Nuclear Magnetic Resonances at Low Temperatures*

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WE have recently completed a preliminary set of experiments on nuclear magnetic resonances at temperatures down to 4°K, using the 9½-inch gap of the M.I.T. cyclotron magnet which was recently made available to us for a period of several days. Following is a summary of the results of these experiments and of a series of room temperature experiments done with a small electromagnet.

Proton or fluorine resonances have been observed in all substances investigated. Among these have been: benzene, ether, paraffin, lithium hydroxide, lithium fluoride, and hydrofluoric acid at room temperature; glycerine down to 195°K (solid CO_2); ammonium chloride, water and ice both as pure H_2O and in the form of a mixture containing 95 percent D_2O+5 percent H_2O down to 77°K (liquid nitrogen); liquid hydrogen at its boiling point; and solid methane down to liquid helium temperature.

In general, broad resonance lines, many gauss wide, were found in solids, with the exception of CH_4, while lines of the order of one gauss and less in width were observed in liquids. In reference to the distilled water and heavy water solutions, the D_2O was found to have no appreciable effect on the width of the resonance line in both the liquid and frozen states. The glycerine resonance line broadened from a width of the order of one gauss to a width of about 16 gauss as the temperature was reduced to 195°K. The LiF gave the broadest resonance observed, greater than 25 gauss wide at room temperature. The resonance line in liquid hydrogen was slightly broader than for protons in water at room temperature. In most cases, narrow lines were observed on an oscilloscope. Because of the lower amplitude of broad resonances, these were investigated on the output meter of a narrow-band 30-cycle amplifier in order to obtain a better signal to noise ratio.

Our observations of narrow lines in liquids and broad lines in solids are in agreement with the theory of line widths outlined by Bloembergen, Pound, and Purcell.[1] In this theory the rotational states in liquids are the key to narrow lines. In solids the internuclear fields serve to broaden the observed resonance line. However, when rotations occur with frequencies greater than the Larmor frequency involved (about 30 Mc for these experiments), the internuclear fields practically average out to zero during one Larmor cycle, thus resulting in a narrow line.

Since rotational states generally lead to narrow lines, it was decided to study the possibility of rotational states above the λ-points of ammonium chloride and solid methane, which have specific heat anomalies at −30°C and 20°K, respectively. Although some slight broadening of the proton line occurred in cooling ammonium chloride from room temperature to 77°K, it was a consistently broad line, such as is characteristic of normal solids. This indicates that the transition across the λ-point is due to an order-disorder phenomenon, in agreement with conclusions drawn by Lawson[2] from an analysis of thermodynamic data. In contrast to this are the observations of proton resonances in solid methane. In a liquid helium bath a broad line, about 12 gauss wide, was found. When the sample was allowed to warm up through the λ-point, the broad line changed to a narrow line, presumably in the vicinity of the λ-point. At liquid hydrogen and nitrogen temperatures, narrow lines, somewhat less than 1 gauss wide, were observed in solid methane.

It should be noted that those molecules with H atoms showing λ-point transitions are among the easiest to study by this method but present considerable difficulty in studies by means of x-rays. More detailed investigations of rotational states in solids are now being undertaken.

Larger signals were observed at low temperatures, approximately following the inverse temperature variation in Curie's formula for the equilibrium magnetization. This is in agreement with results obtained at hydrogen temperatures by Rollin and Hatton[3] and indicates that, in the substances examined, relaxation times do not undergo drastic variations at low temperatures. In the case of resonances in liquid hydrogen, signal-to-noise ratios of from 300 to over 1000 were obtained on an oscilloscope without the use of a narrow-band amplifier. These results indicate that low temperatures may be useful in the study of small samples or of substances with low concentrations of the nucleus under observation, particularly if narrow lines can be retained as in methane. However, in most substances, broad resonance lines are to be expected, and this will tend to reduce the gain caused by the low temperatures. If the structure of resonance lines is to be studied, or if the natural width of narrow lines is to be measured, stringent requirements must be placed on the uniformity of the magnetic field over the sample. Otherwise the line width and shape will be determined by the magnet and not by the sample.

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[1] N. Bloembergen, R. V. Pound, and E. M. Purcell, Phys. Rev. 71, 466(A) (1947).
[2] Rollin and Hatton, Nature 156, 201 (1947).
[3] Andrew W. Lawson, Phys. Rev. 57, 417 (1940).

The Unboundedness of Quantum-Mechanical Matrices

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HILBERT'S definition of a *bounded* infinite matrix A is equivalent to the requirement that the linear substitution $y=Ax$ should define a vector $y=(y_1, y_2, \cdots)$ of finite length whenever $x=(x_1, x_2, \cdots)$ is a vector of finite length