Spin-Lattice Relaxation Time for I^{127} in KI in the Temperature Range 2°K to 20°K*

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The spin-lattice relaxation time, T_1, for I^{127} in both single crystal and powdered KI has been measured in the temperature range 2°K to 20°K using a Pound-Watkins type nuclear magnetic resonance spectrometer. In the liquid hydrogen temperature range T_1 is approximately the same for both the single crystal and the powder specimens, varying from 20 sec at 20°K to 70 sec at 14°K. Both the temperature dependence and the magnitude of T_1 in this temperature range can be explained on the basis of a theory of nuclear quadrupolar spin-lattice relaxation proposed by Van Kranendonk. In the liquid helium temperature range (2°K to 4°K), T_1 is constant within experimental error. For the single crystal $T_1=6.9\times10^3$ sec and for the powder specimen $T_1=6.0\times10^2$ sec in this temperature range. These values of T_1 are less by orders of magnitude than is predicted using Van Kranendonk's theory. The I^{127} resonance (spin $I=\frac{5}{2}$ in units of $\hbar$) consisted of a narrow (less than 1 gauss half-width) central line with broad (>15 gauss) weak wings. This is attributed, according to Pound, to a shift in the nuclear magnetic energy levels brought about by the interaction of the nuclear quadrupole moment with electric field gradients present in the specimens.

INTRODUCTION

THE measurement of the time which characterizes how quickly a spin system may reach equilibrium with its surroundings, i.e., the spin-lattice relaxation time, T_1, is a measure of the strength of the interaction between the spins and the lattice. In the case of nuclear spins imbedded in a solid crystalline lattice, both the magnitude and the temperature dependence of T_1 furnish evidence as to the nature of the dominant relaxation processes involved. To investigate some of these possibilities T_1 has been measured in the temperature range 2°K to 20°K for the I^{127} spin system in KI. I^{127} with a spin of $\frac{5}{2}$ in units of $\hbar$ has a relatively large electric quadrupole moment which provides, in addition to its magnetic moment, another possible mechanism of nuclear spin-lattice interaction. Van Kranendonk[1] has proposed a theory of nuclear electric quadrupolar spin-lattice relaxation in which he considers the most important relaxation processes to be those of a Raman nature. In these Raman processes a lattice vibration is excited and another lattice vibration is de-excited with a small energy balance being made up by the nuclear spin transition. This process depends only on the difference in the frequencies of the two lattice oscillators and advantage is taken of the large density of such oscillators at high frequencies. We shall compare our results with this theory.

EXPERIMENTAL

The nuclear magnetic resonance spectrometer used was of the Pound-Watkins type manufactured by the Nuclear Magnetics Corporation, Boston, Massachusetts. The Pound-Watkins spectrometer detects the nuclear resonance by means of the marginal oscillator principle. For a discussion of the circuitry involved in the marginal oscillator spectrometer, see Pound[2] and Watkins.[3] The actual resonance equipment used in this experiment has been discussed by Low and Squire.[4] A Varian 6-in. electromagnet with associated power supply provided the necessary magnetic field.

The cryogenic features which are conventional in most low-temperature laboratories will not be discussed in any detail. The following details pertain to this particular type of experiment.

The radio-frequency coil used to detect the resonance was wound directly on the $\frac{1}{2}$-in. diameter specimens in order to obtain a maximum filling factor. Connection between the radio-frequency oscillator which was external to the Dewar assembly and the radio-frequency coil was made using RG58/U commercially available coaxial cable. The coaxial cable was reinforced to minimize pickup due to mechanical vibrations by placing it in a $\frac{1}{4}$-in. thin-walled Monel tube. This tube was brought out through the Dewar top plate by means of a stuffing box so that the specimen could be rotated through 180° and raised or lowered if necessary.

The procedure used in determining T_1 was to observe the growth of the absorption signal after saturation by a large radio-frequency field in the following manner. By setting the radio-frequency field at a high enough value, the I^{127} resonance could be completely saturated at the helium temperatures. Since the smallest radio-frequency field obtainable was still large enough to saturate the signal appreciably, it was not possible to simply turn the rf field down to its lowest value and watch the growth of the resonance signal on the oscilloscope. Instead, measurements were made by quickly changing the external magnetic field to a value such

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[1] J. Van Kranendonk, Physica **20**, 781 (1954).
[2] R. V. Pound, *Progress in Nuclear Physics* (Butterworths-Springer, London, 1952), Vol. 2, p. 21.
[3] G. D. Watkins, Ph.D. thesis, Harvard University, 1952 (unpublished).
[4] F. J. Low and C. F. Squire, J. Phys. Chem. Solids **5**, 85 (1958).

that the Larmor resonance condition was not satisfied. The signal was then examined after a certain time by quickly changing the magnetic field back to the resonance condition. The initial magnitude of the absorption signal after this interval of time was measured by using a high-frequency recorder. The signal was allowed to saturate completely again and the procedure repeated with a different interval of time between saturation and observation of the signal. In this way the exponential growth of the absorption signal, which is proportional to the magnetization, could be traced out and a value for T_1 obtained. Both the single crystal and the powder specimens of KI were cut from a 1×1×2-in. single crystal obtained from the Harshaw Chemical Company. The single crystal specimen was

TABLE I. Spin-lattice relaxation times, T_1, for I^{127} in single-crystal KI for the temperature range 2°K to 20°K. Crystallographic orientation with respect to H_0: angle between [001] direction and $H_0=90°$; angle between [100] direction and $H_0=20°$.

T°K	H_0 (kilogauss)	T_1 (sec)
2.16	4.1	$(6.6\pm1.2)\times10^3$
2.16	6.0	$(7.2\pm1.2)\times10^3$
4.20	4.1	$(7.2\pm1.2)\times10^3$
4.20	6.0	$(6.6\pm1.2)\times10^3$
14.41	4.1	63.0±14.0
14.41	4.7	66.0±14.0
14.41	6.0	79.0±14.0
14.93	4.7	52.0±10.0
16.00	4.7	36.0±8.0
16.00	6.0	50.0±8.0
17.00	4.1	27.0±6.0
17.00	4.7	33.0±6.0
17.00	6.0	36.0±6.0
18.01	4.7	28.0±5.2
18.01	6.0	27.0±5.2
20.43	4.1	18.0±3.6
20.43	4.7	18.0±3.6
20.43	6.0	18.0±3.6

a cylinder ½ in. in diameter and ¾ in. long with [100] direction along the axis of the cylinder. The powder specimen was prepared by grinding, with an agate mortor and pestle, a part of the 1×1×2-in. single crystal in an atmosphere of dry nitrogen gas. The particle size ranged from about 1 to 60 μ with an average size of approximately 20 μ. A ½-in. diameter cylinder was formed by lightly pressing the powder in a piston of the correct size.

RESULTS

The experimental values of T_1 for I^{127} in single crystal and powdered KI in the temperature range 2°K to 20°K and in various external magnetic fields are shown in Table I and Table II along with the estimated experimental errors. Figure 1 is a semilogarithmic plot

TABLE II. Spin-lattice relaxation times, T_1, for I^{127} in a powdered specimen of KI in the temperature range 2°K to 20°K. Average particle size = 20 μ.

T°K	H_0 (kilogauss)	T_1 (sec)
4.21	6.0	$(6.0\pm1.2)\times10^2$
3.81	6.0	$(6.0\pm1.2)\times10^2$
2.16	6.0	$(4.8\pm1.2)\times10^2$
20.43	6.0	17.0±3.6
20.43	4.7	18.0±3.6
18.2	6.0	25.0±5.0
16.0	6.0	30.0±6.0
16.0	6.0	33.0±6.0
14.2	6.0	57.0±10.0
14.2	6.0	52.0±10.0
14.4	4.7	49.0±10.0

of T_1 for both the single-crystal and powder specimens in the range 2°K to 20°K. Also, the theoretically predicted values of T_1 according to the theory of Van Kranendonk are seen in Fig. 1. The calculation of T_1 using Van Kranendonk's theory was based on the room temperature value of $T_1=0.014$ sec for I^{127} in KI given by Jennings and Tanttila.[5]

Figure 2 is an enlarged tracing of a photograph of the I^{127} resonance in single-crystal KI at 2.16°K. The total modulation sweep width is approximately 38 gauss.

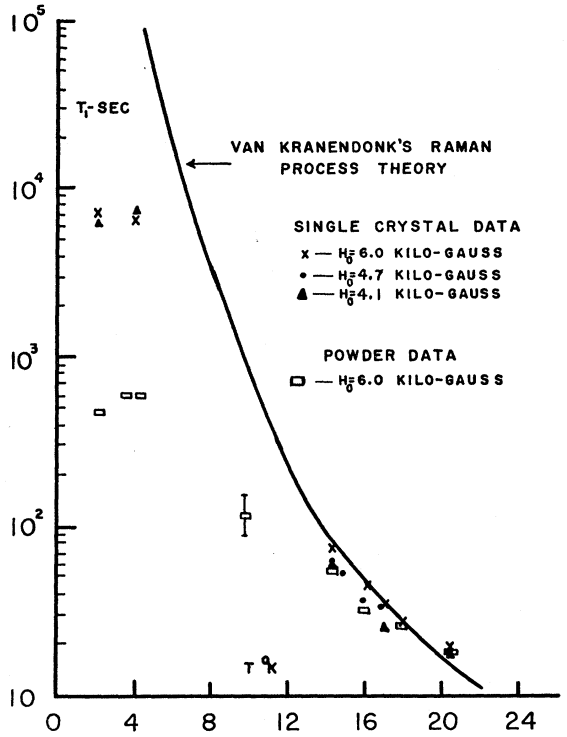

FIG. 1. Spin lattice relaxation time for I^{127} in KI.

[5] D. A. Jennings and W. H. Tanttila, J. Chem. Phys. 28, 976 (1958).

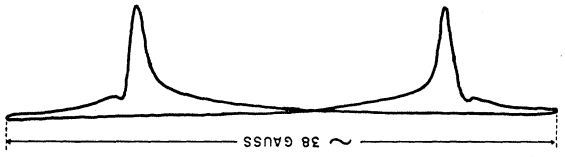

FIG. 2. I^{127} absorption curve in single-crystal KI at a temperature of 2.16°K in a field of 4.1 kilogauss. Total sweep width ≅38 gauss.

The modulation frequency was 10 cps but even at this low frequency there was a slight amount of ringing. As can be seen from Fig. 2, the resonance consists of a narrow (about 1 gauss) central peak flanked by weak broad (greater than 15 gauss) wings. Accurate measurements were not made on the line shape as this was not our primary interest. This resonance shape has been investigated at room temperature by Watkins and Pound[6] and by Solomon.[7]

Watkins and Pound[6] did not observe the wings of the resonance, but from relative intensity measurements they concluded that approximately 86% of the central peak was due to the $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition. The rest of the central peak was due to the other possible transitions in a spin system of $I=\frac{5}{2}$. They proposed that this smearing out in frequency of all the transitions except the central one, i.e., the $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition, was a result of the shifting of the nuclear magnetic energy levels by the interaction of the nuclear electric quadrupole moment with strong electric field gradients in the specimens. The origin of these field gradients was assumed to be strains which are present in even the best single crystals.

Solomon[7] has studied the magnitude of this quadrupolar interaction with the random electric field gradients produced by strains using a spin echo technique. In the specimens of KI he investigated, the interaction expressed in gauss was found to vary from 18 to 36 gauss depending on the specimen (whether powder or single crystal) and its past history. Our results are certainly compatible with Solomon's more careful study of the I^{127} resonance line shape in KI.

DISCUSSION OF RESULTS

As previously stated, I^{127} has a relatively large electric quadrupole moment, $Q=-0.75\times10^{-24}$ cm². Pound[8] first showed that the spin-lattice relaxation time at room temperature was quite short (<0.02 sec) for I^{127} in KI. He attributed this to the interaction of the electric quadrupole moment of the nucleus with fluctuating electric fields produced at a given lattice site by the thermal motion of the surrounding atoms.

Van Kranendonk[1] has given a theoretical discussion of nuclear electric quadrupolar spin-lattice relaxation which we discussed in our introduction. This type of Raman process leads to a transition probability proportional to the seventh power of the temperature at sufficiently low temperatures. Van Kranendonk has calculated the temperature dependence of quadrupolar spin-lattice relaxation assuming a Debye type frequency spectrum for cubic crystals of the KI type. The theoretical curve of T_1 *vs* temperature shown in Fig. 1 for I^{127} in KI was computed from his work using a value of 130°K for the Debye characteristic temperature taken from Norwood and Briscoe.[9] As previously stated, $T_1=0.014$ sec at 300°K from the work of Jennings and Tanttila was used to normalize the computation at room temperature.

As can be seen from Fig. 1, the agreement between theory and experiment for both single-crystal and powdered KI is quite good from 20°K to 15°K. This is interpreted as meaning that at not too low a temperature the quadrupolar spin-lattice relaxation is the dominant relaxation mechanism for I^{127} in KI. Also grinding the single crystal into a fine powder did not eliminate any modes of lattice vibration which are important in the Raman type relaxation process. This is not unexpected since the lattice vibrations eliminated were of a relatively low frequency (10^7 cps and less) and the lattice frequencies important in the Raman type process are generally much higher (10^9 to 10^{12} cps).

In the liquid helium temperature range the experimental values of T_1 fall below the theoretically calculated ones by orders of magnitude. This would indicate that there is a competing mechanism which is becoming more important at the lower temperatures than the Raman type quadrupolar relaxation process. One such mechanism could be the other energy levels of the I^{127} spin system. As stated previously, the I^{127} resonance consisted of a narrow central line with broad weak wings. The central line was interpreted as being almost entirely due to the $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition. Therefore, when the I^{127} resonance was saturated by means of the strong radio-frequency field set on this transition frequency, it is possible that the nuclear systems in the levels characterized by spins of $\frac{5}{2}$, $\frac{3}{2}$, $-\frac{3}{2}$, $-\frac{5}{2}$ remained with a Boltzmann distribution and a cold spin temperature. Thus the "hot" $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ spin system could mix with this "cooler" spin system, thereby furnishing a means of relaxation. Abragam and Proctor[10] have demonstrated a similar type of mixing for a number of spin systems.

Another possible competing relaxation mechanism at low temperatures is the paramagnetic ion relaxation process proposed and experimentally verified by Bloembergen.[11] Low and Squire[4] as well as Bloembergen have reported a $1/T^2$ dependence of T_1 on temperature in the liquid helium temperature range for solids in which this is the dominant relaxation mechanism. In our specimens T_1 was found to be constant in the

[6] G. D. Watkins and R. V. Pound, Phys. Rev. **89**, 658 (1953).
[7] I. Solomon, Phys. Rev. **110**, 61 (1958).
[8] R. V. Pound, Phys. Rev. **79**, 685 (1950).
[9] M. H. Norwood and C. V. Briscoe, Phys. Rev. **112**, 45 (1958).
[10] A. Abragam and W. C. Proctor, Phys. Rev. **109**, 1441 (1958).
[11] N. Bloembergen, Physica **15**, 386 (1949).

range 2°K to 4°K. The paramagnetic ion content of the KI single crystal is some 10^5 per mole.

At 4.2°K, T_1 for the single crystal KI is 6.9×10^3 seconds, while for the powder specimen it is 6.0×10^2 sec. In view of the relaxation times for the two being approximately equal from 20° to 15°K, this order-of-magnitude difference at 4.2°K is puzzling. If the paramagnetic ion relaxation mechanism is responsible for T_1 in the liquid helium temperature range, then one could explain this order-of-magnitude difference by assuming that the paramagnetic ion content of the KI increased in the course of preparing the fine powder. This is ruled out, in our opinion, since considerable care was taken during the grinding process to have the KI always in an inert and dry as possible atmosphere. We realize that Jennings and Tantilla[5] have reported a longer value of T_1 for the powder specimen of KI than for the single crystal at 4.2°K. However, these authors gave no temperature dependence of T_1 in the liquid helium range and have reported elsewhere[12] that their specimens were doped with impurities (presumably for other purposes).

[12] D. A. Jennings and W. H. Tanttila, Program of the Kamerlingh Onnes Conference on Low-Temperature Physics, Leiden University, The Netherlands, June 23–28, 1958 (unpublished), p. 39.

CONCLUSIONS

From this work we can conclude that Van Kranendonk's theory of nuclear electric quadrupolar spin-lattice relaxation gives an explanation for the magnitude and temperature dependence of T_1 for I^{127} in KI in the temperature range 15°K to 20°K and presumably on up to 295°K. We conclude that there is a competing mechanism to the spin-lattice relaxation which becomes important at liquid helium temperatures and suggest that this is caused by the cool I^{127} nuclei which interact with the ones heated in our experimental arrangement. Also, the shape of the resonance line (a sharp central peak with broad weak wings) is in agreement with the work of Watkins and Pound[6] and Solomon.[7]

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