Interruption of Nuclear Spin Diffusion*

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Experimental results are shown in which the nuclear spin diffusion responsible for nuclear relaxation at low temperature, under certain circumstances, can be interrupted by introducing strains into crystals either by the paramagnetic impurity introduced into the crystal or by surface strains made to be significant by grinding the sample to a powder. Nuclei with large quadrupole moments, such as iodine, have their spin diffusion strongly interrupted whereas nuclei with no quadrupole moment, such as fluorine, show no effect of strains on the spin diffusion. The interpretations are made from measured values of the spin–lattice relaxation time at liquid-helium temperature.

INTRODUCTION

NUCLEAR-SPIN diffusion has been long considered an important mechanism for conducting heat in a system of nuclear spins in a solid substance. The heat in the spin system is transferred by means of the mutual interaction of the nuclear magnetic moments of the system.[1] This mutual interaction causes pairwise spin flips of neighboring nuclear moments. These spin flips conserve energy within the nuclear spin system. The process will proceed at a rate that is determined in part by the magnetic dipolar interaction between the nuclei. In addition the Larmor precessions of neighboring nuclei should be close to each other in order that the mutual spin flip take place. This is exemplified graphically in the work of Abragam and Proctor[2] in which the heat from a certain nuclear species could be given to another nuclear species only by dropping the external field essentially to zero.

In cases where there exists a permanent quadrupolar splitting of the nuclear-spin levels, spin diffusion should be seriously curtailed since energy conserving mutual spin flips can only occur if neighboring nuclei are in spin states separated by one in the magnetic quantum number. The curtailment would be the larger, the larger the spin of the nucleus.

Blumberg[3] has shown that in the presence of paramagnetic impurities the magnetic dipolar field from the paramagnetic impurity will limit the spin diffusion between nuclei in the neighborhood of the paramagnetic impurity since the neighboring nuclei will have different Larmor precessions and the nonsecular perturbation between them will not be effective in causing mutual spin flips. This effect has been discussed independently by Bender.[4]

We have been able to show experimentally that it is possible to interrupt the nuclear spin diffusion con-

siderably by introducing strains in crystals to such an extent that the electric field at a quadrupolar nucleus,[5] which has cubic symmetry at the nuclear site in the unstrained crystal, is sufficiently distorted from cubic symmetry to affect markedly the nuclear spin diffusion.

In our work we measure the spin–lattice relaxation time of paramagnetically doped crystals in the temperature region where spin diffusion is the bottleneck in the nuclear spin–lattice relaxation process. We use two methods to introduce strains into the crystal. In one method we grind the samples to fine powder (0.01-cm diam), producing surface discontinuities which are sufficient to introduce strains into the crystal which reduce the spin diffusion rate. Into these crystals we introduce paramagnetic impurities which provide heat contact with the lattice vibrations. In the second method, we merely add paramagnetic impurities to sodium iodide crystal and measure the spin–lattice relaxation time of sodium and iodine nuclei at room temperature and liquid-helium temperature. (The relaxation is principally via quadrupole interaction with time-varying electric-field gradients at room temperature and via spin diffusion at liquid-helium temperature.) The foreign ion distorts the lattice enough that the spin diffusion is interrupted—strongly for the iodine nuclei and considerably less strongly for the sodium nuclei since iodine has a larger quadrupole moment than sodium.

The article is divided into three parts. In part I we describe some of the powder experiments, in part II we describe the experiments on sodium iodide, and in part III we discuss the results of the experiments.

I. FINE POWDERS

We measured spin lattice relaxation time T_1 of iodine nuclei in powdered samples of potassium iodide, doped with $PtO_6^=$, as a function of particle size at liquid-

[1] See, for example, N. Bloembergen, Physica **15**, 386 (1949).
[2] A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958).
[3] W. E. Blumberg, Phys. Rev. **119**, 79 (1960).
[4] P. A. Bender, Ph.D. thesis, University of Colorado, 1960.

[5] Early data on this appeared in an article by us in J. Chem. Phys. **28**, 976 (1958). At that time we attributed effect wrongly to a loss of phonon modes responsible for relaxation. The phenomenon predicted in the above paper has not been detected as yet to the best of our knowledge. The possibility of controlling spontaneous transition probabilities of excited atoms exists if one could limit the size of the cavity containing the atoms so that the zero-point oscillations corresponding to the atomic transition were not present. This has been suggested by M. Mizushima in conversations with him.

helium temperature. We also made similar measurements of T_1 of sodium nuclei in sodium chloride doped with Ni^{++} ions, and of T_1 of fluorine nuclei in potassium fluoride doped with Mn^{++} ions. To introduce the Ni^{++} ion into the sodium chloride lattice we melted sodium chloride in a porcelain crucible with nickel chloride NiCl$_2$ in the melt. In the case of potassium iodide we melted the potassium iodide in a platinum crucible. This process introduced PtO$_6^-$ into the lattice. The potassium fluoride was melted with MnCl$_2$. The melts in each case were air cooled, ground with a mortar and pestle and separated into particle-size fractions using graded screens. No great care was exercised in controlling the amount of impurity added. The amount of the above impurities added to each of the specimens, although changing the relaxation time, did not remove the particle-size dependence exhibited in Fig. 1. The size of the particles given in Fig. 1 is an average size of the particles in a particle-size fraction obtained using the graded screens. We have done the experiments at 1.4, 5, and 10 Mc and find that the results do not depend on the frequency.

For making the measurements the particle fractions were placed in a glass tube with Bakelite plugs between fractions and the tube was then placed in a helium double Dewar in such a manner that the tube passed through the receiver coil of a pulsed free induction spectrometer. A spring attached to the glass tube permitted raising or lowering of the desired particle-size fraction into the receiver coil. Standard pulsed nuclear resonance techniques were employed to measure the spin–lattice relaxation time of these samples. The transmitter coil of the pulsed oscillator was placed outside the helium double Dewar next to the sample. The fractional attenuation of the nuclear induction signal was plotted against time on semilogarithmic paper and the experimental T_1 was determined from the slope of this line. The dependence of the functional attenuation on the time was not perfectly exponential. This can be attributed to two reasons: (1) the range of particle sizes contained in a single powder fraction would have a range of relaxation times, and (2) the spin diffusion process does not lead to an exponential time dependence.[3] However the best straight line was drawn to fit the data and the slope used to calculate the T_1 assuming an exponential behavior.

The significant feature of the data as shown in Fig. 1 is the rapid dependence of T_1 on particle size for iodine, the slower dependence for sodium and the independence of T_1 on particle size for F. These results will be discussed further in conjunction with the results of part II in terms of strains interrupting the nuclear-spin diffusion.

II. SODIUM IODIDE

Several alkali halide crystals are useful in the sense that one can conveniently look at the nuclear resonance of either of the two different nuclei by merely
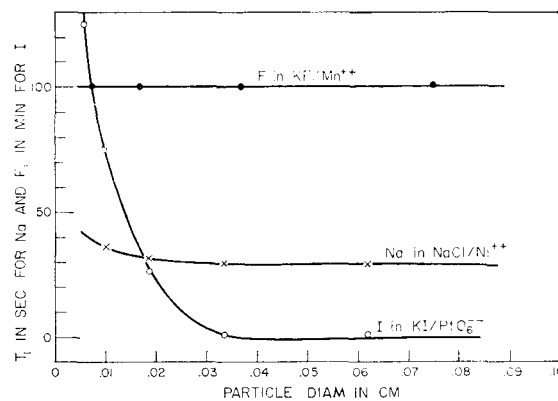

FIG. 1. The particle size dependence of T_1 is shown for fluorine, sodium, and iodine nuclei. The quadrupole moments for sodium, iodine, and fluorine are respectively 0.1, 0.75, and 0.0 b. The quadrupolar antishielding factor should be about 5, >100 and 0.

changing the field while holding the frequency constant. In addition one desires to have a fairly low melting point so that introduction of impurities can be conveniently performed. Sodium iodide crystals satisfy both of these requirements. Cesium iodide is better in that it is not hygroscopic, but it is expensive and more difficult to obtain than sodium iodide. We chose to use sodium iodide. The idea in this experiment was to add a paramagnetic impurity to the sodium iodide and measure the T_1 of each nucleus in the spin-diffusion-limited region (liquid-helium temperature) and compare with the room temperature T_1 at which temperature the relaxation in quadrupolar. Sodium has a smaller quadrupole moment than iodine and one would expect spin diffusion to be seriously limited by strain effects on iodine.

About 1%–0.1% of anhydrous manganese chloride was added to anhydrous sodium iodide and the mixture melted in a helium atmosphere and then removed and permitted to crystallize. The T_1 of sodium at room temperature is 8 sec and of iodine 12 msec. At liquid-helium temperatures the sodium relaxation time ranges from 90 to 300 sec and the iodine relaxation time ranges from 180 to 360 sec in the concentration ranging from 1 to 0.1% MnCl$_2$. The T_1 of sodium doesn't change substantially between liquid-nitrogen and liquid-helium temperatures and the T_1 of both is essentially concentration independent at room temperature. The important result of this experiment is that the iodine relaxation time is longer than the sodium relaxation time at liquid-helium temperature, whereas, the reverse is true at room temperature. This experiment is not as conclusive as the experiments in Sec. I. The primary reason for this is due to the almost equal melting points of manganese chloride (650°) and sodium iodide (651°). In Sec. I the impurities had considerably different melting points from the host crystal. This discrepancy in melting points undoubtedly led to a good deal of separation of the impurity in

localized regions in the host crystal.[6] Evidence for this effect comes from the lack of dependence of the relaxation time on the nominal impurity concentrations. In the experiments on sodium iodide, however, the nominal impurity concentrations was likely the solid solution concentration of the samples whose T_1 was measured. Evidence for this came from the dependence of the length of the free induction decay signal of sodium and iodine at liquid-helium temperatures on the nominal impurity concentration. For the sodium iodide crystals that had the greater manganese chloride concentration the length of the free induction decay signals of sodium iodide were considerably reduced; also those of iodine were so short they were barely detectable following the receiver saturation (15 μsec) and could not be measured. In this case it is unlikely that the relaxation is predominantly by nuclear spin diffusion.

For the more dilute impurity crystals of sodium iodide we performed a particle-size experiment and found that the iodine nuclear relaxation time doubled in the particle-size region where the sodium nuclear-spin relaxation time tripled.

III. DISCUSSION

From the above results it is evident that for the fine-particle experiment the nuclear-spin diffusion is slowed down by the introduction of strains which bring a quadrupole perturbation on the Zeeman spin levels. One can make an estimate of the field gradient introduced by the strains, but this in itself is not helpful unless one is able to relate the field gradient to the strains. On the other hand there is within the data certain other useful information. The penetration of the surface discontinuities into the lattice appears to be about 0.005 cm. We have annealed the KI powders at temperatures 100° below the melting point for several hours and, though we have reduced the dependence of T_1 for iodine on the particle size, we have not been able to remove it. The actual nature of the surface strains appear to be dislocations that penetrate from the surface into the crystallites since it is difficult to imagine that the pure strain field from the surface discontinuity would penetrate 0.005 cm into the crystal. Further, it is of interest to point out that for the powder experiment the spin diffusion in the fine powders is already interrupted by the strains due to the impurities that were introduced as shown in Sec. II. Thus the fine powders have within them two sources of strains: those due to impurities and those

due to surface discontinuities. The surface strains are effective for particle sizes 0.01 cm in diameter and less. The presence of absorbed gases, particularly oxygen, doesn't change our conclusions. The addition of absorbed gases would, if present to a greater extent in the fine powders than in the coarse powders, reduce the relaxation time of fluorine nuclei in KF.

That impurities do, in fact, produce the strains and the consequent broadening of the nuclear line width as we are proposing in these measurements has been shown earlier by Reif and others.[7] From the length of the free-induction decay signal in our experiments on iodine nuclei in KI the observed free-induction decay in the fine powders is less by about a factor of 2 than in the coarse powders. In the sodium iodide crystal the same effect was very pronounced as indicated in Sec. II. The greater the impurity concentration the shorter the free-induction decay.

Our data indicated an initial dependence of the recovery of the nuclear magnetization on time given by Blumberg[3] for the spin diffusion limited case. In the case of sodium nuclei in sodium chloride we got the same relaxation time at 5 Mc as at 10 Mc, thus indicating a field independent relaxation in that case.

The iodine relaxation time in sodium iodide did not show a remarkable particle-size effect. This was likely due to two effects: The dipolar broadening from the paramagnetic impurity had already limited spin diffusion, assuming the electron paramagnetic relaxation time was longer than the reciprocal of the nuclear-spin transition linewidth.[3] Also it is possible that strains due to the impurities had already reduced the spin diffusion to the extent that the reduction by surface discontinuities had a relatively small effect. It is also possible that spin diffusion of iodine nuclei was completely eliminated and the relaxation was via direct magnetic dipolar coupling to the paramagnetic impurity. That iodine in potassium iodide exhibited a strong particle size effect would seem to indicate that the paramagnetic relaxation time of the paramagnetic platinum in the platinate complex was shorter than T_2 of the iodine or that the strains introduced by the platinate complex were not large.

[6] See for example, S. Miyake and K. Suzuki, J. Phys. Soc. Japan 9, 707 (1954); and G. Watkins, Phys. Rev. 113, 79, 91 (1959); D. A. Jennings and W. H. Tanttila, Bull. Am. Phys. Soc. 7, 84 (1962); D. A. Jennings, Ph.D. thesis, University of Colorado, 1962 (to be published); T. T. Chang, Ph.D. thesis, University of Colorado (in preparation).

[7] F. Reif, Phys. Rev. 100, 1597 (1955); R. E. Michels and R. D. Spence, J. Chem. Phys. 26, 954 (1957); A. Monfils and G. Grosjean, Physica 22, 541 (1956); T. J. Rowland, Acta Met. 3, 74 (1955); R. V. Pound and G. Watkins, J. Phys. Chem. 57, 743 (1953); G. Watkins, Phys. Rev. 89, 658 (1953).