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Direct Measurement of Electron Spin-Lattice Relaxation Times*

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A discussion of the experimental problems encountered in making spin-lattice relaxation measurements in electron paramagnetic systems at low temperature is presented. Gadolinium and chrome ion spin-lattice relaxation times, measured by a pulse saturation technique in the time domain, are given. The relation of these spin-lattice relaxation times with relaxation times measured in the frequency domain by observing a saturation parameter is discussed.

INTRODUCTION

FOR more than two decades, physicists have been interested in developing a description of the processes that establish thermal equilibrium between a system of electron spins and its surrounding lattice. Representation of a spin-lattice system by the almost-commuting systems of an atomic electron and Debye lattice vibration is simple and adequate for the consideration of relaxation phenomena. Thermal equilibrium is established by a weak coupling between the spin and the lattice. The Leyden group sensed the basic interest in this problem, developed basic experimental techniques, and carried out the basic thermodynamic interpretation of the experimental measurements under Gorter and Casimir.[1] Their study is well documented, and the published work of this group is a monument to their efforts (essentially single-handed) in the experimental understanding of this problem. In truth, to the present time, no change has been made in the basic experiments and their interpretation. To be sure, improvements and extensions of the original techniques have been made; for example, in considering nuclear spin relaxation, and in applying resonance techniques to the measurement of the relaxation time of the individual lines in the paramagnetic spectrum. But always interpretation of experimental results has been dependent upon the physical model assumed for the process because the measurements have, for the most part, been made in the frequency domain (cw power saturation techniques). So that the interpretation of the experimental results will be less dependent upon the physical models, we have measured electron spin-lattice relaxation times in the time domain.[2]

To review briefly: by the mutual inductance method of Gorter and Broer a weighted mean of the relaxation times of all of the states of the pertinent paramagnetic spectrum is measured, since the maximum rate at which the magnetic moment of the specimen can be made to follow a changing magnetic field is determined. This may be interpreted as a direct measure of relaxation times averaged over the several component spectral lines. Relatively little average power is put into the spin system; corrections for size and thermal conductivity to be applied to these measurements have been calculated by Eisenstein.[3] However, even at 2°K, and for chrome alum specimens as large as 1 cm in radius, he concludes that size and thermal conductivity do not seem to cause measurable effect. In the spirit of the Leyden measurements, Bloembergen, Purcell, and Pound[4] measured nuclear relaxation times, using nuclear resonance absorption, both in the frequency domain and in the time domain. The frequency-domain measurements were made on appropriate systems by observing the onset of nonlinearity (saturation) between the measuring power and the absorbed power, and relating this saturation behavior, by means of the Bloch equations,[5] with spin-spin and spin-lattice relaxation times. Measurements of nuclear spin-lattice relaxation times can also be made by saturating the resonance with high rf power and then monitoring the recovery of the nuclear susceptibility of the sample with time by using a weak monitoring field. If the nuclei are in an inhomogeneously broadened system, it is possible to saturate a limited section of a nuclear spin-resonance absorption line. In this case, the spectral diffusion of nuclear magnetization weakly couples the saturated nuclei with a reservoir of unsaturated nuclear magnetization. Thus the interpretation of this experiment must take into account not only relaxation through spin-lattice coupling, but also spin relaxation through spectral spin diffusion.

We immediately note that in electron paramagnetism, inhomogeneously broadened systems appear to be rare, although they are readily identifiable by experimental measurement.[6] We feel that the paramagnetic systems that we report here are not inhomogeneously broadened, and in any case, applicable spectral diffusion times

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[1] C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Inc., New York, 1947).

[2] C. F. Davis and M. W. P. Strandberg, Bull. Am. Phys. Soc. Ser. II, 2, 226 (1957); Strandberg, Davis, and Kyhl, Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957 (to be published); Davis, Strandberg, and Kyhl, Bull. Am. Phys. Soc. Ser. II, **3**, 9 (1958).

[3] J. Eisenstein, Phys. Rev. **84**, 548 (1951).

[4] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 678 (1948); C. P. Slichter and E. M. Purcell, Phys. Rev. **76**, 466 (1949).

[5] F. Bloch, Phys. Rev. **70**, 460 (1946).

[6] A. M. Portis, Phys. Rev. **91**, 1071 (1953).

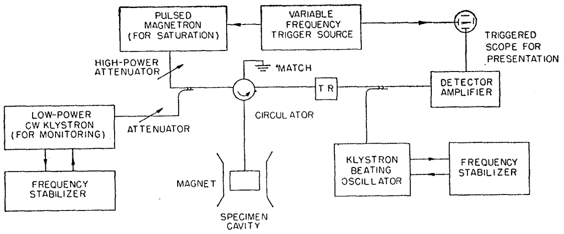

FIG. 1. Block diagram of equipment for measuring relaxation time by pulse saturation method.

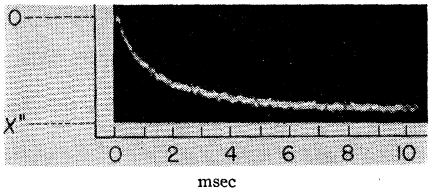

FIG. 2. Typical oscilloscope trace. Oscilloscope photograph of $La(Gd)(C_2H_5SO_4)_3 \cdot 9H_2O$ at 4.2°K with crystal axis parallel to magnetic field. The transition is $\frac{5}{2}$, $\frac{3}{2}$ at 2240 gauss and 8745 Mc/sec.

would be too long to require consideration in the present discussion.[7]

There have been several measurements of power saturation behavior in the microwave region of electron paramagnetic systems.[8] These measurements were made by observing the resonant susceptibility of the electron paramagnetic-spin system as a function of the microwave energy density at the paramagnetic crystal. Again, the data were interpreted in terms of spin-spin and spin-lattice relaxation time by means of the Bloch equations. Unfortunately, the applicability of the Bloch equations cannot be considered universal. It has been pointed out[9] that phonon relaxation processes may, in some cases, influence paramagnetic saturation measurements as a strong function of the saturation parameter; such multiple relaxation processes are particularly probable at low temperatures; at the present time their presence or absence can be evaluated by experimentation only. A generalized model of electron paramagnetic systems must be made flexible enough so that conditions which make the Bloch equations applicable, or not, can be investigated. In the presence of arguments such as those advanced in reference 7, measurement of spin-lattice relaxation times in electron paramagnetic systems will always be somewhat suspect. For this reason, we decided to abandon frequency-domain measurements in favor of time-domain measurements.[2] These measurements make it possible to study the behavior of the susceptibility over several time constants after its saturation. Thus, any deviation from a simple relaxation process can be evaluated. It is frequently possible to establish, as described below, that the measured relaxation times must arise from the spin-lattice step only. Furthermore, by using pulse saturation of the system with very low pulse recurrence frequency, the average power level necessary for making the measurements can be reduced to any desired value.

The measurements presented below should be taken in the spirit of the foregoing remarks. We feel that the experiments measure the quantities that we wish to measure, and that the interpretation of the data is direct and subject to less criticism than cw power saturation measurements in the frequency domain.

EXPERIMENTAL TECHNIQUES

A block diagram of the pulse saturation apparatus is given in Fig. 1. A tunable magnetron (wavelength, 3 cm) is fed through a high-power attenuator and a circulator to the specimen cavity. The cavity is immersed in appropriate low-temperature Dewars and is in a controllable magnetic field. The magnetron pulse is approximately 1 μsec in duration and has a carrier frequency that is identical with the frequency of the sample cavity. A low-power, cw klystron is also coupled into the magnetron transmission line, and the signal reflected from the cavity is led through a T-R switch to a sensitive superheterodyne receiver and amplifier system. Since the superheterodyne receiver has micromicrowatt sensitivity, millimicrowatts (or less) can conveniently be used as the monitor power. The high-power attenuator can be used to increase the magnetron power until it produces a usable amount of saturation of the paramagnetic susceptibility. The magnetron recurrence frequency is variable and is approximately one pulse a second. Since the receiver is linear, the output displayed on an oscilloscope with a linear time base provides a direct measurement of the magnitude of the reflection coefficient of the cavity as a function of time. The magnitude of the reflection coefficient is related to the Q of the cavity, Q_0; of coupling, Q_e; and of the specimen, Q_x; by the following equation:

$$|r| = \frac{1/Q_e - 1/Q_0 - 1/Q_x}{1/Q_e + 1/Q_0 + 1/Q_x}. \tag{1}$$

The filling factor was essentially constant because the crystal was usually small, and the measurements were made under resonance conditions. Thus Q_x is related to the instantaneous specimen susceptibility and the constant filling factor as

$$Q_x^{-1} = 4\pi\eta\chi'',$$

where χ'' is the imaginary part of the susceptibility. Figure 2 shows a typical oscilloscope trace. A semilogarithmic plot of $[1-(Q_\infty/Q_x)]$ against time is shown in Fig. 3, from which the relaxation time is evaluated as the slope of the best straight line through the experimental points. Here, Q_∞ is the limiting Q_x as saturation is decreased.

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[7] A. M. Portis, Phys. Rev. **104**, 584 (1956).

[8] A. H. Eschenfelder and R. T. Weidner, Phys. Rev. **92**, 869 (1953); G. Feher and H. E. D. Scovil, Phys. Rev. **105**, 760 (1957).

[9] M. W. P. Strandberg, Phys. Rev. **110**, 65 (1958).

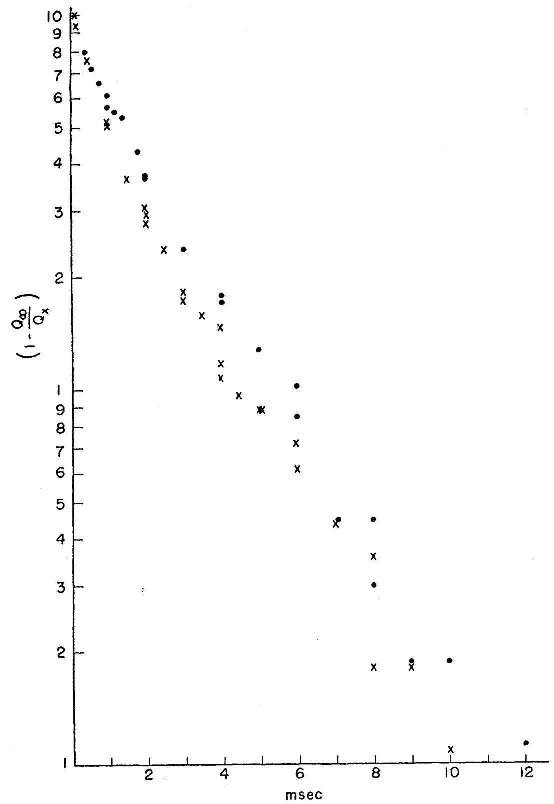

FIG. 3. Typical relaxation curve for line of Fig. 2. Data from two experiments are included. Calculated relaxation time is 2.59 msec.

In order to assure the validity of the data, certain precautions are required during the running of each experiment. The klystron monitoring power must be maintained at a level that is sufficiently low to assure that its action, alone, does not cause saturation. The monitoring level can be checked simply by increasing the klystron power several orders of magnitude and simultaneously increasing the attenuation in the detector arm by the same amount. An observation of the same reflection coefficient under both conditions indicates absence of saturation from monitoring power. This test must be performed on each spectral line before it is possible to state that the monitor itself does not partially saturate the line. Since the monitoring system that we used for the data described here was not designed to reject the real part of the susceptibility, great care was taken to adjust the magnetic field exactly to the resonance field of the paramagnetic system at the sample cavity frequency, and to stabilize the microwave monitoring field to exactly the cavity frequency. Under these circumstances, the cavity and specimen provide resistive loads, and the cavity reflectivity is truly a known function of the instantaneous imaginary part of the susceptibility. A slightly misadjusted magnetic field or klystron frequency can produce reactive effects that vary as a function of time.

EXPERIMENTAL RESULTS

As the first in a continuing series of measurements of spin-lattice relaxation times by the methods described above, we present here observations of relaxation times in three crystal specimens which appear to us to be direct measurements of spin-lattice relaxation times, or at least the direct measurement of relaxation times controlled predominantly by spin-lattice relaxation. The measurements on gadolinium ethyl sulfate diluted with lanthanum, $(La_{0.995}Gd_{0.005})(C_2H_5SO_4)_3\cdot 9H_2O$, on ammonium chrome alum diluted with aluminum, $(NH_4)(Al_{0.98}Cr_{0.02})(SO_4)_2\cdot 12H_2O$, and on the chromium impurity in a single crystal of ruby (Al_2O_3) are shown in Table I. These data were obtained from measurements of the decay of the sample susceptibility for at least two, and in many cases as many as four, time constants. In our measurements, the graphs were essentially straight or barely concave upward, as shown by a typical graph, Fig. 3.

All seven lines of a gadolinium specimen were run, in order to compare the various relaxation times. The crystal axis was parallel to the dc magnetic field; measurements were made at 4.2°K and a frequency of 8750 Mc/sec. The observed differences in relaxation times between lines can only be interpreted as being the result of the spin-lattice step, since all experiments were performed at the same frequency. Hence all lines couple to the same lattice modes. In a further experiment, the klystron power was increased, and the relaxation times of two gadolinium lines were measured as a function of monitoring power. The relaxation times were relatively constant with power until a level capable of saturating the paramagnetic resonance was approached. Increasing the power above this point by 6 db caused the measured relaxation time to drop by a factor of ten. These results are given diagrammatically in Fig. 4.

Two ammonium chrome alum samples of different size were run as a check to pick up any volume effects

TABLE I. Measured relaxation times of $(La_{0.995}Gd_{0.005})(C_2H_5SO_4)_3\cdot 9H_2O$ with the crystal axis parallel to the dc magnetic field. Temperature, 4.2°K; frequency, 8750 Mc/sec.

Field (gauss)	Transition	Relaxation time (msec)	Cw measurement (similar conditions)[a]
2000	$\frac{5}{2}\rightarrow\frac{7}{2}$	6.3	
2240	$\frac{3}{2}\rightarrow\frac{5}{2}$	2.6	
2650	$\frac{1}{2}\rightarrow\frac{3}{2}$	4.0	
3070	$-\frac{1}{2}\rightarrow\frac{1}{2}$	5.2	0.060 msec
3570	$-\frac{3}{2}\rightarrow-\frac{1}{2}$	5.8	0.060
3910	$-\frac{5}{2}\rightarrow-\frac{3}{2}$	4.8	0.075
4280	$-\frac{7}{2}\rightarrow-\frac{5}{2}$	9.8	0.167

Measured relaxation times of $(NH_4)(Al_{0.98}Cr_{0.02})(SO_4)_2\cdot 12H_2O$

	Relaxation time (msec)	Frequency (Mc/sec)
Large specimen	7.5±4	8726
Small specimen	9.0±1	8753

Relaxation time of measured synthetic ruby line, 37 msec.

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[a] See reference 10.

that might exist. The dc magnetic field was parallel to one crystal axis (perpendicular to a face). Measurements were made at 4.2°K and frequencies of 8753 Mc/sec (smaller specimen) and 8726 Mc/sec (larger specimen). At 4.2°K, this material (diluted 1:50) displays its spectrum as one misshapen line. Care was taken to measure the center of the line, although other portions of the line gave equivalent relaxation times. The volume ratio between the two samples is thirty; the linear dimensions are in a ratio of 3:1.

Relaxation data in the artificial ruby were determined from observation of relaxation of the sample susceptibility for the $\frac{1}{2}\longrightarrow\frac{3}{2}$ transition with the magnetic field at an angle of 90° with the crystal C axis. The measured data describe an exponential decrease of the susceptibility, the measurements having been made over a time span of three relaxation times.

DISCUSSION OF RESULTS

As has been indicated in reference 9, a relaxation process in which the phonons play a dominant role must be characterized by a relaxation time that depends upon the saturation level. The solution of Eqs. (2) and (7) of reference 9 for the transient decay of the saturation of a paramagnetic system, after the saturation pulse, indicates that the relaxation of the spin paramagnetic susceptibility must have a variation in slope if phonon "holdup" exists; that is, if phonon excitation builds up to a point that is sufficient to restrict the transfer of energy from the spins to the crystal lattice. This follows from the fact that if the phonon excitation starts from thermal equilibrium with the bath after the saturation pulse, and increases by the subsequent transfer of energy from the spins at the normal spin-lattice relaxation rate to an excitation level sufficient to restrict the transfer of energy from the spins to the lattice, a change in slope in the recovery of the susceptibility of the sample must occur at the time when the phonon excitation has been built up to a level sufficient to restrict the energy transfer between the spin and the lattice. For this reason we have demanded that our data, in order to be considered a significant measure of a single spin-lattice relaxation process, shall be describable by a simple exponential decay over several decay constants. This criterion was met by the data presented in Table I.

Gadolinium

All of our measurements were made at a single frequency, and hence the phonon spectrum with which the spins interacted was a constant. We believe that the spin-lattice relaxation time is a function of the electron-spin dipole-matrix elements. Therefore, we would expect different relaxation times for different components of the paramagnetic spectrum. This variation of spin-lattice relaxation time with spin quantum numbers is indicated in the results for gadolinium. The connection between the relaxation times and the dipole-moment matrix elements is, of course, not direct—all of the levels of the paramagnetic system partake in the relaxation process. However, qualitative agreement with the data is apparent, since the extreme lines in the spectra have the longest relaxation times and also the smallest dipole-moment matrix elements. Note that the experimental results that we present consist of relaxation times some fifty to sixty times as long as those reported by Feher and Scovil.[8] The relaxation times of gadolinium lines that they reported in reference 8 were said[10] to have been four times as long as 1.2°K as at 4.2°K. It should be noted, too, that the Feher and Scovil measurements were made as power saturation experiments in which the susceptibility was reduced by 10 db. Our results indicate that one should measure a shorter relaxation time as the power level is increased. It appears that in order to obtain agreement between the pulsed and cw measurements on gadolinium, the spin-lattice relaxation time would have to be measured by cw methods as a function of the power level. Our relaxation times should then correspond to the spin-lattice relaxation time deduced from saturation measurements extrapolated to the limit of zero saturating power. We intend to carry out this type of experiment.

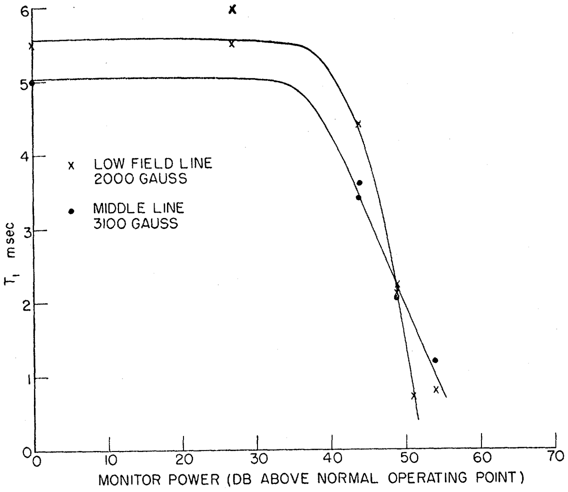

FIG. 4. Decrease in relaxation time of two lines of the gadolinium spectrum as a function of monitor power level. Same specimen as in Fig. 2.

The behavior of the rare-earth ions is somewhat different from the behavior of chromium, for example, in that indirect or second-order processes produce spin-lattice relaxation times which are the order of, or even less than, spin-spin relaxation times at room temperature. The sharp change of spin-lattice relaxation time with monitoring power level would indicate a faster variation for the spin-lattice relaxation constant

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[10] H. E. D. Scovil, Massachusetts Institute of Technology Physics Colloquium, May 9, 1957 (unpublished).

than with the reciprocal of the temperature. This situation needs further clarification by experiment. It does seem that the shortening of the relaxation time with monitoring power may be simply the result of an increase (in the conventional sense) in the lattice temperature with resultant shortening of the spin-lattice relaxation time. If the lattice temperature is increased in the conventional sense, that is, by an appropriate increase in excitation of all lattice modes, this might be due to this crystal having a very short phonon-phonon relaxation time, or due to the predominance of indirect or second-order Raman processes in the spin-lattice relaxation for gadolinium.[11] These considerations will be the subjects of further experimentation.

Ammonium Chrome Alum

Since at low temperatures ammonium chrome alum has a vanishing trigonal crystalline electric-field splitting, the transitions for the degenerate quartet occur almost at a single value of the magnetic field. Hence, the relaxation time is a weighted mean over the spin-lattice relaxation times of the whole system. But since these elements of the spectrum overlap, spin-spin relaxation should equilibrate the decay of all the quantum states. The essential conclusion derived from the results for chrome alum that are presented here is that we are not operating with a volume-dependent effect. Although the accuracy of the experiment is not all that could be desired, the agreement is satisfactory in view of the large change in linear dimension, i.e., a factor of three.

The chrome alum relaxation times reported here are approximately the same as those reported by Gorter.[1] On the other hand, Eschenfelder and Weidner measured relaxation times in a similar chrome alum at this temperature by a cw saturation method and obtained spin-lattice relaxation times of less than 1 msec. Since our measurements of the relaxation time are supported by a simple exponential decay over several relaxation times, we feel that our experiments measure the spin-lattice step more truly than does cw saturation. In order to obtain significant data by the saturation method, it would seem, as we indicated above, that one would have to measure the saturation parameter as a function of power level and be assured by the measurements that a simple and single spin-lattice relaxation time is being measured. Only in this way can a change in effective lattice temperature be uncovered.

Ruby

The measurement of the ruby relaxation time that we present here is the longest true spin-lattice relaxation that we have measured. The ruby crystal is an interesting structure to study because a good deal is known of its thermal conducting characteristics. These characteristics give hints of its phonon scattering properties. (See reference 9 for a discussion of our interest in these effects.) For this reason we feel that the ruby structure is an ideal medium for basic study of the over-all spin-relaxation process at low temperature. From this point of view, the single measurement of a ruby spin-lattice relaxation presented here is to be taken only as an interesting fact, the physical significance of which will be made apparent in later experimental and theoretical work.

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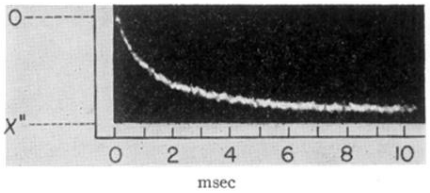
[11] S. A. Altshuler, Zhur. Eksptl. i Teoret. Fiz. 24, 681 (1953).



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