

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

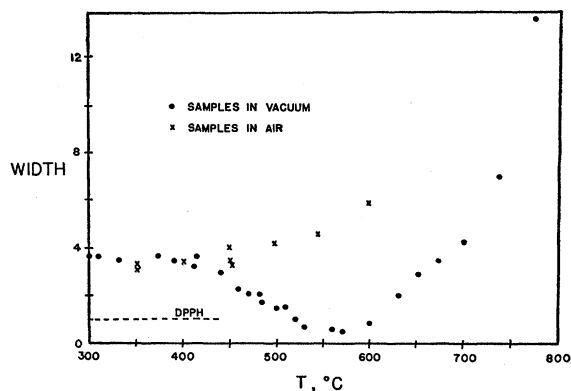


Fig. 1. Width of electron spin resonance absorption (relative to DPPH width = 2.70 gauss) vs temperature of charring.

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.

We have examined the effect of the inclusion of these terms on the theory of the cohesion of the alkali metals. In the cellular approximation, the potential V in (1) is the ion core potential, and we consider the change in the ground-state energy E_0 and in the reciprocal of the effective mass E_2 . We may treat the corrections in first-order perturbation theory to sufficient accuracy (the error may be as large as 6% for cesium), using ordinary nonrelativistic wave functions. Since the ground state is, to good approximation, a pure S -state, the change in the ground-state energy is

$$\Delta E_0 = - \int \psi^* \left[\frac{(E_0 - V)^2}{2mc^2} + \frac{\hbar^2}{4m^2c^2} \frac{dV}{dr} \frac{d}{dr} \right] \psi d\tau, \quad (2)$$

where ψ is the wave function for the ground state Γ_1 . The change in the effective mass is a little more difficult to obtain. If we consider Bloch functions $u_k e^{i\mathbf{k} \cdot \mathbf{r}}$, u_k satisfies

$$\left\{ H + \mathbf{k} \cdot \left[\left(1 - \frac{E - V}{2mc^2} \right) \frac{\hbar \mathbf{p}}{m} - \frac{i\hbar^2 \nabla V}{4m^2c^2} + \frac{\hbar^2}{4m^2c^2} (\boldsymbol{\sigma} \times \nabla V) \right] \right\} u_k = \left[E_k - \left(1 - \frac{E - V}{2mc^2} \right) \frac{\hbar^2 k^2}{2m} \right] u_k, \quad (3)$$

where H is the Hamiltonian of (1). The correction terms transform as vectors. To find the energy to second order in \mathbf{k} and first order in the relativistic corrections, we calculate

$$E_k = \int e^{-i\mathbf{k} \cdot \mathbf{r}} u_k^*(r) H e^{i\mathbf{k} \cdot \mathbf{r}} u_k(r) d\tau / \int u_k^* u_k d\tau. \quad (4)$$

For the alkalis, we may use Bardeen's form³ of u_k , $u_k = u_0 + i\mathbf{k} \cdot \mathbf{r} u_1$, where u_1 vanishes on the surface of the atomic sphere. We find, using (3)

$$E_k = E_0 + \frac{\hbar^2 k^2}{2m} E_2 - \left\{ \Delta E_0 \left(1 - \frac{4\pi}{3} k^2 \int (ru_1)^2 r^2 dr \right) + \frac{4\pi}{3} k^2 \int ru_1 \left[\frac{(E_0 - V)^2}{2mc^2} + \frac{\hbar^2}{4m^2c^2} \frac{dV}{dr} \frac{d}{dr} \right] (ru_1) r^2 dr \right\}, \quad (5)$$

plus some terms which are negligibly small. Here E_0 and E_2 have their nonrelativistic values.

A detailed numerical analysis of these effects is being carried on by the author and Mr. V. Sirounian for the cases of potassium and cesium, using self-consistent field wave functions. Some of the essential features of the results, which will be published in detail at a later date, are as follows: The corrections yield an increased binding. This occurs because the probability that a valence electron will be found near the nucleus, is, on the average, greater in the solid than in the free atom, owing to the compression of the valence electron

charge within the atomic sphere. The effect is not negligible (order of 1 kcal/mole) in potassium, and may be quite large in cesium because of an expected Z^4 dependence on atomic number. In cesium, one would expect an effect of the same order of magnitude as the entire cohesive energy.

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Multiple Thermal Relaxation Times and Nuclear Spin Energy Transfer in Liquids*

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WE offer several lines of evidence to suggest that just as distinguishable protons in a molecule may show discrete nuclear induction lines, they may also have their own characteristic time for return to the ground state from an excited spin state. This would lead to different optimum values of the rf field H_1 . We have observed such differences for protons in groups such as CH_3 , CH_2 , CH , OH and others. Further, one frequently notes the appearance of more "wiggles" after one line has been traversed than for others of similar intensity and width. Thus, for example, a long spin-spin relaxation time t_2 is indicated for the OH protons in some phenols. Since $t_2 \leq t_1$, one has an indication of a relatively

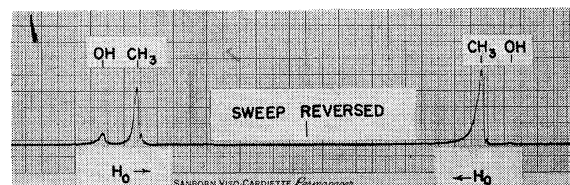


FIG. 1. The proton lines for the OH and CH_3 groups appear as expected when the field is increasing. For decreasing field the OH line is missing. The field H_1 is large and constant.

long time t_1 . The nonidentity of t_1 for distinguishable protons in the same molecule leads to line intensities which are not proportional to their number. Inferences from such intensities must therefore be made with caution.

For large values of H_1 , the relative intensities of multiple lines may depend on the direction of field