

⁸D. J. Scalapino, in *Tunneling Phenomena in Superconductors*, edited by E. Burstein and S. Lundquist (Plenum, New York, 1967).

⁹In order to focus on the charge which enters the electrostatic part of $\Delta\mu$ the effects of the rf field have not been included.

¹⁰See, e.g., F. Low, Phys. Rev. **110**, 974 (1958).

¹¹We follow the conventions of J. D. Bjorken and S. D. Drell, *Relativistic Quantum Fields* (McGraw-Hill, New York, 1965).

¹²That it cannot be a more singular distribution than

$\delta(\omega)$ will become apparent from the explicit analyses of diagrams below.

¹³P. W. Anderson, *Concepts in Solids* (Benjamin, New York, 1964), pp. 106–111.

¹⁴D. N. Langenberg and J. R. Schrieffer preceding paper, Phys. Rev. B **3**, 1776 (1971).

¹⁵P. W. Anderson and A. H. Dayem, Phys. Rev. Lett. **13**, 195 (1964); M. J. Stephen and H. Suhl, *ibid.* **13**, 797 (1964); P. W. Anderson, N. R. Werthamer, and J. M. Luttinger, Phys. Rev. **138**, A1157 (1965).

Comments on Effects of Electron-Electron Interactions on Nuclear Spin-Lattice Relaxation Times in Aluminum[†]

F. Y. Fradin

Argonne National Laboratory, Argonne, Illinois 60439

and

T. J. Rowland

University of Illinois, Urbana, Illinois 61801

(Received 8 July 1970)

The results of measurements of ²⁷Al spin-lattice relaxation and local field in the rotating frame in aluminum are inconsistent with the model presented by Tunstall and Brown.

Recently Tunstall and Brown¹ have reported the results of nuclear dipolar relaxation in aluminum for $1.3 < T < 295^\circ\text{K}$. They interpreted their results using a three-bath model and an analysis extending the coupled rate equations of Schumacher.² For their sample, filed from a "high-purity zone-refined aluminum single crystal," they found the ratio δ of the dipolar spin-lattice relaxation rate to the Zeeman spin-lattice relaxation rate to be 2.15 ± 0.07 independent of temperature. The quantity $\delta - 2.0$ is a measure of the effect of electron correlations. Their analysis relied on an estimate of the relative heat capacities of the dipolar, small quadrupolar, and large quadrupolar systems to be in the ratio of 2:1:5. They pointed out that at low temperatures, where the spin-lattice relaxation times are long, all systems contribute to the measured relaxation rate. At high temperatures, where spin-lattice relaxation times are short, cross relaxation is ineffective at coupling the quadrupolar systems to the dipolar system and thus the quadrupolar systems do not contribute to the measured relaxation rate.

We have measured the spin-lattice relaxation time in the rotating frame $T_{1\rho}$ in nominally 99.9999% pure aluminum at 300°K . Some of our results have been reported in earlier publications,^{3,4} where details of the experimental procedure can be found. The spin system is prepared in the rotating frame using the spin-locking pulse sequence.⁵ At exact resonance the initial quasiequilibrium ($t \ll T_{1\rho}$) magnetization

in the rotating reference frame is given by⁴

$$M = M_0 [H_1^2 / (H_1^2 + H_D^2 + H_Q^2)], \quad (1)$$

where M_0 is the equilibrium magnetization in the laboratory frame, H_1 is the amplitude of the rf field, H_D^2 is the square of the dipolar field in the rotating frame (equal to one-third⁶ of the Van Vleck second moment), and H_Q^2 is the square of the effective quad-

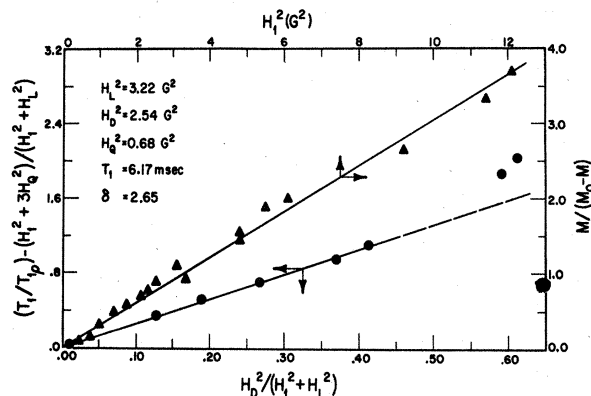


FIG. 1. Experimental determination of H_D^2 and δ for nominally 99.9999% purity aluminum at 300°K . The triangles are for the data $M / (M_0 - M)$ vs H_1^2 and the circles are for the data $(T_1/T_{1\rho}) - (H_1^2 + 3H_D^2) / (H_1^2 + H_D^2)$ vs $H_D^2 / (H_1^2 + H_D^2)$.

the apparent values of δ found in a number of experiments on aluminum are considerably greater than 2.¹⁰

of magnetization against time and (b) with the amplitude of H_1 , due to the mixing effect of the presence of H_1 . As further support for our value we may note the value of $\delta = 2.07$ measured by Pifer.⁵ rupolar field in the rotating frame (equal to one-third the quadrupolar contribution to the second moment of the absorption line for a powder⁷). It is assumed throughout that cross relaxation is sufficiently fast to establish a common spin temperature for the Zeeman, dipolar, and quadrupolar systems. In Fig. 1, $M/(M_0 - M)$ is plotted against H_1^2 ; the reciprocal of the slope of the straight-line plot yields $H_L^2 \equiv H_D^2 + H_Q^2 \equiv 3.22G^2$.

If we take H_D^2 equal to the theoretical value of the Van Vleck second moment $2.54G^2$, then $H_Q^2 = 0.68G^2$. Thus we find the relative heat capacity of the dipolar system to quadrupole system to be 3.7:1, whereas Tunstall and Brown estimate the ratio of heat capacities of their dipolar and small quadrupolar systems to be 2:1. In fact a study of the effect of substitutional solutes⁴ on H_L^2 indicates that a value of $H_D^2/H_Q^2 = 2$ requires in excess of 0.1-at. % solute, hardly likely in high-purity aluminum.

At exact resonance the relaxation rate in the rotating frame is given by⁴

$$\frac{1}{T_{1\rho}} = \frac{1}{T_1} \frac{H_1^2 + \delta H_D^2 + 3H_Q^2}{H_1^2 + H_D^2 + H_Q^2}. \quad (2)$$

Here we have taken the quadrupolar spin-lattice relaxation rate to be three times the Zeeman rate⁸ $1/T_1$ unaffected by electron-spin correlations. In Fig. 1, $(T_1/T_{1\rho}) - (H_1^2 + 3H_Q^2)/(H_1^2 + H_L^2)$ is plotted vs $H_D^2/(H_1^2 + H_L^2)$. We have taken $H_D^2 = 2.54G^2$, $H_Q^2 = 0.68G^2$, $H_L^2 = 3.22G^2$, and $T_1 = 6.17$ msec. The slope of the straight-line plot yields $\delta = 2.65$. The large value of δ found using Eq. (2) is indicative of the failure of the equation to correctly describe the field-dependent relaxation rate.

Thus, we feel that the arguments given by Tunstall and Brown do not solve the enigma in aluminum. The problem is at least twofold. First, there is the large second moment that exceeds the theoretical Van Vleck second moment. Large experimental values of the second moment have been found by a variety of techniques, using different methods of sample preparation, by a number of investigators.^{4,9} It has not been demonstrated in a conclusive manner that the discrepancy in the second moment is due to the nuclear electric quadrupole interaction. However, a much smaller residual quadrupole interaction has been found³ in aluminum just below the melting temperature. Second, there is the large apparent dipolar relaxation rate. The effect of electron correlations in aluminum is expected to increase the value of δ by no more than 10% above the uncorrelated value of 2. However,

[†]Work performed under the auspices of the U. S. Atomic Energy Commission.

¹D. P. Tunstall and D. Brown, Phys. Rev. B **1**, 2881 (1970).

²R. T. Schumacher, Phys. Rev. **112**, 837 (1958).

³F. Y. Fradin and T. J. Rowland, Appl. Phys. Letters **11**, 207 (1967).

⁴T. J. Rowland and F. Y. Fradin, Phys. Rev. **182**, 760 (1969).

⁵S. R. Hartmann and E. L. Hahn, Phys. Rev. **128**, 2042 (1962).

⁶L. C. Hebel, in *Solid State Physics*, edited by F. Seitz

and D. Turnbull (Academic, New York, 1963), Vol. 15.

⁷L. S. Brown, IBM J. Res. Develop. **6**, 338 (1962).

⁸A. G. Anderson and A. G. Redfield, Phys. Rev. **116**, 583 (1959).

⁹J. J. Spokas and C. P. Slichter, Phys. Rev. **113**, 1462 (1959); N. Fernelius, in *Proceedings of the International Conference on Magnetic Resonance and Relaxation, Fourteenth Colloque Ampère, Ljubljana, Yugoslavia, September 1966*, edited by R. Blinc (North-Holland, Amsterdam, 1968), p. 497.

¹⁰L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959); L. C. Hebel, *ibid.* **128**, 21 (1962).