

Letters to the Editor

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Paramagnetic Resonance in Irradiated Ice

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(Received February 5, 1954)

WE have recently detected the presence of paramagnetic resonance in samples of ice previously exposed to ionizing radiation at 77°K. The detection equipment utilized a regenerative 350-Mc one-quarter wave coaxial line oscillator incorporated into a double-wall Dewar. The auxiliary circuits have been described previously.¹ The irradiation source was a 400-curie Co⁶⁰ gamma source² with total dosages used in the range $(2-20) \times 10^{20}$ ev/g, yielding signal-to-noise values of 10 to 1000. Irradiations were carried out by using cylinders of ice approximately 5 mm in diameter and 50 mm in length; the resonance-sensitive volume being, however, about 0.1 cc. Measurements were made at temperatures ranging from 4°K (in liquid helium) to 225°K with most of the data taken at 77°K (liquid nitrogen).

At 77°K the H₂O ice displayed a doublet resonance structure at a gyromagnetic ratio of 2.0 with a separation of *ca* 30 gauss and line widths of 6 gauss, each component of equal intensity. Using D₂O ice, a triplet structure was obtained with component separation of 5 gauss and line width of 2 gauss; intensity ratios along the structure were in the ratio 1:2:1.

The results indicated represent substantial evidence for the existence of a free spin (i.e., unpaired electron) existing near an H or D nucleus, with resultant hyperfine structure. Relative line intensities substantiate this assumption, and the line widths are also in the correct ratio if one assumes that neighboring protons or deuterons are the source of the line broadening. The ratio of the hyperfine splitting constants in H₂O ice and D₂O ice, 4.0, is in good agreement with the corresponding atomic beam ratio of $W_H/W_D=4.3$.³ However, the splitting values (e.g., 85.5 Mc/sec in H₂O ice) are considerably less than the free-atom values (e.g., 1420 Mc/sec for H).³ One may attribute this reduction in interaction, at least qualitatively, to the polarization effect of the ice. In fact, the required effective dielectric constant is 2.55, approximately equal to the determined high-frequency value.⁴

In measurements at 4°K, a second doublet structure was revealed in H₂O ice with a separation of 10 gauss, while the D₂O ice resonance spectrum showed a distortion attributable to a second close triplet structure.

In the radiation chemistry of aqueous systems the presence of H and OH is deduced by indirect evidence, and it is suggested that the OH free radical may be responsible for this second resonance. The reversible disappearance of this doublet at higher temperatures remains to be explained. On irradiation of H₂O ice containing H₂O₂, a second doublet structure 12 to 15 gauss in separation becomes prominent at 77°K, while the 30-gauss doublet is weakened or disappears. It is plausible to assign this doublet to OH also, and this weakening of the 30-gauss doublet would be expected if the thermodynamically favorable reaction, $H+H_2O_2 \rightarrow H_2O+OH$, occurs. The persistence of the OH doublet at the higher temperatures may be taken to be a manifestation of the stabilization of the resonance of this radical. Annealing experiments indicate a greater stability for this radical than that

attributed to the H atom. Results with D₂O₂ in D₂O are in agreement with the effects obtained in H₂O₂-H₂O.

We have also investigated the free radical species formed in solid NH₃ and solid HCOOH irradiated at 77°K. These reveal a more complex resonance spectrum with the formation of an intermediate paramagnetic species during annealing. A more complete report of this work will be published shortly.

¹ B. Smaller and E. Yasaitis, *Rev. Sci. Instr.* **24**, 991 (1953).

² Blomgren, Hart, and Markheim, *Rev. Sci. Instr.* **24**, 298 (1953).

³ J. E. Nafe and E. B. Nelson, *Phys. Rev.* **73**, 718 (1948).

⁴ N. E. Dorsey, *Properties of Ordinary Water Substance* (Reinhold Publishing Corporation, New York, 1940), pp. 496-500.

The Heat Capacity and Entropy of Liquid He³ from 0.42°K to 1.06°K

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(Received February 8, 1954)

PRELIMINARY measurements have been made on the heat capacity of liquid He³ between 0.42°K and 1.06°K. These results, when combined with vapor pressure and melting pressure data, show that the entropies of both the liquid and the solid are approximately $R \ln 2$ at 0.42°K, and it is concluded that there is no appreciable alignment of the nuclear spins in either liquid or solid He³ down to 0.42°K.

The calorimeter consisted of a cylindrical copper container, in the center of which was located a 1.87-cc copper vessel connected to an external He³ filling line through a small cupronickel tube. Ferric ammonium alum (74 g) was hand-tamped around the He³ vessel to about 0.7 times the crystal density. Four copper vanes were hard-soldered to the He³ vessel to provide a large area of contact with the alum, and a strip carbon resistor, which served both as a resistance thermometer and as a heater, was fastened to one of the vanes. The free volume in the container was filled with He³ gas to about 1 atmos pressure at room temperature in order to improve the heat transfer within the calorimeter.

The temperature scale was obtained by calibrating the resistance thermometer and the susceptibility of the iron alum against the vapor pressure of liquid He³ from 1.1 to 4.2°K. Below 1.1°K the resistance thermometer was calibrated against the susceptibility of the iron alum. Kistemaker's corrections¹ were applied to the "agreed" helium temperature scale,^{2,3} and corrections for the difference between the magnetic temperature and the thermodynamic temperature were made on the basis of the results of Kurti, Simon, and Squire.⁴ A smooth table of resistance versus thermodynamic temperature was then constructed from the calibration data.

The heat capacity of the empty calorimeter was determined before making the measurements with He³. The first liquid He³ experiments were made with 1011 cc (STP) of gas, or approximately 1.7 cc of liquid. It was found that with this quantity of He³ the available magnetic field was insufficient to cool the calorimeter below about 0.7°K; consequently, for runs at lower temperatures the amount was reduced to 601 cc or 315 cc (STP). The heat capacity of liquid He³ along the saturation line is expressed by the equation:

$$C_{\text{sat}} = 0.53 + 0.48T \text{ cal deg}^{-1} \text{ mole}^{-1}. \quad (0.42 \leq T \leq 1.06^\circ\text{K}). \quad (1)$$

Because of a rather large heat leak in these experiments the results may be in error by as much as 5 percent.

The entropy of liquid He³ at 1°K, including the nuclear spin entropy, has been calculated from vapor pressure measurements to be $2.09 \pm 0.14 \text{ cal deg}^{-1} \text{ mole}^{-1}$.^{5,6} From this result and from Eq. (1) it follows that the entropy of the liquid at its saturated vapor pressure is

$$S_{\text{liq}} = 2.09 + 0.53 \ln T + 0.48(T - 1) \text{ cal deg}^{-1} \text{ mole}^{-1} \quad (2)$$

in the temperature range 0.42 to 1°K. At the lowest temperature of the measurements, 0.42°K, the entropy of the liquid is 1.35 ± 0.15

cal deg⁻¹ mole⁻¹, or very nearly equal to $R \ln 2 = 1.38$ cal deg⁻¹ mole⁻¹, the value for random orientation of the nuclear spins. If the reasonable assumption is made that the contribution of phonon excitation to the total entropy is small at this temperature, it can be concluded that the nuclear spins are not appreciably ordered in liquid He³ at 0.42°K, in agreement with our previous prediction.⁶ The results also indicate, contrary to suggestions by others,⁷⁻⁹ that liquid He³ cannot be treated as an ideal Fermi-Dirac gas having the same molecular weight and density as liquid He³; for the entropy of such a gas at 0.42°K would be 0.84 cal deg⁻¹ mole⁻¹, instead of the measured value of 1.35 ± 0.15 cal deg⁻¹ mole⁻¹.

The present results may also be combined with data on the melting pressure to obtain the entropy of solid He³. It has been found¹⁰ that the slope of the melting pressure curve becomes zero near 0.42°K, and hence from the thermodynamic relation,

$$dp/dT = \Delta S/\Delta V, \quad (3)$$

the difference in entropy between the compressed liquid and the solid becomes zero near this temperature. Provided that the entropy change on compression of the liquid is small, the entropy of solid He³ at 0.42°K must therefore be 1.35 ± 0.15 cal deg⁻¹ mole⁻¹, which corresponds to random orientation of the nuclear spins in the solid. This conclusion substantiates Pomeranchuk's assumption¹¹ regarding nuclear spin alignment in solid He³.

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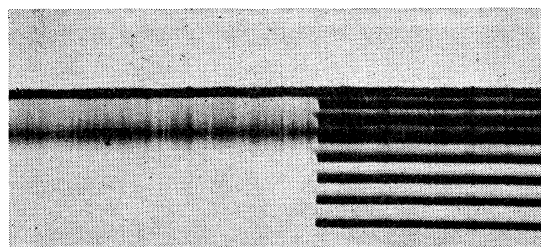
Energy Loss of Electrons in Passage Through Thin Films*

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(Received February 8, 1954)

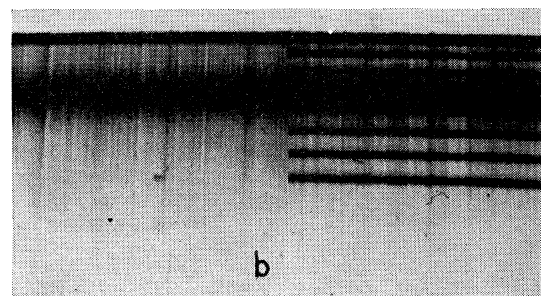
THIS is a preliminary report on measurements of the energy loss spectrum of 30-kev electrons passing through thin films of metals and insulators. These losses are of the same type as those measured by Ruthemann,¹ Lang,² and Möllenstedt,³ and as those calculated by Pines and Bohm⁴ by means of their "plasma oscillation" theory of metals.

To make these measurements, we modified an electrostatic electron microscope by replacing its two projection lenses with a slit and a "cylindrical" lens. The analysis of the scattered primary beam is accomplished by utilizing the off-axis chromatic aberration of the "cylindrical" lens.³ The slit has a fixed spacing of approximately 2 microns, and was built into the shell of one of the projection lenses with provision made for rotation and translation from outside the vacuum of the instrument. The "cylindrical" lens was made using the shell and outer electrodes of the other projection lens, and replacing the center electrode by an element with an elongated aperture. These were placed in the former projection lens positions with the slit above the lens. After proper alignment, as described by Möllenstedt, it was found that the projected image of the slit could be shifted parallel to itself when the accelerating potential was changed relative to the lenses. With this arrangement we have obtained an energy resolution of 1 part in 35 000.

The thin films, which were between 50 and 100A thick, were prepared by evaporation onto salt crystal faces, floated off on water, and mounted on 200-mesh screens. These were placed



(a)



(b)

FIG. 1. Examples of the type of spectra obtained. Fig. 1(a) is the spectrum of germanium, and Fig. 1(b) is the spectrum of beryllium. The top line in each case represents the primary energy. The diffuse line on the left is the energy spectrum of electrons transmitted through the scatterer, and on the right are calibration markers spaced 6 ev apart.

in the normal object position of the microscope so that an enlarged image appeared on the slit. In cases where the material oxidized rapidly in the air, it was evaporated onto another thin film substrate in the vacuum of the analyzer itself.

Figure 1 shows examples of the type of spectra obtained. On the left is the energy spectrum of electrons transmitted through the film, and on the right are calibration markers spaced 6 ev apart. The spectrum contains, besides the undisturbed baseline, one or more lines which in some cases are quite sharp. Table I lists preliminary values of the energy losses corresponding to the maxima of these lines for the materials which we have measured so far. The letters *a*, *b*, *c*, *d*, and *e* shown as subscripts to the

TABLE I. Energy loss values in ev for approximately 30-kev electrons passing through thin films of various materials. The subscripts refer to estimated widths of the lines (see text).

Material	Energy loss values in ev
Beryllium	6.5 _a 18.9 _a
Na on quartz	5.4 _a 10.7 _a 13.3 _a 17.5 _c
Na on collodion	5.1 _a 10.8 _a 17.5 _b 18.6 _c
Magnesium	9.7 _a 20.3 _a
Aluminum	6.2 _a 13.9 _a 19.2 _b 27.8 _a 35.0 _b
Silicon	5.2 _a 16.9 _a
K on silicon	7.8 _a 11.3 _a 15.0 _a 18.7 _a 22.6 _a 27.8 _b
K on collodion	8.0 _a 11.0 _a 14.9 _a 19.5 _a 22.7 _a 25.8 _b
Titanium	11.4 _a 21.4 _b 42.9 _b
Chromium	9.7 _a 21.8 _d 45.0
Manganese	9.9 _a 22.1 _d
Iron	15.8 _b 19.4 _b 56.1
Cobalt	5.7 _a 18.3 _c
Nickel	5.8 _a 9.4 _a 13.2 _a 17.6 _c 23.4 _c
Copper	6.9 _a 11.3 _a 19.6 _d
Germanium	16.0 _b 30.1 _b
Palladium	15.7 _a 21.5 _a
Silver	16.0 _c
Cadmium	14.5 _a
Tin	4.5 _a 12.4 _a 18.0 _a 23.9 _a
Antimony	14.2 _a 24.3 _a
Gold	16.5 _a 21.5 _a
Bismuth	13.0 _a 25.2 _a
Collodion	4.5 _a 19.3 _d
Quartz	5.5 _a 19.4 _a
Air (nitrogen)	12.9 _a