

PARAMAGNETIC RESONANCE ABSORPTION IN GRAPHITE*

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Graphite usually gives rise to an electron spin resonance, which is relatively weak and furthermore sensitive to thermal treatment of the graphite. The spin center concentration decreases as the measuring temperature is lowered. The concentration measured at room temperature is decreased by heating near 1200°C and restored by heating at 1500°C. The thermal stability of the centers is furthermore a function of the crystal size and perfection and is decreased by oxygen. The centers have tentatively been identified with irregularities in the mosaic and peripheral boundaries.

Paramagnetic resonance absorptions near a g value of 2 have been observed in carbon,¹ in coal,² graphite,³ in chemical compounds of graphite⁴ and in irradiated graphite.⁵ The resonance induced by irradiation and by chemical reactions differ in line width, intensity, and temperature dependence from the other resonances listed, which must therefore be attributed to different types of spin centers. The resonances in coals, carbons, and graphites also differ considerably from each other, yet it appears possible to assign these resonances to somewhat related disturbances in the carbon structure of these substances.

The apparatus and its calibration against an organic free radical have been described earlier.⁶ All samples were powdered and measured in quartz or Pyrex tubes, of 6 mm outside diameter. The graphite was either high purity artificial graphite or natural flake graphite (Madagascar or Ceylon) re-purified after subdivision, by acid treatment and heating in inert atmospheres to 3000°C. Sugar char was prepared by heating sucrose in air to about 400°C, and powdering the residue.

RESULTS

The number N , of spin centers per carbon atoms at or below room temperature was found to be

$$N = A \exp \{-B/kT\} \quad (1)$$

where A was 10^{-3} within a factor of 2 or 3 for artificial graphites and somewhat less for natural graphites, and B was 0.05 ev for artificial graphites and 0.04 ev for natural graphites.

The spin centers of artificial graphite disappeared during heat treatment in inert atmospheres or *vacuo* above 1100°C. Similarly, they disappeared when natural graphite

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¹ D. J. E. Ingram and J. E. Bennett, *Philos. Mag.* **45**, 545 (1954); D. J. E. Ingram and J. G. Tapley, *ibid* **45**, 1221 (1954); J. E. Castle, *Phys. Rev.* **94**, 1410 (1954); **95**, 846 (1954).

² Ingram, Tapley, Jackson, Bond, and Mur-naghan, *Nature* **174**, 797 (1954); A. Etienne and J. Uebbersfeld, *J. Chem. Phys.* **51**, 328 (1954).

³ G. R. Hennig and B. Smaller, Argonne National Laboratory Progress Report, ANL-5101 (August, 1953) unpublished; J. E. Castle, *Phys. Rev.* **92**, 1063 (1953).

⁴ G. R. Hennig, B. Smaller, and E. L. Yasaitis, *Phys. Rev.* **95**, 1088 (1954); *ibid* **97**, 239 (1955).

⁵ G. R. Hennig and B. Smaller, Argonne National Laboratory Report ANL-5385 (January, 1955), unpublished.

⁶ M. S. Matheson and B. Smaller, *J. Chem. Phys.* **23**, 521 (1955).

TABLE I

Electrical Properties of Artificial Graphite Before and After Annealing

Treatment	Measuring Temperature (°C)	Relative Resistance† (ρ/ρ_0)	$10^{10} \times$ Magneto† Resistance ($\Delta\rho/\rho$ gauss ⁻²)	Hall Coefficient (emu)‡
Unannealed	25	1.00	6.63	-0.604
	-196	1.673	17.38	-1.603
Annealed*	25	0.988	6.69	-0.608
	-196	1.661	17.51	-1.608

* Heated for 5 min in helium at 1175°C.

† Estimated error $\pm 0.2\%$

‡ Estimated error $\pm 2\%$.

ite powdered to a particle size of several microns, was heated to 1100°C. Coarser flakes of natural graphite did not lose their spin centers during heat treatment.

Heat treatment of artificial and powdered natural graphites above 1400°C restored the resonance absorption without appreciable changes in line width or temperature dependence. These regenerated spin centers were stable during further heat treatments between 25°C and 1800°C, as long as air was excluded. Admission of air or oxygen at room temperature converted the centers to the unstable form which can be destroyed by heating to 1100°C. The rate of this reaction with oxygen differed by orders of magnitude for different artificial graphite samples prepared from different raw materials. In finely powdered natural graphite the rate of this oxygen reaction was too slow to be detected after several days' exposure.

The concentration of spin centers was not altered appreciably by partial combustion of the samples in air at 600°C. Samples whose spin centers had previously been destroyed by heat treatment, retained their lack of resonance absorption.

A few experiments were conducted with sugar chars which showed a resonance absorption near a g value of 2.0. The intensity of this absorption was at least ten times as

large as the intensity of graphite. Furthermore, the concentration of spin centers in the chars did not change at measuring temperatures below room temperature, (i.e., B in Eq. (1) is zero). The absorption disappeared after heat treatment near 600°C, and reappeared after heating to about 1500°C. The spin centers in this heat treated carbon were not destroyed by further reheating at 1100°C, even after prolonged standing in air.

DISCUSSION

The relatively high concentration of potential spin centers (10^{-3} per atom) excludes the possibility that they are metallic impurities since the maximum ash concentration is at least an order of magnitude less. The concentration of conduction electrons in graphite is probably of the same order of magnitude as the spin center concentration, but the behavior of the spin centers during annealing or at low temperature can hardly be attributed to conduction electrons. Measurement of several electrical properties have confirmed that the conduction electrons are not affected by the annealing treatment (Table I). The sensitivity of the electrical properties to changes in the electron population had been determined previously⁷ and shows that less than 2×10^{-5} electrons have been removed by annealing. The properties indicate further that the temperature dependence of the spin center concentration below room temperature is not associated with trapping or releasing of trapped conduction electrons or holes.

The only structural defects which are known to be present in graphite in sufficient concentration to account for the resonance are internal and external surfaces. The external surfaces of artificial graphite amount to $1 \text{ m}^2/\text{g}$ or about 5×10^{-4} surface atoms per carbon atom. However, the burning experiments described above have shown

⁷ G. R. Hennig, J. Chem. Phys. **19**, 922 (1951).

that removal of external surfaces by burning does not affect the resonance absorption. Thus, the spin centers must be defects at internal surfaces or mosaic boundaries. The crystallite size determined by the x-ray line width of artificial graphites amounts to about 1000 Å at right angles to the hexagonal axis, and somewhat more in natural graphites. Therefore, the mosaic boundaries between artificial graphite crystallites contain at least 2×10^{-3} boundary atoms. It appears that a special configuration of some or all of these boundary atoms separating the perfect crystallite regions, must be responsible for the resonance absorption. To explain the observed behavior one must assume furthermore, that oxygen is able to dissolve in the mosaic boundaries of artificial graphite and thus penetrate close to the spin centers. Some evidence for such solubility has repeatedly been reported.⁸ The structure of natural graphite is sufficiently more compact that oxygen diffuses much more slowly through or over the mosaic boundaries, and reaches the spin centers

only after very long exposure to air and only in very finely powdered material. The oxygen desorbes, probably as an oxide of carbon, at 1100°C and thereby destroys the spin centers. Desorption of chemisorbed oxygen near this temperature has been detected by Gulbransen.⁹

The disordered structures responsible for paramagnetism are recreated above 1400°C by thermal disordering of the mosaic surface atoms.

The disappearance of the resonance below room temperature implied in Eq. (1) might be due to reversible interaction of adjacent spin centers. It is tempting to attribute this interaction to centers in adjacent layer planes, so that centers of the same type present in ungraphitized carbons and chars cannot interact at low temperatures, because the layer planes in these materials are considerably further apart than in graphite.

The actual structure of the spin centers is still unknown. They might possibly be either singly bonded carbon atoms or incipient vacancies. } 12

⁸ L. Meyer, Z. Phys. Chem. **B17**, 385 (1932); H. Boersch and L. Meyer, Z. Phys. Chem. **B29**, 59 (1935).

⁹ E. A. Gulbransen and K. F. Andrew, Ind. Eng. Chem. **44**, 1034 (1952).