Nuclear-resonance study of Rb^{87} in $RbMnF_3$

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The Rb^{87} nuclear spin-lattice relaxation time in the antiferromagnet $RbMnF_3$ has been measured from 1.5 to 300 K. The results, extrapolated to infinite temperature, agree within experimental error with theory using newly evaluated spin-pair correlation functions. The temperature dependence is compared with Moriya's theory in the paramagnetic region.

I. INTRODUCTION

$RbMnF_3$ is one of the most ideal magnetic materials occurring in nature—a simple-cubic antiferromagnet described well by the isotropic Heisenberg Hamiltonian.[1] The physical magnetic properties of the system are described theoretically in terms of the spin correlation functions, the evaluation of which is the subject of continual interest.[2] Nuclear-magnetic-resonance relaxation times provide good tests of the short-range correlation functions. In a previous paper[3] the F^{19} relaxation times were reported over a wide range above and below the Néel temperature. Here we give (i) the results of measurements on the Rb^{87} nucleus over the same temperature range, (ii) show that the results, extrapolated to infinite temperature, can be calculated within experimental error using newly derived correlation functions, and (iii) compare Moriya's adaptation of the Weiss molecular-field approximation to the data in the paramagnetic region.

II. THEORY

A. General

The relaxation of the Rb^{87} nuclei is assumed to be caused by the hyperfine interaction with the Mn^{++} ions. The Hamiltonian for the pth Rb nuclear spin $\vec{I}_p$ subjected to an external field $\vec{H}$ is given by

$$\mathcal{H}_p = -g_N\mu_N\vec{I}_p\cdot\vec{H}+\sum_j \vec{I}_p\cdot\overleftrightarrow{A}_{pj}\cdot\vec{S}_j + g_N\mu_N g\mu_B\sum_j \frac{1}{r_{pj}^3}\left(\frac{3(\vec{I}_p\cdot\vec{r}_{pj})(\vec{S}_j\cdot\vec{r}_{pj})}{r_{pj}^2}-\vec{I}_p\cdot\vec{S}_j\right) . \quad (1)$$

The first term is the usual Zeeman energy where g_N is the nuclear g factor and μ_N is the nuclear magneton. The second term is a contact hyperfine interaction resulting from a fractional unpairing of the S electrons of the nonmagnetic Rb^+ ion due to the Mn^{++} d-electrons's spin S_j in the Rb-Mn bond.[4,5] The summation is restricted to the eight nearest-neighbor Mn^{++} ions. $\overleftrightarrow{A}_{pj}$ is the contact hyperfine-coupling term and assumed to have the form

$$A_{pj}^{\mu\nu} = A\delta_{\mu\nu} , \quad (2)$$

where μ and ν represent x, y, or z. The value of A is reported as -11.4×10^{-6} cm^{-1} by Payne *et al.*[4] and $-(12.10\pm0.73)\times10^{-6}$ cm^{-1} by Walker and Stevenson.[5] The third term is the dipolar interaction where g is the gyromagnetic ratio and μ_B is the Bohr magneton. The summation is taken over all sites occupied by Mn^{++} ions. We rewrite the Hamiltonian (1) as follows:

$$\mathcal{H}_p = -g_N\mu_N\vec{I}_p\cdot\vec{H}+\sum_j \vec{I}_p\cdot\overleftrightarrow{F}_{pj}\cdot\vec{S}_j , \quad (3)$$

where $\overleftrightarrow{F}_{pj}$ contains both the contact and dipolar interactions.

In $RbMnF_3$ the Mn^{++} ions ($S=\frac{5}{2}$) form a simple-cubic magnetic system that is described by the isotropic Heisenberg Hamiltonian

$$\mathcal{H} = \frac{1}{2}\sum_{j,j'} J_{jj'}\vec{S}_j\cdot\vec{S}_{j'} , \quad (4)$$

where the exchange integral J is nonzero only between nearest neighbors and has the value 6.8 $\pm$0.6 K.[1]

The nuclear spin-lattice relaxation time T_1 is given by Moriya[6] for the Hamiltonian (3) as

$$\frac{1}{T_1} = \frac{1}{2\hbar^2}\int_{-\infty}^{\infty} dt\cos\omega_0 t \times\sum_{j,j'}\sum_{\nu,\nu'}[(F_{pj}^{x\nu}+iF_{pj}^{y\nu})(F_{pj'}^{x\nu'}-iF_{pj'}^{y\nu'})] \times\langle\{\delta S_j^{\nu}(t)\delta S_{j'}^{\nu'}(0)\}\rangle , \quad (5)$$

where ω_0 is the nuclear resonant frequency. Since ω_0 is of the order of 10^8 sec^{-1} and the correlation functions decay on a time scale of 10^{-13} sec, $\cos\omega_0 t$ may be set equal to 1. The z direction is along the average local field at the nucleus, $\delta\vec{S}_j=\vec{S}_j-\langle\vec{S}_j\rangle$, where $\langle O\rangle$ represents a thermal average of the operator O in terms of the Hamiltonian of the electronic spin system, and $\{AB\}=\frac{1}{2}(AB+BA)$.

Our main interest is in the calculation of T_1 in the paramagnetic region where the spontaneous

magnetization is zero. Because of the isotropic exchange integral we can write Eq. (5) as follows:

$$\frac{1}{T_1}=\frac{1}{\hbar^2}\sum_{jj'}\sum_{\nu}(F^{x\nu}_{pj}F^{x\nu}_{pj'}+F^{y\nu}_{pj}F^{y\nu}_{pj'})\tilde{\sigma}_0(\vec{r}_{jj'}) , \quad (6)$$

where

$$\tilde{\sigma}_0(\vec{r}_{jj'})=\int_0^\infty dt\,\sigma(\vec{r}_{jj'},t) \quad (7)$$

and

$$\sigma(\vec{r}_{jj'},t)=\langle S^z_j(t)S^z_{j'}(0)\rangle . \quad (8)$$

The quantity $\sigma_0(\vec{r}_{jj'},t)$ is the two-time spin-pair correlation function and $\tilde{\sigma}_0(\vec{r}_{jj'})$ is its time integral which is equal to the spectral weight function at zero frequency. Once $\tilde{\sigma}_0(\vec{r}_{jj'})$ is known, the nuclear-spin–lattice relaxation time can be calculated.

B. Infinite temperature

At infinite temperature a satisfactory result for the two-time spin-pair correlation functions is obtained[7] from the knowledge of the short time expansion coefficients of $\sigma(\vec{r}_{jj'},t)$[8] in the calculation based on the generalized-Langevin-equation formalism.[9] It is also shown that the correlation functions obtained in that calculation have correct long-time tails.[10] The time integrals of $\sigma(\vec{r}_{jj'},t)$ are given for several values of the spin for the simple-cubic Heisenberg magnet.[11] In Table I, we reproduce from Ref. 11, the values of $\tilde{\sigma}_0(\vec{r}_{jj'})$ which are needed here. The values for $\vec{r}_{jj'}=(0,0,0)$ and $(a,0,0)$ have been used to calculate the spin-spin relaxation time T_2 of F^{19} in $RbMnF_3$ at infinite temperature and have resulted in nice agreement with the experimental value.[12]

We now substitute these values into Eq. (6) to evaluate $T_{1\infty}$. Because of the long-range character of the dipolar interaction the summations on j and j' are carried out to $\vec{r}_{pj}=(\frac{11}{2}a,\frac{11}{2}a,\frac{11}{2}a)$. In Fig. 1 we show how $T_{1\infty}$ converges as a function of $|\vec{r}_{pj}|$

TABLE I. Time integral of the two-time spin-pair correlation function $\tilde{\sigma}_0(\vec{r}_{jj'})$ in units of $\hbar[S(S+1)]^{1/2}/6J$ at infinite temperature for the simple-cubic lattice.

$\vec{r}_{jj'}$	$S=\frac{1}{2}$	$S=\frac{5}{2}$
(0, 0, 0)	1.660	1.687
(a, 0, 0)	0.481	0.499
(a, a, 0)	0.308	0.318
(a, a, a)	0.243	0.251
(2a, 0, 0)	0.237	0.246
(2a, a, 0)	0.199	0.206
(2a, a, a)	0.178	0.183
(2a, 2a, 0)	0.155	0.160
(2a, 2a, a)	0.145	0.150
(3a, 0, 0)	0.152	0.157

TABLE II. Variation of $T_{1\infty}$ with the range of the time integral of the two-time spin-pair correlation function for $S=\frac{1}{2}$ and $\frac{5}{2}$.

$\vec{r}_{jj'}$	$T_{1\infty}$(msec) $S=\frac{1}{2}$	$T_{1\infty}$(msec) $S=\frac{5}{2}$
(0, 0, 0)	2.42	2.39
(a, 0, 0)	2.20	2.16
(a, a, 0)	2.17	2.13
(a, a, a)	1.96	1.92
(2a, 0, 0)	2.00	1.97
(2a, a, 0)	2.05	2.01
(2a, a, a)	2.02	1.98
(2a, 2a, 0)	2.02	1.99
(2a, 2a, a)	2.02	1.98
(3a, 0, 0)	2.02	1.98

when the values of $\tilde{\sigma}_0(\vec{r}_{jj'})$ up to the ninth nearest neighbors are taken into account. Table II shows how $T_{1\infty}$ converges as longer-ranged correlations are included—the sum over $|\vec{r}_{pj}|$ being taken up to $(\frac{11}{2}a,\frac{11}{2}a,\frac{11}{2}a)$. It is therefore apparent that $T_{1\infty}$ converges for both variables.

The value for T_1 thus obtained is 2.0 ± 0.2 msec for both $S=\frac{1}{2}$ and $S=\frac{5}{2}$ by using the value of A reported by Payne *et al.*[4] Walker and Stevenson's[5] data yield a 4% smaller value for $T_{1\infty}$.

C. Paramagnetic region

We now investigate the temperature dependence of T_1 in the paramagnetic region making use of Weiss molecular-field approximation (WMFA) as given by Moriya.[6] Because of the isotropic exchange Hamiltonian for the electronic spin system we have

$$\begin{aligned}\sigma(la,ma,na,t)&=\sigma(\pm la,\pm ma,\pm na,t) ,\\ &=\sigma(\pm ma,\pm la,\pm na,t) ,\\ &=\cdots , \text{ etc.},\end{aligned} \quad (9)$$

where $\vec{r}_{jj'}$ is denoted as (la,ma,na). Then it follows from Eq. (6) that

$$\frac{1}{T_1}=\frac{1}{\hbar^2}\sum_{l\geq m\geq n\geq 0}c(l,m,n)\int_0^\infty\sigma(la,ma,na,t)\,dt . \quad (10)$$

Here $c(l,m,n)$ is defined by the equation

$$c(l,m,n)=\sum_{j,j'}\sum_{\nu}(F^{x\nu}_{pj}F^{x\nu}_{pj'}+F^{y\nu}_{pj}F^{y\nu}_{pj'}) , \quad (11)$$

where the first summation is taken only over the values of j and j' which satisfy the condition that $(|r^x_{jj'}|/a,\ |r^y_{jj'}|/a,\ |r^z_{jj'}|/a)$ is equal to one of the permutations of (l,m,n). We define the Fourier space transform of the two-time spin-pair correlation function as

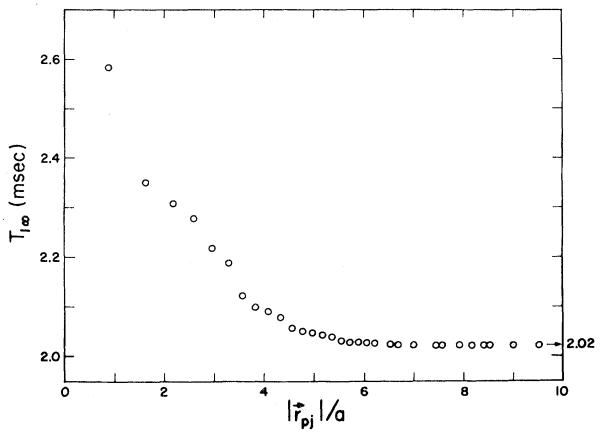

FIG. 1. Convergence of $T_{1\infty}$ as a function of $|\vec{r}_{pj}|$. Correlations between Mn^{++} spins up to the ninth nearest neighbor are taken into account.

$$\sigma(la, ma, na, t) = \frac{1}{N}\sum_{\vec{k}} I(\vec{k}, t)\exp[-i(lk_x a + mk_y a + nk_z a)]$$

$$= \frac{1}{N}\sum_{\vec{k}} I(\vec{k}, t)\cos(lk_x a)\cos(mk_y a)\cos(nk_z a), \tag{12}$$

where

$$I(\vec{k}, t) = \frac{k_B T}{g^2\mu_B^2}\chi_z(\vec{k}) f_{\vec{k}}^z(t) \tag{13}$$

and $\chi_z(\vec{k})$ is the static wave-vector-dependent susceptibility and $f_{\vec{k}}^z(t)$ is a relaxation function assumed to be characterized by an exponential decay with a rate $\Gamma_{\vec{k}}$. Substituting Eqs. (12) and (13) into Eq. (10) yields

$$\frac{1}{T_1} = \frac{k_B T}{\hbar^2 g^2 \mu_B^2}\frac{1}{N}\sum_{\vec{k}} \frac{\chi_z(\vec{k})\tilde{c}(\vec{k})}{\Gamma_{\vec{k}}} \tag{14}$$

where $\tilde{c}(\vec{k})$ is defined by

$$\tilde{c}(\vec{k}) = \sum_{l\geq m\geq n\geq 0} c(l, m, n)\cos(lk_x a)\cos(mk_y a)\cos(nk_z a). \tag{15}$$

Following Moriya, $\Gamma_{\vec{k}}$ is determined by assuming a Gaussian decay of the correlation function of the torque and the WMFA is used for $\chi_z(\vec{k})$. We obtain the expression

$$\frac{T_{1\infty}}{T_1} = \frac{1}{6[3(\delta+1)G(3(\delta+1); 0, 0, 0) - 1](\delta+1)^2}\frac{g(\infty)}{g(\delta)}, \tag{16}$$

where

$$g(\delta) = \sum_{l\geq m\geq n\geq 0} c(l, m, n)\{G(3; l, m, n) + (-1)^{l+m+n}$$

$$\times[G(3(\delta+1); l, m, n) - 3(\delta+2)G'$$

$$\times(3(\delta+1); l, m, n)]\}, \tag{17}$$

and

$$\delta = (T - T_N)/T_N. \tag{18}$$

$G(t; l, m, n)$ and $G'(t; l, m, n)$ are the lattice Green's functions of the simple-cubic lattice and its derivative with respect to t, respectively, and their evaluation is reported for $0 \leq l, m, n \leq 5$ in Ref. 13. The Néel temperature T_N is 82.9 K.[3]

III. EXPERIMENTAL RESULTS AND DISCUSSION

The experiments were carried out using the same samples and apparatus described in Ref. 3. The much improved precision, ±2%, throughout the paramagnetic region and through some of the antiferromagnetic region results from the use of boxcar integration techniques made possible because of the convenient relaxation time. The data were taken with the magnetic field applied in the [1, 0, 0] direction except as noted.

A. Paramagnetic region

The data are plotted in Fig. 2 as a function of $1000/T$ on semilog scales. The value, $T_{1\infty} = 2.0 \pm 0.1$ msec, is found by making a straight-line extrapolation through the six highest temperature points. This value is in excellent agreement with our calculated value of 2.0 ± 0.2 msec. We feel this is strong evidence for the correctness of the correlation functions.

The line shown in Fig. 2 is the result of Eq. (16) using 2.02 msec as the value of $T_{1\infty}$. As is expected, the WMFA works best at high tempera-

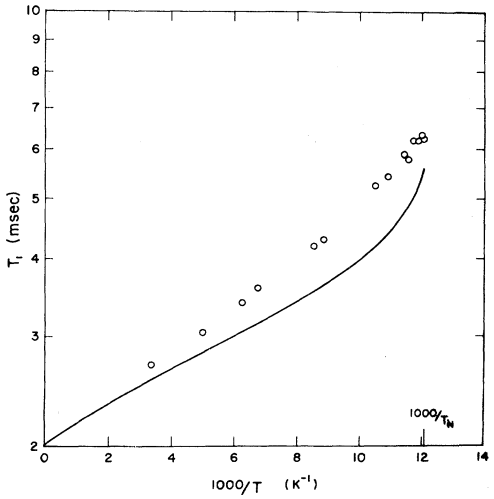

FIG. 2. Spin-lattice relaxation times (circles) in the paramagnetic range as a function of inverse temperature taken at a frequency of 10.02 MHz. The line is the result of Moriya's theory using 2.02 msec as the value of $T_{1\infty}$.

tures, as can be seen from the slope there, where the effects of short-range order are not important. Scherer *et al.*[14] have very recently included these effects in a calculation of the F^{19} linewidths in MnF_2 and $KMnF_3$ and find an improved fit.

B. Antiferromagnetic region

In Fig. 3 representative values of T_1 are plotted vs temperature on log-log scales. Above 10 K the temperature dependence of the data is virtually identical to the F^{19} data.[3] At $T \sim 12$ K, $T_1 \propto T^{-7}$ and the slope decreases continuously as the temperature increases. It was suggested in Ref. 3 and more recently by Lowe and Whitson[15] that an Arrhenius plot may be more appropriate. We find that

$$T_1^{-1} = (1/3.8)e^{-1.17T_N/T}\ \text{msec}^{-1} \qquad (19)$$

represents the data very well over the three decades in T_1 from 12 to 50 K. The magnitude of T_1 is 10^3 times larger than $T_1 (= T_2)$ of F^{19}, as it is at infinite temperature.

As in the case of the F^{19} resonance we find a different relaxation mechanism in the liquid-He temperature range. It is relatively ten times stronger, however, than the F^{19} mechanism and has a different magnetic field dependence. For fields between 4 and 10 kG, we find that $T_1 \sim H^3$. The temperature dependence appears to be less than that of $1/T$. Both of our samples, which come from different sources, give the same results. This relaxation mechanism is not understood and more experiments, extending the temperature range to 0.1 K, are in progress.[16]

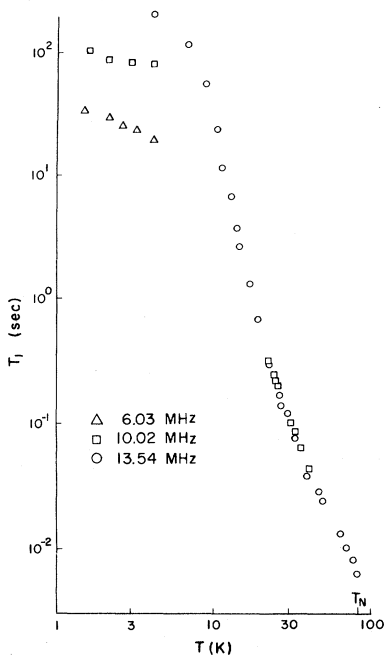

FIG. 3. Spin-lattice relaxation times in the antiferromagnetic range as a function of temperature.

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