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Paramagnetic Resonance in Anthracite and Other Carbonaceous Substances

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Paramagnetic resonance was measured in a number of substances containing free carbon. The measurements were carried out at 295° and 90° K at the frequencies 9450, 536.76 176.1 and 20 mc.

IN 1953 Castle[1] detected paramagnetic resonance in thin layers of graphite. In 1954 a number of investigators[2-5] established that paramagnetic resonance is present in certain other forms of carbon (in activated wood charcoal, charred organic substances). We undertook to investigate various types of coal, organic tars and certain other substances containing free carbon.

1. Procedure

A block diagram of the installation is shown in Fig. 1. High frequency vibrations were produced by a klystron generator which was fed by a stabilized source of current. The frequency of the generator was measured by a wave meter with an accuracy of ± 0.03%. The high frequency power of the generator was controlled by a thermistor bridge. The high frequency signal from the generator was introduced to the resonance cavity through an attenuator (5-10 db). After the signal emerged from the cavity it was rectified, amplified, and finally introduced to the vertical plates of an oscillograph. In the different measurements two types of amplifiers were used: 1) a narrow band amplifier at 400 cycles for observing the maxima of the curves $X''=X''(H)$ and 2) a broad band amplifier for observing the overall shape of the curves $X''=X''(H)$

The specimen of the substance under investigation was placed into the resonance cavity, which was located between the poles of the electromagnet producing the static magnetic field H of a strength up to 10000 oersteds. The magnetic field was modulated by coils wound on the pole pieces of the electromagnet. The modulations coils were fed by a 50 cycle current from the line circuit (during broad band amplification) or a 200 cycle current from a sonic frequency generator (during narrow band amplification). The amplitude of modulation was kept strictly constant during the experiment. During narrow band amplification, values from 0.1 to 50 oersteds could be assigned to it and during broad band amplification values from 0.5 to 700 oersteds. The modulated current was introduced through a phase changer to the horizontal plates of an oscillograph. The determination of the H^* values was carried out by proton resonance. For this purpose a generator was used the frequency of which could be varied gradually from 10 to 20 mc. The measuring coil of the proton generator, containing an ampoule with a weak aqueous solution of $MnCl_2$ (0.01 mole / l) was placed in the field of the electromagnet, directly under the resonance cavity. The uniformity of the static magnetic field was such that when the measuring coil containing the solution of $MnCl_2$ was placed into that position in the field which (during measurements) was occupied by the specimen of the substance under investigation, there was hardly any change in the picture of the proton resonance on the screen of the oscillograph. Proton resonance was registered by the method of Zavoiskii from the changes in the anode current.[6] By means of successive switching it was possible to obtain signals on the screen of the oscillograph from the three centimeter generator and from the proton generator. The amplitude of modulation in the measurements of proton resonance had the value 0.2 oersted. For a value of field $H=H^*$; corresponding to electron resonance, the frequency of the proton generator was changed until such time when no proton resonance line appeared on the screen of the oscillograph.

The frequency, corresponding to proton resonance, at a given value of H^*, was measured by a heterodyne wave meter with an accuracy up to 0.1%. It is this value which mainly determines the accuracy of the experiment. The calibration of the magnetic

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[1] J. G. Castle, Phys. Rev., 92, 1063 (1953).

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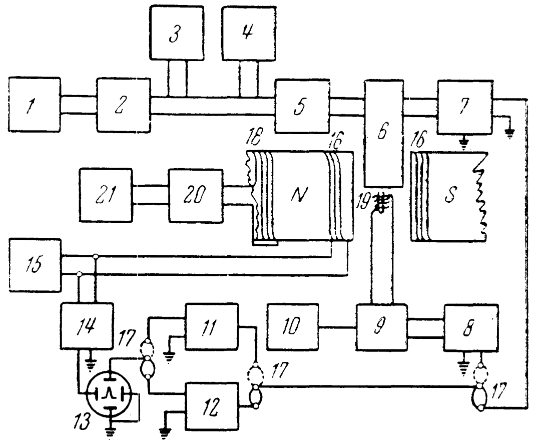

FIG. 1. Block diagram of the high frequency apparatus. *1*-stabilized power of supply, *2*-klystron generator, *3*-wave meter, *4*-power control, *5*-attenuator, *6*-resonance cavity, *7*-crystal detector, *8*-stabilized power supply, *9*-generator of proton resonance, *10*-heterodyne wave meter, *11*-narrow band amplifier, *12*-wide band amplifier, *13*-oscillograph, *14*-phase changer, *15*-audio frequency generator, *16*-modulation windings of the electromagnet, *17*-change-over switches, *18*-electromagnet windings, *19*-measuring coil of the proton generator, *20*-apparatus for the field strength H of the electromagnet, *21*-source of supply for the electromagnet.

field during broad band amplification was carried out by the luminous modulation of the oscillograph tube.

The measurements at the frequencies 536.71 and 176.1 mc were carried out by the Zavoiskii method of the grid current.[6] The grid current of the appropriate generator was connected to the input of the narrow band amplifier instead of the current from the detector of the three centimeter installation. The calibration of the magnetic field in this case was carried out by the free radical α,α-diphenyl-β-trinitrophenylhydrazyl, the g-factor of which was determined at the frequency 9450 mc by means of proton resonance and found to equal 2.004 ± 0.002, which is in agreement with the measurements of other authors.[7]

The width of line in the free radical, determined at the frequency of 9450 mc, was found to equal 2 ± 0.5 oersteds, which is in agreement with the data of Chu et al.[7] The absorption curve of the free radical obtained at the frequency 9450 mc is given in Fig. 2a.

2. Measurements of paramagnetic resonance in anthracite

An easily measurable effect with a very narrow resonance line was found in the anthracite specimens. The shape of the absorption curves was found to be strongly dependent on the form of the specimens and on the frequency of the oscillating magnetic field.

The photographs of the signals observed on the screen of the oscillograph by the method of broad band amplification at 9450 mc are shown in Fig. 2. The anthracite specimens had equal areas 11.3 x 4.4 mm and differed in the thickness ($2d$). For the specimen *b* the thickness $2d = 0.25$ mm, for $c = 0.5$ mm, for $d = 0.8$ mm, for $e = 1$ mm and for $f = 2$ mm.

The specimens were located on the bottom of the resonator with the long axis along the magnetic lines of force. They were insulated from the metallic bottom of the cavity with parchment. The characteristic distortion of the shape of the absorption line, which was observed in the thicker specimens and which becomes almost unnoticeable in the samples with the thickness of $2d \leq 0.25$ mm, finds an explanation in the considerable electroconductivity of the anthracite. The effect of the electroconductivity on the shape of the line of magnetic absorption was theoretically analyzed by Bloembergen.[8]

For an infinite flat conducting plate he found that in the limiting case, when the depth of penetration of the field into the plate $\delta \gg d$, the magnetic losses should be proportional to $1 + 2\pi(X' + X'')$. In the other limiting case, when $\delta > > d$, the magnetic losses should be the same as in semiconductors.

A qualitatively experimental substantiation of the effect of conductivity on the shape of the absorption line was obtained by Bloembergen by comparing the curves of the derivative of the coefficient of paramagnetic absorption, produced by the Cu^{63} nuclei in metallic copper when taken as a fine powder. Our experiments represent one of the first verifications of the effect of conductivity in electronic paramagnetics.

As is evident from curve *b* (Fig. 2), at a thickness of plate $2d \leq 0.25$ mm the influence of X' on the effective absorption coefficient is negligible. As d increases, the part of X' in the absorption effect increases and at $2d \geq 2$ mm it becomes sharply predominating, since the shape of curve *f* practically coincides with the predicted shape for $X'(H)$.

Thus the effective coefficient of absorption X''_{eff} in anthracite can be expressed as $A(d)X' + X''$, where the numerical coefficient $A(d) \ll 1$ when $\delta > d$ and $A(d) \gg 1$ when $\delta < d$. The discrepancy

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[7] T. L. Chu, E. Pake, D. E. Paul, J. Tawsend and S. I. Weissman, J. Phys. Chem. 57, 504 (1953).

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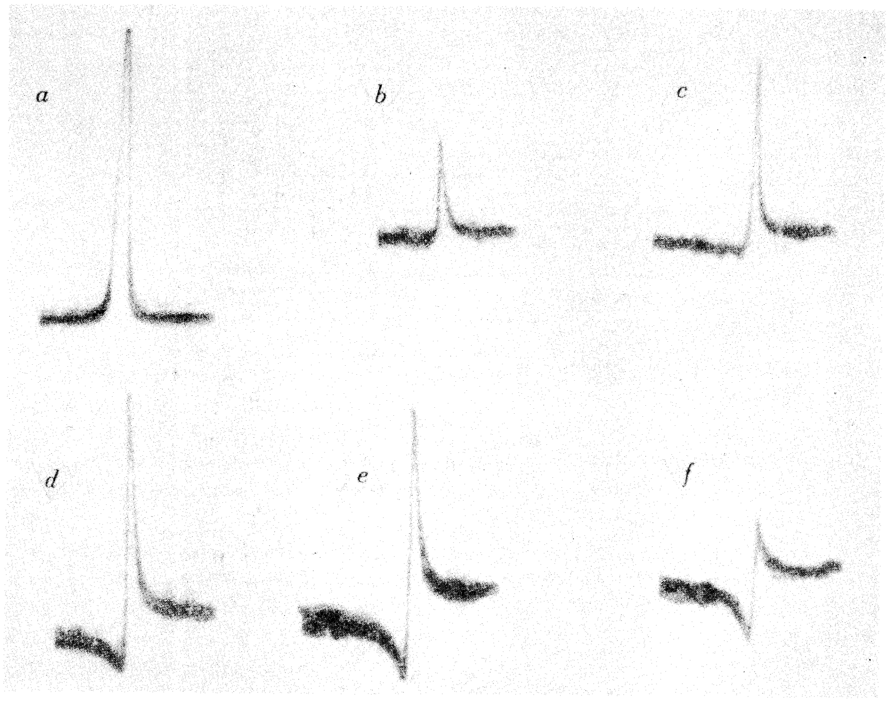

FIG. 2.

in the result we obtained and the Bloembergen formula for the latter case is not surprising, since in our experiments with the thick specimens the thickness of the plate was commensurable with the linear dimensions of its area.

At the lower frequencies, the distortion in the shape of the absorption line in anthracite becomes much less noticeable owing to the increase in the depth of penetration δ. It was possible to observe this distortion in the thick cylindrical specimen (diameter 8 mm) at the frequency $\nu=536$ mc. The same specimen at the frequencies 176 and 20 mc gave the ordinary curve $X''=X''(H)$.

The effective g-factor of the absorption line in anthracite was determined on the specimen b by the method of proton resonance at the frequency 9450 mc. It was found to equal 2.004 ± 0.002.

The measurement of the width of the absorption line* ΔH in anthracite was carried out at the frequency 9450 mc in the specimen b, as well as at the frequencies 176 and 20 mc. The width was determined by comparing with the line resulting from the free radical. It was found that for anthracite the value $\Delta H = 0.7$ oersted over the entire range of frequencies investigated. The relative error in the determination of ΔH did not exceed 20%. (The absolute value of ΔH cannot claim to such accuracy owing to the possible error in the determination of ΔH for the free radical)

The fact that the width of the line in anthracite is independent of frequency shows that the main share of the effect cannot be ascribed to the electrons of the conductivity, since in graphite, in accord with Refs. 1,2, the width of line varies from 40 oersteds at $\nu = 9000$ mc to 0.1 oersted in the region of radio frequencies.

Thus, either the free radicals or the "broken bonds" between the carbon atoms can be responsible for the effect. A substantiation of this statement is given by the experiment with the anthracite which was finely pulverized in an agate mortar. When the pulverization is carried out in the presence of air, the effect is greatly diminished and in a short time (10-15 min.) it cannot be observed at all. When, however, the pulverization of the anthracite in the mortar is carried out under a layer of liquid, preventing oxidization, then the effect continues to be observed for a long time. Twenty four hours later it can still be measured; however, the absorption curve has broadened considerably. After anthracite had been heated to a temperature of red heat and then allowed to cool to room temperature, the effect disappears completely.

At the temperature of liquid oxygen the effect in anthracite increases by approximately 3 times as compared with its value at room temperature; more-

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* By width of line we mean the distance in oersteds between the points, corresponding to an intensity of the effect equal to one half the maximum intensity.

over, the width of the absorption curve remains unchanged. This can also be observed in the free radical, the susceptibility of which obeys the Curie law.

On the basis of all of the results given above, one can consider that it has been established that either the free radicals present in the anthracite or the " broken bonds" are responsible for the effect observed in anthracite. Evidently, between the paramagnetic particles in anthracite there exist very strong exchange interactions.

3. Measurements of paramagnetic resonance in other substances

We have also observed paramagnetic resonance in a number of other substances containing carbon: coal, freshly prepared wood charcoal, petroleum asphalt, carbolite and black rubber. Of the substances named, the most intense effect was observed in petroleum asphalt and in carbolite. At 90° K a weak effect $g \approx 2$ was found in specimens of petroleum from Bavlinskii region (Tartariia).

The effective g-factor for all of the substances mentioned was found to equal 2.004 ± 0.002. It was established that, upon cooling to the temperature of liquid air, the intensity of the effect in all cases increases by approximately 3 times, in the free radical as well as in the anthracite. No distortion of any kind in the shape of line was observed in the above substances. The width of lines was measured at the frequency 9450 mc by comparing with the free radical. The widths of lines obtained for the substances investigated are given below (in oersteds):

1. Coal (gaseous)	4.4	± 0.5
2. Freshly prepared wood charcoal . . .	4.8	± 0.5
3. Petroleum Asphalt . . .	4.3	± 0.5
4. Carbolite	3.8	± 0.5
5. Black Rubber	11	± 2

Thus the substances we studied can be subdivided into 3 types differing in width of line. Anthracite belongs to the first type having the narrowest curve (0.7 oersted). To the second type belong the substances 1-4 given in the Table above; in these the width of lines is equal, within the limits of experimental error, and on the average it is approximately 4.4 oersted. Finally, black rubber belongs to the third group of substances having the broadest curve.

The agreement in the value of the g-factors and identical temperature dependence of the intensity of the effect make plausible the assumption that in all cases the free radicals or the " broken bonds" between the carbon atoms are responsible for the effect.

In conclusion the authors wish to express their deep gratitude to Academician A. E. Arbuzov and to F. G. Valitova for the preparation of the substance ∝ ∝ -diphenyl- β - trinitrophenylhydrazyl, which made it possible to carry out easily quantitative determinations of the width of lines in the substances investigated.

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