

III. LOW TEMPERATURE PHYSICS

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A. NUCLEAR MAGNETIC RESONANCE IN SOLID METHANE

Measurements of the nuclear magnetic resonance absorption spectrum in the temperature range from 2° K to 4° K have been made for pure solid methane (CH_4) and for three mixtures of methane with krypton. We obtain traces of the first derivative of the absorption curve as a function of magnetic field, and our results can best be described with reference to two characteristics of these traces: (a) the linewidth, which we take to be the difference between the values of magnetic field characterizing the maximum and minimum values of the first derivative, and (b) the second moment of the absorption curve, or the average value of $(H-H_0)^2$, calculated by using the absorption at each value of H as a weighting factor. (H_0 is the field characterizing the center of the line.) The second moment can be calculated theoretically from an equation derived by Van Vleck. For a molecule such as methane which has several protons, the second moment is the sum of two contributions: an intramolecular part, arising from interactions among the four protons within a given molecule, and an intermolecular part, arising from interactions among the protons on one molecule and those on neighboring molecules.

Our experimental results for pure methane below 4°K give us 7.1 gauss² for the second moment, and 7.1 gauss for the linewidth. We observe no changes in these quantities with temperature which are greater than ± 5 per cent, our experimental uncertainty. For a methane molecule completely at rest, the intramolecular contribution to the second moment alone is greater than 30 gauss², so it is clear that the methane molecules cannot be standing still. It is known that the carbon atoms in methane form a face-centered cubic lattice in the solid. If one calculates the intermolecular contribution to the second moment, assuming that the four protons are smeared out uniformly over a shell surrounding each carbon atom, a value of 10 gauss² is obtained, which, of course, is too large. A more realistic model would be one in which the molecules are assumed to have definite orientations with respect to various directions in the lattice, and to jump from one equivalent orientation to another. Calculations for the various possibilities are in progress.

In order to study the intramolecular contribution to the second moment, we made measurements in krypton-methane mixtures. Both substances have face-centered cubic lattices with approximately equal lattice constants, and are known to form solid solutions at all concentrations. As the (almost) magnetically inert krypton atoms replace methane molecules in the lattice, the second moment should decrease, falling

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linearly with increasing krypton concentration either to zero or to some finite value, which would be interpreted as the intramolecular contribution to the second moment. Our measurements were made for methane lattices having 15 per cent, 50 per cent, and 90 per cent of their sites occupied by krypton atoms. The three second moments, together with the value for pure methane, lie on a straight line which extrapolates to a value of approximately 1.8 gauss^2 for isolated methane molecules. The linewidth does not fall linearly with increasing krypton concentration, but decreases in such a way that it may become zero; however, further points are needed at higher krypton concentrations before a definite statement can be made. The indications are, nevertheless, that the shape of the absorption curve is changing, and we believe that our results at high krypton concentrations may pose problems of interpretation which are not necessarily related to those that arise in connection with pure methane.

Our plans for the immediate future are to study the absorption spectra of methane-krypton mixtures at additional concentrations and to extend the measurements for all of our samples to temperatures in the range 4°K - 77°K . Work has commenced on CH_3D and will soon begin on CH_4 - CD_4 mixtures. These experiments are all part of our long-range program to study the λ -point in solid methane and in the various solid deuterated methanes.

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