

## Nuclear Spin Relaxation in Gallium Metal

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The nuclear spin-lattice relaxation time  $T_1$  has been measured in a fine powder of gallium metal from near the superconductivity transition temperature 1.1°K to near the melting point 307°K. The experiments were performed with pure nuclear quadrupole resonance using pulsed-nuclear-resonance techniques. Between approximately 4.2 and 300°K the product of  $T_1$  and the absolute temperature is found to be temperature-dependent, varying from 1.01 sec°K between 1.1 and 4.2°K to 0.73 sec°K at 300°K. The relaxation mechanism is magnetic in origin, as determined from the ratio of the relaxation times for the  $\text{Ga}^{69}$  and  $\text{Ga}^{71}$  nuclei. Various explanations for the temperature dependence of  $T_1T$  are discussed.

### I. INTRODUCTION

IN the formulation of the nuclear-spin relaxation time  $T_1$  in metals, the tensor hyperfine interaction between the electron-spin system and the nuclear-spin system usually provides the principal mechanism by which the nucleus exchanges energy with the lattice. This interaction, first discussed by Heitler and Teller<sup>1</sup> and calculated in detail by Korringa,<sup>2</sup> normally arises from the interaction of the nucleus with the  $s$  conduction electrons because of the density maximum of these electrons at the nucleus. Later, Mitchell<sup>3</sup> extended this calculation of the contact part of the interaction to include both the noncontact part, i.e., the non- $s$ -electron's contribution to the hyperfine interaction, and the nuclear quadrupole interaction with the conduction electrons. These theories predicted that  $1/T_1T$  is temperature-independent and proportional to the electronic density of states  $\rho(E_F)$ . This leads to the possibility that measurements of  $T_1$  can be used to give information on  $\rho(E_F)$  and consequently on the electronic band structure. Additional information can be obtained on the density of states by measurement of the Knight shift. However, in gallium, the large quadrupole interaction has as yet precluded any resonance measurements being made in large dc magnetic fields although efforts are under way. This paper then is concerned only with the measurement of  $T_1$  for  $\text{Ga}^{69}$  and  $\text{Ga}^{71}$  in the nuclear quadrupole resonance from near the superconducting transition temperature,  $\sim 1.1^\circ\text{K}$  to 300°K. The quadrupole resonance frequencies have previously been determined.<sup>4</sup> It is found that  $T_1T$  is temperature-dependent between 4.2 and 200°K, varying from 1.01 sec °K between 1.1 and 4.2°K to 0.73 sec °K at 300°K.

In the succeeding sections we shall discuss the experimental apparatus and method, the experimental results and their interpretation.

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<sup>1</sup> W. Heitler and E. Teller, Proc. Roy. Soc. (London) **A155**, 637 (1936).

<sup>2</sup> J. Korringa, Physica **16**, 601 (1950).

<sup>3</sup> A. H. Mitchell, J. Chem. Phys. **26**, 1714 (1957).

<sup>4</sup> W. D. Knight, R. Hewitt, and M. Pomerantz, Phys. Rev. **104**, 271 (1956); M. Pomerantz, thesis, University of California, Berkeley, 1958 (unpublished).

### A. Experimental Procedure

#### 1. Sample

The sample, obtained from Aluminum Co. of America, is stated to be 99.999% pure. In its final forms, the sample consisted of a dry powder mixture of one-half gallium and one-half quartz powder of comparable particle size. The gallium particles were made by exposing the molten metal to ultrasonic radiation in a volatile liquid containing a stabilizing agent. The particles were found to be very nearly spherical and approximately 90% of the diameters were between 2.0 and 3.2  $\mu$ .

#### 2. Experimental Technique and Equipment

Standard pulsed-nuclear-resonance techniques<sup>5,6</sup> were used in the measurement of the nuclear spin-lattice relaxation times. Sequenced 180°–90° pulses were employed and the pulse widths,  $\sim 20$   $\mu\text{sec}$ , were narrow compared to the free induction decays.

The electronic equipment is similar to that of Clark<sup>7</sup> with some minor modifications made since single coils rather than crossed coils are necessary. To protect the input of the receiver, the circuit shown in Fig. 1 was used.

In this circuit,  $C_1$ ,  $C_2$  and  $L_1$  (sample coil) form a matching network to maintain a high- $Q$  sample coil, which minimizes loading by the transmitter. This condition is determined by the relationship

$$R_{\text{in}} = QX_L / (C_1/C_2 + 1)^2,$$

where  $R_{\text{in}}$  is the transmitter impedance, about 500 ohms. The capacitance  $C_3$  is chosen such that the rf current through the diodes is limited to a safe value. The diodes serve to limit the maximum voltage applied to the preamplifier tube grid.  $C_4$  is chosen much larger than  $C_3$  so as to minimize the signal drop across  $C_4$  and  $L_2$ .  $C_3$ ,  $C_5$  and  $C_6$  are tuned to the sample resonance frequency such that the maximum signal occurs across  $L_2C_5$ .

<sup>5</sup> E. L. Hahn, Phys. Rev. **80**, 580 (1950).

<sup>6</sup> H. Y. Carr and E. M. Purcell, Phys. Rev. **94**, 630 (1954).

<sup>7</sup> W. G. Clark, Rev. Sci. Instr. **35**, 316 (1964). The authors would like to thank Dr. Clark for making his circuits available to us before publication and for many helpful discussions.

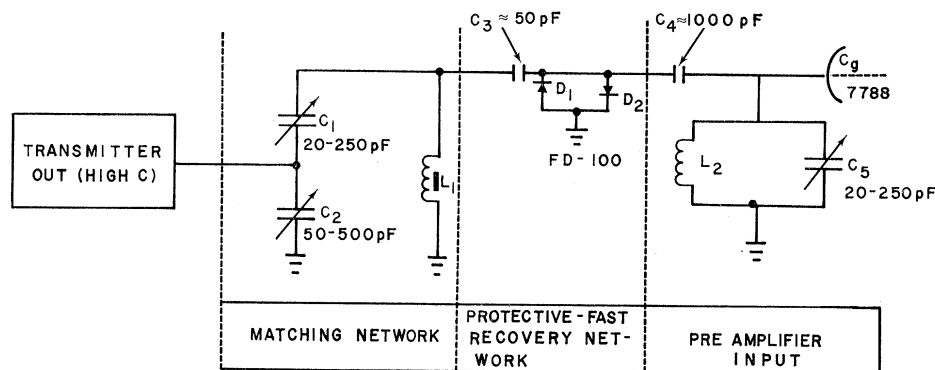


FIG. 1. Protective input circuit for receiver.

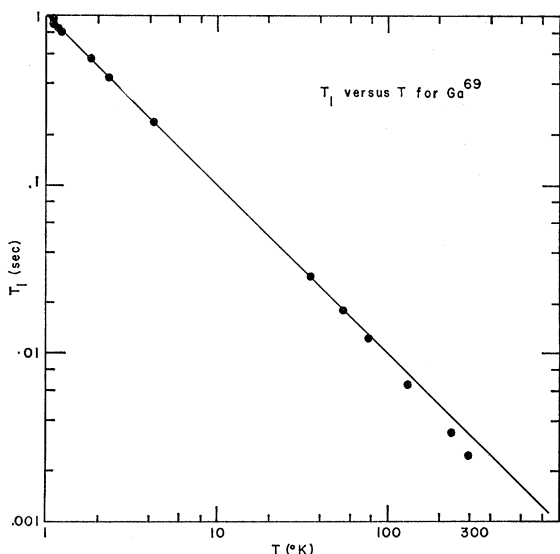
Other minor modifications were made necessitated by the availability of certain tubes and the need for some protective circuitry in the boxcar integrator.

### 3. Temperature Measurement

Down to 35°K, thermocouples were used to measure the temperatures. Below 4.2°K, a resistance thermometer was employed which was calibrated against the vapor pressures of He<sup>4</sup> and He<sup>3</sup>.

### B. Experimental Results

The experimental results for Ga<sup>69</sup> are shown in Figs. 2 and 3 where, respectively,  $T_1$  versus  $T$  and  $T_1T$  versus  $T$  are plotted. Similar results are obtained for Ga<sup>71</sup>. Figure 2 shows the range in the measured values of  $T_1$ , 0.92 sec to 2.45 msec, and Fig. 3 clearly shows the deviation of  $T_1T$  from the expected constant value. There is an 8% deviation between the measured  $T_1T$  at 77.4°K and the extrapolated low-temperature value (1.01 sec °K), as denoted by the dotted line. At 300°K

FIG. 2. Relaxation time for Ga<sup>69</sup> versus temperature.

this deviation has become 30%. Since the experimental accuracy is about  $\pm 2\%$  these deviations are outside the experimental uncertainty.

Also according to the magnetic-hyperfine-relaxation theories,<sup>2,3</sup>  $T_1$  should be inversely proportional to the square of the nuclear magnetic moment,  $\mu_N$ . Therefore the ratio of the relaxation times should obey the following relationship

$$T_1(\text{Ga}^{69})/T_1(\text{Ga}^{71}) = [\mu_N(71)/\mu_N(69)]^2 = 1.61.$$

Table I shows the results for this ratio at various temperatures and to within  $\pm 2\%$ , the relaxation mechanism is clearly magnetic in origin. Quadrupole relaxation mechanisms are excluded, for otherwise one should obtain

$$T_1(\text{Ga}^{69})/T_1(\text{Ga}^{71}) = [Q(71)/Q(69)]^2 = 0.388$$

which obviously is not the case.

## II. DISCUSSION

In a metal, the interaction responsible for the nuclear spin-lattice relaxation can be expressed in terms of the density of states at the Fermi surface  $\rho(E_F)$ , and in terms of the  $s$  (contact) part and the non- $s$  (non-contact) part of the Korringa interaction in the following manner:

$$1/T_1T = A^2(T) (\mathbf{I} \cdot \mathbf{S}) \rho^2(E_F),$$

where  $\mathbf{I}$  and  $\mathbf{S}$  are the respective spins of the nucleus and electron. The latter parts may also be influenced by core polarization, i.e., by the exchange interaction

TABLE I. Ratio of relaxation times for Ga<sup>69</sup> and Ga<sup>71</sup>.

$T$ (°K)	$T_1$ (Ga <sup>69</sup> ) (sec)	$T_1$ (Ga <sup>71</sup> )	$T_1$ (Ga <sup>69</sup> )
			$T_1$ (Ga <sup>71</sup> ) (sec)
4.2	0.24	0.15	1.60
77.4	0.012	0.0075	1.59
80	0.0115	0.00715	1.61
131	0.0065	0.00400	1.63
235	0.0033	0.00242	1.62
300	0.00245	0.00154	1.59

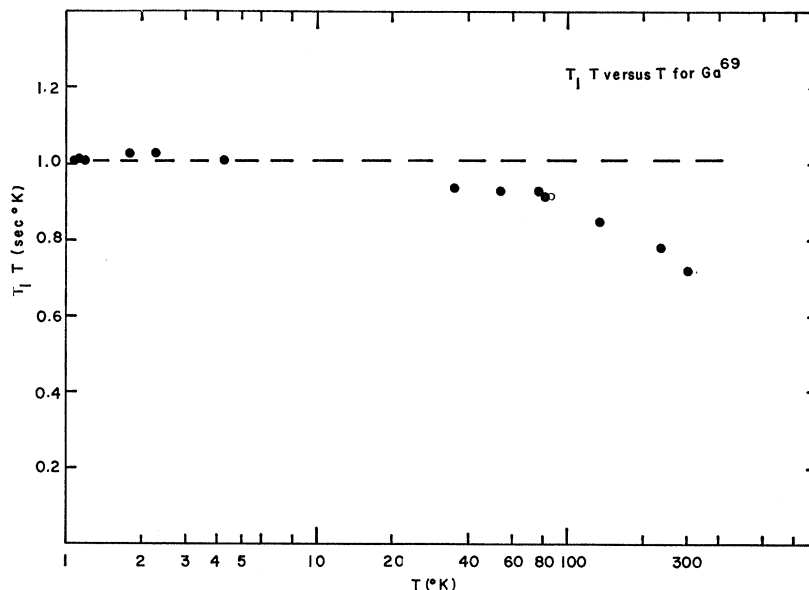


FIG. 3.  $T_1T$  for  $\text{Ga}^{69}$  versus temperature.

between the core electrons and the unpaired valence electrons, as considered by Yafet and Jaccarino for transition metals.<sup>8</sup> The influence of core polarization has been calculated for Li on the Knight shift and it was found that contribution of the  $p$  and  $s$  parts were equal and opposite.<sup>9</sup> However, the core polarization was only about 10% of the direct contribution. It is doubtful whether it would be an order of magnitude larger in Ga and dominate the hyperfine interaction responsible for  $T_1$ .

The influence of the density of states and the amplitude of the electronic wave function on the relaxation time has been treated in some detail by Weger and Silbernagel.<sup>10</sup> Assuming no singularities in the density of states but allowing for an energy-dependent  $|\Psi(0)|^2$ , it has been shown that

$$\frac{1}{T_1T} = \left( \frac{1}{T_1T_0} \right) \left[ 1 + \frac{(\pi k_B T)^2}{6} \left( \frac{1}{h} \frac{d^2 h}{dE^2} - \frac{1}{h} \frac{dh}{dE} \frac{1}{\rho} \frac{d\rho}{dE} \right) \right],$$

where the second term arises from the shift in Fermi energy and  $h$  is defined as

$$h = \rho^2 \langle |\Psi_E(0)|^2 \rangle_{\text{constant energy surface}}.$$

As far as the density of states is concerned, it can be seen from this expression<sup>11</sup> that a change in  $\rho(E_F)$  can either be brought about by additional bands becoming important as the temperature increases (or possibly through a change in the contribution of the bands

<sup>8</sup> Y. Yafet and V. Jaccarino, Phys. Rev. **133**, A160 (1964).

<sup>9</sup> See Table II of Gaspari *et al.*, Phys. Rev. **134**, A852 (1964).

<sup>10</sup> M. Weger and B. Silbernagel (to be published). The authors would like to thank Professor Weger for communications of this result.

<sup>11</sup> This equation is quite similar in form to that used in connection with normal transport phenomena in metal; see A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1958).

initially present) or even if the energy versus  $k$  dependence of a single band is nonparabolic. Gallium is known to have four bands contributing to the electronic properties at low temperatures.<sup>12</sup> It would not be surprising if the band structure becomes even more complicated as the temperature increases.<sup>13</sup>

To interpret our results in terms of a change in the amplitude of the conduction-electron wave function would necessitate an increase in the  $s$  part (or non- $s$  part) amplitude at the nucleus as the temperature increases. Whether such a large increase is possible is not known.

Thus far the discussion has only dealt with nuclear-spin-electron-spin interaction. In addition the departure of  $T_1T$  from constancy can arise from the electron-orbit-nuclear-spin interaction. Obata<sup>14</sup> has calculated the nuclear-spin-electron-orbit interaction (which is analogous to a  $k \cdot I$  interaction in the tight-binding approximation) which can lead to temperature dependence of the product  $T_1T$  and moreover of  $T_1K^2$ . Both the electrons on the Fermi-surface as well as those not on the Fermi-surface can contribute to the Knight shift through a Van Vleck-Ramsey-type mechanism. The relaxation time, on the other hand, arises from the electrons near the Fermi surface alone. Since the

<sup>12</sup> J. H. Wood (private communication). The authors would like to thank Dr. Wood for communicating his results prior to publication and one of them (EGW) would like to thank him for an enlightening discussion.

<sup>13</sup> One calculation has been carried out by W. B. Teutsch [Bull. Am. Phys. Soc. **7**, 483 (1962)] to account for the experimental results. It is based on two assumptions, that there are two overlapping parabolic bands (one electron and one hole) and that the Fermi energy is about  $kT$ . An approximate fit for the data can be obtained for an overlap energy of 0.12 eV and an  $E_F$  of 0.11 eV as measured from the bottom of the electron band. In view of the rather stringent assumptions the fit could be fortuitous however.

<sup>14</sup> Y. Obata, J. Phys. Soc. Japan **18**, 1020 (1963).

Korringa relation holds when both  $T_1$  and  $K$  are contributed to only from the electrons near the Fermi surface, we would expect to observe a departure from the Korringa relation in the present case. Measurement of the Knight shift would enable one to differentiate between this mechanism and the other mechanisms discussed previously, since they do not lead to a departure of  $T_1K^2$  from constancy.

### III. CONCLUSIONS

It is not possible at this time to establish the exact mechanism which is responsible for the temperature-

dependent product of  $T_1T$ . The observation may well be a reflection of the rather complicated band structure of Ga. When the results of the Knight shift are available, it is hoped that some additional insight will be gained into the problem although it will not be possible to differentiate between the influence of the density of states and the amplitude of the electronic wave function.

### ACKNOWLEDGMENTS

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## Systematic Variation of Quadrupole Crystal-Field Shielding in Rare-Earth Ethyl Sulfates\*

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Quadrupole-coupling constants were obtained from measurements on  $\text{La}^{140}$ ,  $\text{Eu}^{154}$ ,  $\text{Gd}^{159}$ , and  $\text{Lu}^{177}$  nuclei oriented in neodymium ethyl sulfate at temperatures down to  $0.01^\circ\text{K}$ . These results are combined with the other available quadrupole-coupling data on La, Dy, Tm, and Lu in ethyl sulfate lattices to determine the quadrupole-antishielded term transforming as  $Y_2^0$  in the crystal-field potential, i.e.,  $(1-\gamma_\infty)A_2^0$ . This term increases fairly slowly throughout the rare earths, with an average value of approximately  $(3 \times 10^4 \text{ cm}^{-1})a_0^{-2}$ . These values were compared with theoretical estimates of  $-80$  for  $\gamma_\infty$  to yield the quantities  $A_2^0$ . Comparison of the  $A_2^0$ 's with the corresponding  $V_2^0$ 's taken from optical spectroscopy, using Hartree-Fock radial moments  $\langle r^2 \rangle$  for the  $4f$  electrons, together with some extrapolation, gives a complete set of shielding factors  $(1-\sigma_2)$  for the crystal-field component  $V_2^0$ . These factors vary from 0.6 in  $\text{Lu}^{3+}$  to 0.4 in  $\text{Eu}^{3+}$  and drop to  $-0.2$  in  $\text{La}^{3+}$ . Thus not only is there substantial shielding of  $V_2^0$ , but this shielding seems to vary considerably in the  $4f$  series. The  $\sigma_2$ 's are typically larger by about 50% than theoretical estimates.

### I. INTRODUCTION

THE splitting of ionic terms and levels in crystals<sup>1</sup> comprised the first extensive application of group-theoretical methods to quantum-mechanical problems. Applied first to the iron ( $3d$ ) group, these methods were also used in the early 1930's for the rare earths.<sup>2</sup> Elliott and Stevens introduced a systematic formulation of crystal-field theory for the rare earths,<sup>3-6</sup> using the method of operator equivalents. The remarkable success of this formulation in explaining optical spectra of rare-earth ethyl sulfates, where many

energy levels can be fitted with only four adjustable parameters, is among the best experimental evidence for the validity of crystal-field theory.

Even in the relatively straightforward rare earths there are several levels of sophistication at which crystal-field theory may be applied. The simplest assumptions are that only the lowest term(s) of the appropriate  $4f^n$  configuration need be considered, and that the crystalline field is adequately represented by point charges of appropriate magnitude at neighboring lattice sites. A rigorous treatment would consider all configurations of the ion in question, including those arising from promotion of electrons from closed shells, and would account for such subtleties as covalent bonding.<sup>7</sup> That these refinements are necessary for a realistic description of the problem is clearly demonstrated by the lack of agreement between the crystal-field parameters  $V_L^M$  deduced by fitting optical data and those calculated from lattice sums,<sup>8</sup> as well as by the effects

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<sup>1</sup> H. Bethe, *Ann. Physik* **3**, 133 (1929).

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<sup>3</sup> K. W. H. Stevens, *Proc. Phys. Soc. (London)* **A65**, 209 (1952).

<sup>4</sup> R. J. Elliott and K. W. H. Stevens, *Proc. Roy. Soc. (London)* **A215**, 437 (1952).

<sup>5</sup> R. J. Elliott and K. W. H. Stevens, *Proc. Roy. Soc. (London)* **A218**, 553 (1953).

<sup>6</sup> R. J. Elliott and K. W. H. Stevens, *Proc. Roy. Soc. (London)* **A219**, 387 (1963).

<sup>7</sup> C. K. Jorgensen, R. Pappalardo, and H. H. Schmidte, *J. Chem. Phys.* **39**, 1422 (1963).

<sup>8</sup> E. Y. Wong and I. Richman, *J. Chem. Phys.* **36**, 1889 (1962).