

As nuclei, was of electronic origin, was as follows: the magnetic field was left at zero field for several minutes. It was then switched on to a value near the electronic resonance field, and subsequently swept through the resonance field. The signal observed was very small, since one had not allowed sufficient time (i.e., several electronic T_1 's) for the Boltzmann difference in population of the electron spin states to be established. It was possible to observe the growth of the Boltzmann population difference by looking at the amplitude of the resonance signal as a function of the time that the magnetic field was left on near the resonance field.

This long relaxation time, very unusual for an *electronic* time, is frequently encountered among nuclear spins. Hence, some of the fast-passage features of the resonance signal have been seen in nuclear resonance experiments.^{2,3} However, in the present case, the behavior is further complicated by the inhomogeneous broadening⁴ of the resonances, brought about by the magnetic Si^{29} nuclei contained within the electron's orbit and by the small amplitude magnetic field modulation at 600 cycles, used for greater sensitivity.

The intensity and form of the resonance signal, as well as the final state of the magnetization immediately after passage through resonance, depend on the value the sweep speed has in comparison with T_1 and T_2 .⁵ This dependence arises as a consequence of the inhomogeneous broadening of the resonances and the situation that even in the fast-passage case, the signal intensity at any point is made up largely of contributions from the wings of distant spin packets. One can either turn around by 180° the net magnetization M belonging to a particular spin packet by sweeping through the packet in a time *short* compared with T_2 , or reduce the M nearly to zero via the T_2 relaxation if one sweeps through the packet in a time *long* compared with T_2 . After having been thus reduced near to zero, or turned 180° , the M then recovers its original magnitude and orientation via T_1 relaxation. Thus, since the signal intensity at a point on the over-all resonance curve depends partly on the state of the magnetization of the packets behind it, and since the state of the magnetization of the packets depends on the rate at which they were swept through resonance and on the amount of time elapsed afterwards, we get a fairly complicated dependence of signal intensity on sweep rate. We will not discuss here all of the possible cases that can arise.

The purpose of the present note is primarily to call attention to the unusually long electronic relaxation time. This and associated effects now explain most of the phenomena which previously were attributed to a very large nuclear polarization.

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Narrow Electron Spin Resonance in Charred Dextrose*

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A STRONG electron spin resonance, with full width at half-height of at most 1.1 gauss, was found for charcoal prepared in the following way: Anhydrous dextrose, charred preliminarily in air at approximately 300°C , was heated at various higher temperatures in vacuum. A minimum in width, with the above value, was found for evacuated samples heated to 570°C and measured at room temperature. Samples of this type should be useful since they are more easily obtained than DPPH and have narrower, almost as intense (about 10^{20} spins/cm³), resonances.

The resonance, at $g=2.003$, was studied at 9400 Mc sec⁻¹ using a standard microwave spectrometer, with a 723A/B klystron and a rectangular transmission cavity, and using a dc magnetic field modulated at 37 cps. The absorption signals were amplified and displayed on an oscilloscope. The narrowest widths were probably limited by the homogeneity of our magnetic field, even though samples in capillary tubes were used and gave widths at the minimum somewhat less than 1 gauss. The resonance was also observed at 51.7 Mc/sec, using a Hopkins oscillator,¹ with the dc magnetic field supplied by Helmholtz coils and modulated at 60 cps. The samples showed a minimum width of 1.1 ± 0.1 gauss occurring at $570 \pm 5^\circ\text{C}$. This width was not limited by field inhomogeneity, as indicated by the fact that *n*-picryl-9-aminocarbaryl² showed a width of about 0.63 gauss.

The high-frequency widths obtained with evacuated samples, as a function of charring temperature, are shown in Fig. 1. The peak intensity rose from a signal-to-noise ratio of 10 at 300°C to 10^3 - 10^4 at 570°C. At temperatures above the minimum, a broadening and

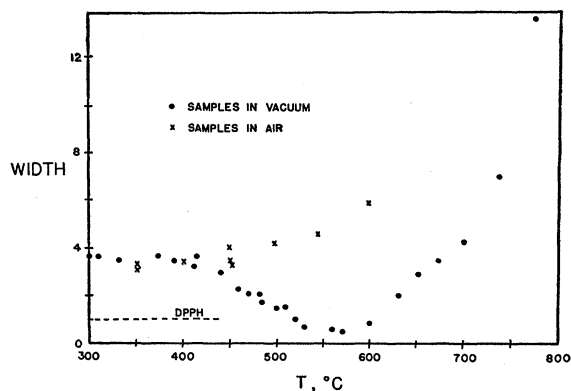


Fig. 1. Width of electron spin resonance absorption (relative to DPPH width = 2.70 gauss) vs temperature of charring.

diminution of intensity were observed until the resonance was no longer observable at 780°C. Above 525°C, an increase in dielectric loss was observed. Some effects of evacuation on the resonance of low-temperature carbons have been independently observed.³

The rate of attainment of the equilibrium value A_e of the area under the absorption curve was studied for evacuated samples heated at 450°C and 550°C. The time required for the area to reach $(1 - e^{-1})A_e$ was found to be 2.2 hr for both temperatures. All evacuated samples were heated for at least 8 hr at the charring temperature.

For samples charred in air and not evacuated, the magnetic absorption increased in intensity with temperature, as previously reported.^{4,5} The width of the absorption in this range, reported to be constant (8 ± 2 gauss),⁴ was found to increase slightly with temperature. A typical set of results is included in Fig. 1. It was found that samples charred in air and then evacuated at room temperature gave narrow widths, equal to those of the vacuum-charred material.

The effect of various gases on the evacuated samples was investigated. The possibility of such effects has been previously mentioned.^{3,4} The samples were found to be sensitive to small amounts of O_2 and another paramagnetic gas, NO, but were unaffected by N_2 and H_2 . The width increases rapidly above an O_2 (or NO) pressure of 0.1 mm Hg, becoming broader than 60 gauss for pressures above 100 mm. The peak intensity also decreases markedly. In order to reobtain the original width and peak intensity, it was necessary to evacuate the sample for 10 min at 25°C in the case of O_2 , and for 30 min at 150°C in the case of NO. Adsorption isotherms have been determined and show (a) that carbon treated in this way has a large surface area (about 580 m² g⁻¹)

and (b) that O_2 is adsorbed at room temperature on only a small fraction (about 2%) of the available surface. More extensive results will be published elsewhere.⁶

Measurements made on samples cooled to liquid nitrogen temperature showed no change in width, for both the vacuum-treated and for the O_2 -poisoned carbon.

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Relativistic Corrections to the Cohesive Energies of the Alkali Metals*

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RECENT investigations¹ on the effect of relativistic corrections on electronic energy bands in solids have been almost entirely concerned with the spin-orbit coupling. The purpose of this note is to point out that there are other relativistic effects of the same order of magnitude which will affect the numerical values of the calculated effective mass and the calculated values of cohesive energies.

The theory is based on the second approximation to the Dirac equation²:

$$E\psi = H\psi = \left[\left(1 - \frac{E-V}{2mc^2} \right) \frac{p^2}{2m} + V - \frac{\hbar^2}{4m^2c^2} \nabla V \cdot \nabla + \frac{\hbar}{4m^2c^2} \sigma \cdot (\nabla V \times p) \right] \psi. \quad (1)$$

In the case of a spherically symmetric potential, the last term on the right represents spin-orbit coupling. The other terms, $[(E-V)/2mc^2](p^2/2m)$ and $(\hbar^2/4m^2c^2) \nabla V \cdot \nabla$, may be, however, of the same order of magnitude. They do not change the symmetry properties of the energy bands as predicted on the basis of spin-orbit coupling alone, but they may strongly affect numerical predictions of the theory.