samples are shown in Fig. 1. Since the level of ferromagnetic impurities is rather low compared to the net magnetization of supported iron catalysts, in principle, these impurities would not have affected the general trend of the σ results for the iron catalysts, which will be reported separately[10]. However, since the true diamagnetic susceptibility (χ_0) was of *prime importance* in the characterization of these carbons, the well-known

Table 1. Description of undoped and boron-doped carbons

Sample Code	Carbon Black	HTT (K)	Duration of HTT (h)	Surface Area (m^2g^{-1})	Sulfur Content (wt.%)
MC (AR)	Monarch 700	-	-	200	1.34
MC (DS)	Monarch 700	1273	12	206	0.03
CSX-203 (AR)	CSX	-	-	-	0.80
CSX-203 (DS)	CSX	1273	12	1500	0.33
C-2 (AR)	Carbolac-2	-	-	714	0.05
C-2 (DS)	Carbolac 2	1273	12	850	0.02
CMC	Monarch 700	3023	1	80	nil
BCMC1	MC + 170 ppm B	2073	1	92	nil
BCMC2	MC + 260 ppm B	2773	½	87	nil
BCMC3	MC + 110 ppm B	2773	1	-	nil
BCMC4	MC + 140 ppm B	2773	1	-	nil
BCMC5	MC + 220 ppm B	2773	1	110	nil

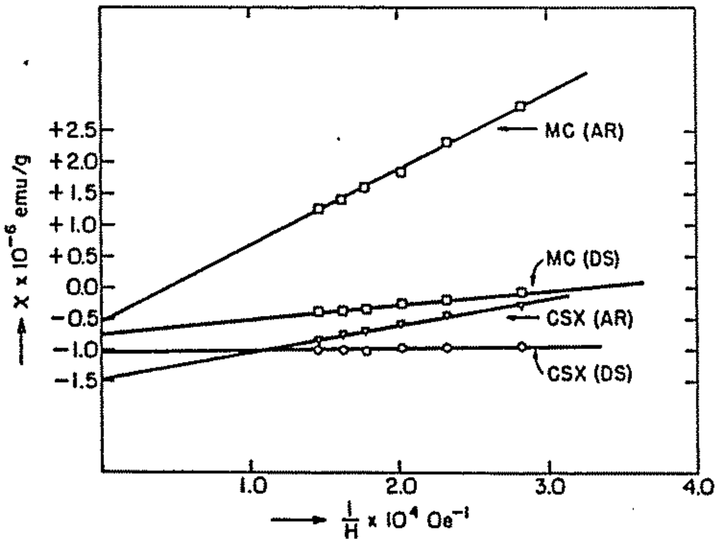

Fig. 1. Variation of diamagnetic susceptibility with 1/H. Typical Honda–Owen plots, for MC and CSX carbons, described in Table 1.

Honda-Owen plots[11] indeed proved very useful in obtaining χ_0).

The variations in diamagnetic susceptibility with temperature (80–300 K) for the non-boronated samples are shown in Fig. 2. This figure shows that the diamagnetic susceptibility decreases with lowering of temperature for the amorphous MC, CSX and C-2 samples. These carbons show typical diamagnetic susceptibilities at room temperature which cross over to positive values at ~80 K. With diamagnetic materials, an "increase" in χ means that it is more "negative". From the magnitude of the susceptibility, it can be inferred that these carbons are "turbostratic" (disordered) in nature. The observed value in χ at 80 K can be ascribed to paramagnetic impurities or surface complexes which have free radical character. A similar trend has been observed by Kiive and Mrozowski[12] for various cokes.

For GMC, however, the diamagnetic susceptibility increases as the measurement temperature T is lowered. A similar increase has been observed for a variety of graphitic carbons by a number of investigators. One of the earliest approaches to account for such behavior was that of Ganguli and Krishnan[13]. Several modifications appeared later for a two-dimensional electron gas model[14]. Pacault and Marchand[15] succeeded in describing such a change in the observed diamagnetic susceptibility χ_0 with measurement temperature by the following equation:

$$\chi = \chi_0 [1 - \exp(-T_0/T)]. \qquad (2)$$

where χ_0 is the limiting value of χ, which is essentially reached at 80 K[16], and T_0 is the degeneracy temperature related to E_F, which is measured from the top of the valence band ($E_F = kT_0$, where k is the Boltzmann constant). This approach yielded *relative* changes in E_F of carbons by boron doping. In a later 1974 paper Pacault[15] modified the above equation by considering the "core" diamagnetism of carbon.

Pacault and Marchand's approach has been successfully employed by Santiago *et al.*[16] to characterize a number of carbons in terms of the band parameters that can be computed from the above model. Thus, according to these authors, T_0 is a measure of the metallic behavior of a given graphitic carbon. That is, the lower the T_0, the closer the carbon is to perfect graphite. The same approach[16] was used here to estimate the band param-

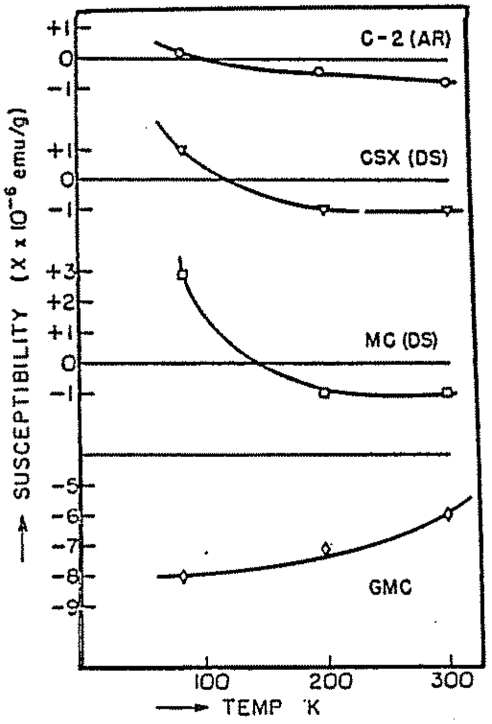

Fig. 2. Variation of diamagnetic susceptibility with temperature for various carbons. The GMC shows a typical Landau diamagnetic behavior, which is represented in Fig. 4 in which χ is plotted vs $1/T$.

Table 2. Parameters calculated for GMC

Parameter	Present Study	Literature Values (8)
T_o	388 K	230 to 550 K
α	113	68 to 139
ν	$0.32 \times 10^{19}/g$	$(0.16 \text{ to } 0.7) \times 10^{19}/g$

eters in the case of GMC. The parameters obtained are changes in E_F (ΔE_F), T_0, the mass coefficient $\alpha = m/m^*$, where m and m^* are the rest and effective mass of the electron, respectively, and ν the number of excess charge carriers. Values presented in Table 2 fall within the range of literature values, summarized by Mulay and Boudreaux[8].

The characteristics of the GMC support were modified by the introduction of boron as described before. The temperature dependence of χ for typical samples between 80 and 300 K is given in Fig. 3. It is seen in this figure that the diamagnetic susceptibility of the GMC exhibited a temperature-dependent Landau diamagnetism. This is characteristic of a free electron gas and has been considered in the earlier section. Sample BGMC1 (HTT 2073 K) showed a paramagnetic behavior superimposed on a less pronounced diamagnetic susceptibility of carbon. However, sample BGMC2 (HTT 2773 K) showed an almost temperature-independent Langevin type of diamagnetism, characteristic of materials with complete pairing of spins, e.g. KCl, consisting of closed-shell configurations for K^+ and Cl^- [8].

The above observations are in general agreement with those of Delhaes and Marchand[17] and can be explained as follows. For BGMC1, the initial part of the curve is similar to that of GMC, but as the temperature is lowered (i.e. as $1/T$ increases), a decrease in χ_0 is observed. Apparently, the HTT for BGMC1 was not high enough to drive all the boron atoms into trigonal (sp^2) sites as a substitutional impurity. Under such conditions, boron can occupy different positions: substitutional, interstitial, and surface defect sites[18]. The boron atoms at the defect sites can therefore exist as localized paramagnetic spin centers and, hence, be responsible for the observed decrease in χ with lowering of temperature. A similar idea was proposed by Mrozowski[19]. On the basis of ESR results for boron-doped P 33 carbon black, he suggested that boron atoms can act not only as acceptors, but neutralize some of the existing localized spin centers; and under special conditions these act as spin centers. In the case of the BGMC2, the HTT appeared sufficient to diffuse practically all boron atoms into substitutional sites. According to the band theory of McClure[20], which was subsequently confirmed by Soule[21], the progressive addition of substitutional boron lowers E_F of graphite. As the E_F is shifted in the valence band, the semimetallic graphite behaves more like a metal and, as a consequence, exhibits Pauli paramagnetism, analogous to that of alkali metals. Indeed, this has been observed in the case of the BGMC2, where the observed χ_0 was independent of temperature. Having established the optimum HTT for boron doping, various samples were prepared with different boron concentrations. The diamagnetic susceptibilities of these samples are plotted against $1/T$ and are shown in Fig. 4.

As explained by Soule[21], the diamagnetic susceptibility in graphite is a summation of diamagnetic susceptibility contributions from conduction electrons and localized spins. With the progressive addition of boron, the number of conduction electrons is reduced until eventually the diamagnetic susceptibility approaches that contributed by the core diamagnetism which is temperature independent. According to the McClure band model, from the change in susceptibility, the corresponding change in

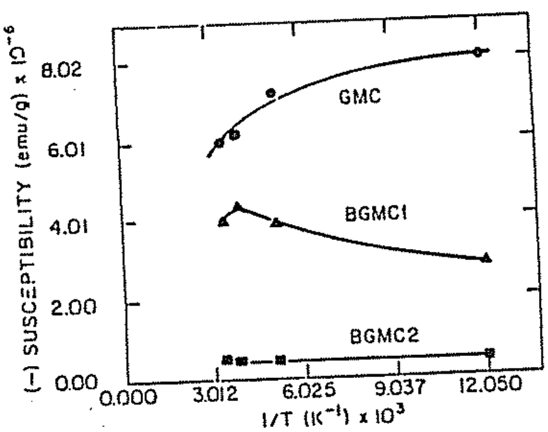

Fig. 3. Variation of diamagnetic susceptibility with $1/T$ for boronated carbons, showing the effect of HTT. GMC shows a typical Landau diamagnetic behavior.

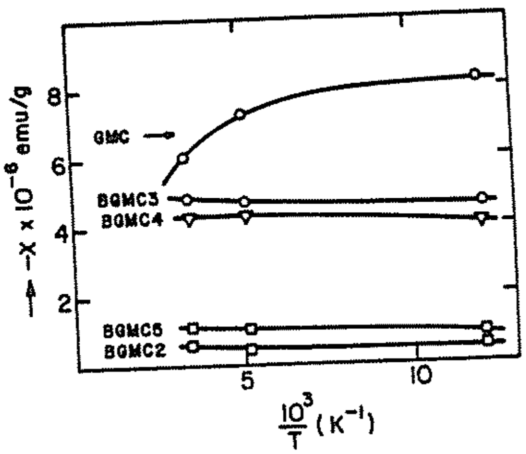

Fig. 4. Variation of susceptibility as a function of $1/T$ for different boronated samples.

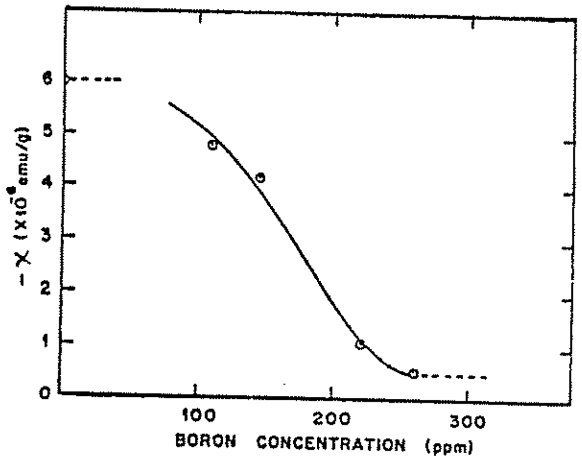

Fig. 5. Variation of diamagnetic susceptibility of carbons as a function of boron concentration.

E_F can be estimated. This has been done by Soule and, as expected, a decrease in E_F was observed with an increase in acceptor concentration. The variation in susceptibility with boron concentration, and the corresponding changes in E_F for various boronated samples are shown in Figs. 5 and 6, respectively. The observed trend agrees well with that of the theoretical predictions by Sharma *et al.*[22].

3.2 *Characterization of carbons by electron spin resonance (ESR) spectroscopy*

Various carbon samples were further studied by ESR spectroscopy. The parameters of interest are the "*g*" value, the line width δH, the line shape, and the line intensity *I*. Before outgassing, the ESR signals for both the AR and boron-doped samples were very weak and considerably broad. In some cases the line widths were as broad as 250 G. However, when the samples were treated at 673 K for 16 hr in a stream of H_2 and then sealed after being evacuated to 10^{-4} Pa, they gave intense signals with line widths of the order of 25–60 G. This result is considered to arise from adsorbed oxygen and has previously been reported for some carbon blacks[23]. However, the exact mechanism of oxygen interaction with the existing spins on the surface of carbon is not yet clearly understood. Most of the physically adsorbed O_2 is in triplet Σ state. Samples in contact with air or O_2 gave ESR signals, typically with Gaussian shape, whereas the outgassed samples gave signals of a true Lorentzian shape. In either case, the *g*-values were found to be the same, but narrowing in the line shape suggests that the removal of O_2 increases the exchange interaction between the localized spins in the carbon framework, presumably via the electron cloud. The *g*-values and the corresponding parameters for various carbons are given in Table 3. Typical ESR spectra for the MC, GMC, and B-doped BMC samples are shown in Figs. 7(a)–(c) and 8(a)–(c), in order to emphasize the subtle changes with boron doping and/or measurement temperatures.

Results in Table 3 show that both the *g*-values and the line widths change with boron doping. Mrozowski[19] has shown that the single ESR absorption line arises from both the conduction electrons and localized spin centers, and the observed *g*-value of the composite line arises from an exchange mixing mechanism. The trend in the observed *g*-values falls within the range reported by Mrozowski[19]. The change in δH also follows a similar trend in the present study. Samples BGMC2 (RT) and BGMC5 revealed a sharp line superimposed on the broad line (Figs. 8a and b). These lines did not show any variation in *g*-value even under low scan. Similar spectra have been observed by Retkofsky and coworkers[24] for Pittsburgh bituminous coal samples. These authors also showed that these two lines could not be better resolved any further even at 35 GHz. All samples in this study, except the BGMC2, could be satisfactorily described by the Lorentzian line shape.

The number of spins in each case is also shown in Table 3. It should be noted that determining absolute spin concentrations from ESR is extremly difficult, since it involves a number of variables such as "Q" of the cavity, relative electrical conductivity of the samples and their skin depth. Some of these parameters can be controlled by making measurements with a dual mode cavity and a two-step integral method[6]. In the present study, spin

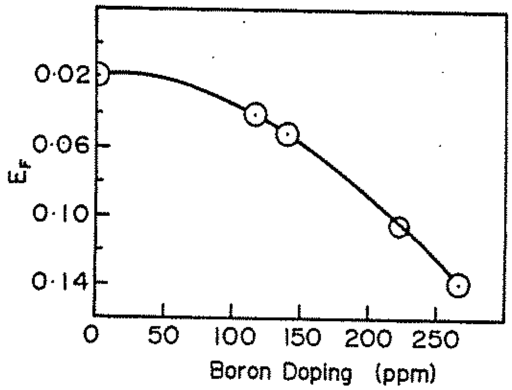

Fig. 6. Relative shifts in Fermi levels $|E_F|$ in eV, derived from the observed degeneracy temperature (T_0), as a function of boron doping in GMC.

Table 3. ESR parameters for various carbons

Sample*	B-Level (ppm)	g-Value	δH* (Gauss)	Line Shape	Relative Number of Spins/g ($\times 10^{19}$)
GMC	0	2.0057	60	Lorentzian	50
BGMC1	170	2.0049	38	Lorentzian	45
BGMC2	260	2.0012	26	Not Lorentzian	5
MC	0	2.0014	37	Lorentzian	15

* See Table 1 for the description of samples.

** Line widths are often expressed in Gauss, which is the same as Oersted.

concentrations were obtained in a single cavity and, therefore, are subject to error. However, the relative number of spins show that their concentration is reduced by a factor of ten from GMC to BGMC2, that is, boron doping clearly reduces the number of spins.

The relative variation in spin concentration of the MC and GMC samples can be explained as follows. In general, there are two types of bonding involved in carbon blacks. Some carbon atoms are tetrahedrally (sp^3) bonded to four neighboring carbon atoms, whereas other carbon atoms are bonded to only three other neighbors by sp^2 hybridization. In the second case, each carbon atom would still be left with one unpaired electron. The number of such free electrons in a given carbon, therefore, depends on the ratio of sp^2 to sp^3 bonding involved. The presence of tetrahedral bonding in carbon blacks has been alluded to by Lijima[25]. In the process of graphitization, tetrahedral bonding is predominantly eliminated so that carbon atoms in each plane have only sp^2 hybridization. The unpaired electrons associated with each carbon form a delocalized electron cloud above and below a given plane. The spin concentration in GMC, therefore, arises from a combined contribution of localized spins and delocalized spins.

For the BGMC2, the g-value is slightly lower than the accepted free spin value of 2.0037. This may be ascribed to an exchange interaction between neighboring spins, which apparently takes place via the delocalized π electron cloud. This situation is reminiscent of the RKKY interaction[26] observed in diamagnetic alloys. The effect of progressive addition of boron on the g-value is presented in Table 3, along with the corresponding changes in δH and line shapes. These results clearly show that the addition of boron decreases the g-value, which stems from a decrease in the E_F of the GMC. This observation is in conformity with the theory of McClure and Yafet[27]. Furthermore, these observations substantiate the conclusions drawn from the susceptibility results presented earlier.

In general, the ESR line intensities observed at 300 K and at 80 K for the (a) highly graphitized carbons and (b) "amorphous" materials can be explained in a straightforward manner. Typical ESR spectra for the BGMC2 samples which belong to type (a) are shown in Fig. 8(a). For the samples of type (a), the ratios $[I(80\ \text{K})/I(300\ \text{K})]$ lie in a range from 1.14 to 1.20. Figure 8(c) depicts the ESR intensities for sample MC which belongs to the (b) carbon type. In this case the ratio $[I(80\ \text{K})/I(300\ \text{K})]$ is 2.2, which is considerably higher than that for the type (a). This higher ratio is attributed to both a larger contribution from the localized spins residing at various defect sites in the carbon framework, and a smaller contribution from conduction electrons.

4. SUMMARY

Various commercial as-received, desulfurized, graphitized, and boronated graphitized carbon blacks were successfully characterized by magnetic susceptibility (χ) and ESR studies. High-surface area desulfurized carbons were found to be turbostratic (disordered) in nature from measurements of χ as a function of temperature. The graphitized carbon showed a temperature-dependent Landau diamagnetism, whereas the graphitized sample subsequently boronated at 2073 K, displayed a paramagnetic behavior superimposed on the Landau type diamagnetism. The sample boronated at 2773 K showed an almost temperature-independent Langevin diamagnetism, suggesting that most of the boron (at the 260 ppm level) entered substitutional sites. The role of boron as an electron acceptor was thus well established, in agreement with previous studies. Various band parameters, such as the effective electron mass and number of charge carriers (conduction electrons and holes), calculated for the graphitized samples using the conceptual approximations of a two-dimensional model, agreed reasonably well with those reported by previous workers. The χ values were found to decrease systematically with progressive addition of boron, and estimates of the lowering in the Fermi level could be obtained from the χ data.

The ESR results, in general, confirmed the findings from the susceptibility data, in that a systematic lowering in the "g" value, the line width, and the relative spin concentration was observed with progressive doping of graphitized carbon black with boron.

These boron-doped carbon blacks should be interesting supports for Fe which would represent a new family of Fe/C catalysts. Their characterization by magnetic and

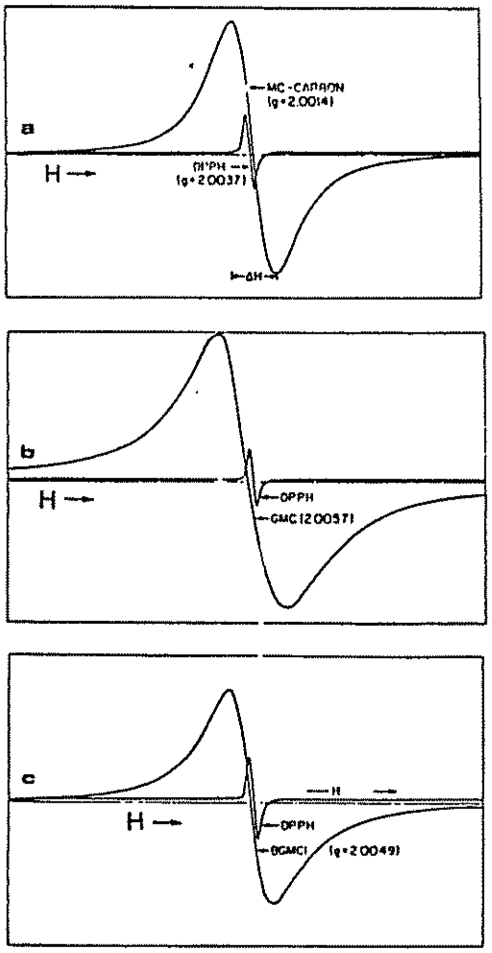

Fig. 7.(a–c) ESR spectra obtained at room temperature (*RT*) which show changes in the "*g*" values (with respect to DPPH), δH and *I*, for MC, GMC and BGMC1, respectively. These spectra show the effect of graphitization of MC to GMC and that of boronation of GMC to BGMC1 (see Table 3 and text).

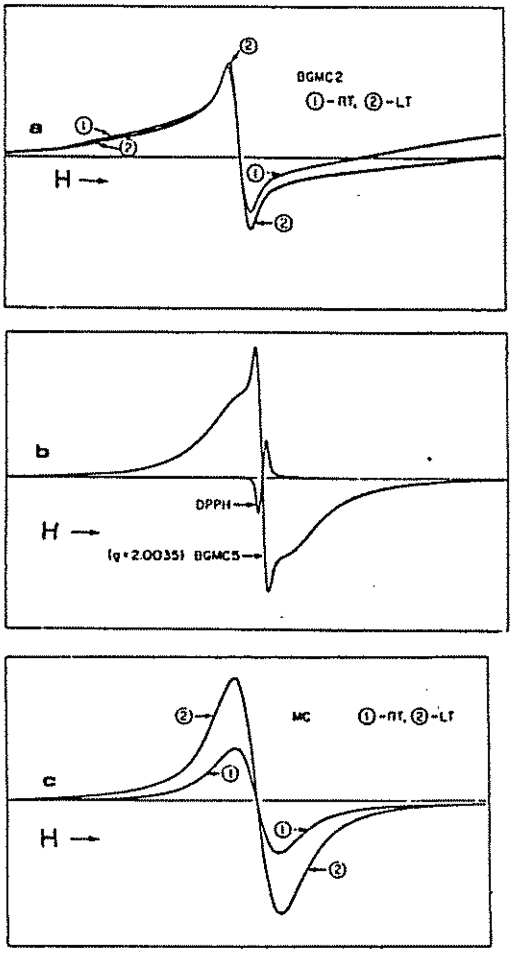

Fig. 8.(a–c) ESR spectra for BGMC2, BGMC5 and MC, respectively. BGMC2 and MC spectra were obtained at room temperature and at a low cryogenic temperature (*LT*) (see Table 3 and text). BGMC5 reveals the superposition of broad and sharp spectra.

Mössbauer measurements, adsorption properties, and their catalytic behavior in the CO hydrogenation reaction are reported separately[10].

Acknowledgements—We are grateful to the National Science Foundation, USA, for supporting this work with an NSF Grant No. CPE 7915761. One of us (Prasad Rao) is thankful to the Government of India for providing him with a fellowship during 1979–83.

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