

SPIN AUTOCORRELATION OF Ni IN $K_2Mn_{0.975}Ni_{0.025}F_4$ STUDIED BY NUCLEAR
 SPIN–LATTICE RELAXATION

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From the nuclear spin–lattice relaxation of the out-of-layer ^{19}F nuclei in magnetic fields perpendicular to the c -axis the low-frequency component of the autocorrelation function $\langle S^z(t)S^z(0) \rangle$ of Ni in ordered $K_2Mn_{0.975}Ni_{0.025}F_4$ is found to be substantially reduced relative to the Mn host. The experimental rates vs temperature are in accord with those for relaxation involving two spin excitations calculated with local Green's functions.

IN THIS COMMUNICATION we examine, as a function of the temperature, the low-frequency component of the correlation function $\langle S_0^z(t)S_0^z(0) \rangle$ of an isolated impurity spin embedded substitutionally in an antiferromagnetically ordered lattice. As a model system we have used the well-known two-dimensional (2D) antiferromagnet K_2MnF_4 doped with small concentrations (≈ 2.5 at.%) of Ni spins. In this system the correlation function $\langle S_0^z(t)S_0^z(0) \rangle$ of the Ni spins may be probed via the part of the nuclear spin–lattice relaxation of the out-of-layer ^{19}F nuclei ($^{19}F^I$) due to processes involving two spin excitations, which become operative in an external field perpendicular to the tetragonal axis. Previous work [1] has already evidenced that the excitation spectrum associated with the Ni impurity is substantially different from that of the host. It is dominated by a localized s mode lying far above the spin-wave band [2].

In zero external field, the out-of-layer ^{19}F nuclei located adjacent to the Ni resonate in a transferred hyperfine field $H_i = A_2 \langle S_0^z \rangle / g_N \mu_N$ (~ 40 kG), with minute corrections due to the further-out Mn neighbors. The resonance appears as a weak line at a frequency, extrapolated to zero temperature and field, of about 165 MHz, slightly dependent on the Ni concentration; the resonance of the $^{19}F^I$ NMR associated with the Mn host spins occurs at about 150 MHz. The measurements of the relaxation times were carried out by tracking the echo intensity following a $\pi/2 - \pi/2 - \pi$ pulse sequence as a function of the time span between the $\pi/2$ pulses. The external field, ranging up to 15 kG, was set at right angles to the c -axis. Its precise orientation was accomplished by seeking coincidence of the NMR of ^{19}F nuclei adjacent to the Ni spins on the up and down sublattices. It should be noted that the signal-to-noise is substantially reduced, in particular at the lower external fields, by the inhomogeneous spread of the

internal hyperfine field. For resonance in a perpendicular field H_0 , the spread is magnified by a factor H_i/H_0 due to the pulling apart of the spin packets when projecting the total resonance field back on the transverse direction. At 10 kG, for example, the line is already over 200 G in width.

The effect of a perpendicular magnetic field H_0 is to break the symmetry by a canting of the quantization axis of the nuclear spin I over an angle $\theta = \arctan(H_0/H_i)$ from the c -axis. The part of the hyperfine interaction relaxing the nuclei, i.e. the part containing I^\pm , is for the present system then given by [3, 4]

$$\mathcal{H}_{hf} = \frac{1}{4}A_1 [I^+S^-(1 + \cos \theta) - I^-S^+(1 - \cos \theta)] - \frac{1}{2}A_2 I^+S^z \sin \theta + \text{c.c.} \quad (1)$$

In equation (1) the canting of the electronic spin S , at 15 kG amounting to 0.6° compared to $\theta \approx 20^\circ$, has been neglected. Accordingly, S^z still refers to the tetragonal axis. The terms proportional to A_1 give rise to a relaxation involving three spin excitations (processes involving a single spin excitation would violate energy conservation), while the term with A_2 invokes relaxation by two excitations. The total relaxation rate, to be compared to experiment, thus reads

$$1/T_1 = (1/T_1^{(3)}) \frac{1}{2} (1 + \cos^2 \theta) + (1/T_1^{(2)}) \sin^2 \theta. \quad (2)$$

A typical experimental result, at 6.0 K, is given in Fig. 1, where the angle θ is determined from $\theta = \arcsin(H_0/H_{res})$, with $\hbar\omega = g_N \mu_N H_{res}$ the NMR transition energy. It is observed from Fig. 1 that first $1/T_1^{(2)}$ is larger than $1/T_1^{(3)}$ by two or three orders of magnitude [5], and second the dependence of $1/T_1$ on field is almost entirely contained in $\sin^2 \theta$. Detailed calculations indeed reveal that the effects of the variation of the excitation energies and Bogoliubov coefficients with the transverse

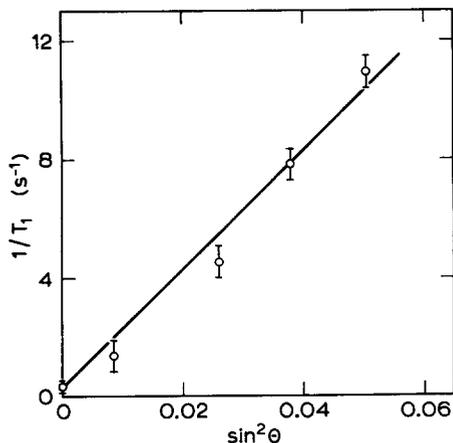


Fig. 1. Typical set of experimental data for $1/T_1$ of ^{19}F adjacent to Ni impurities in K_2MnF_4 at $T = 6.0$ K vs $\sin^2\theta$ [cf. equation (2)]. Data point at $\sin^2\theta = 0$ corresponds to $1/T_1^{(3)}$ only. The slope of the solid line represents the rate $1/T_1^{(2)}$.

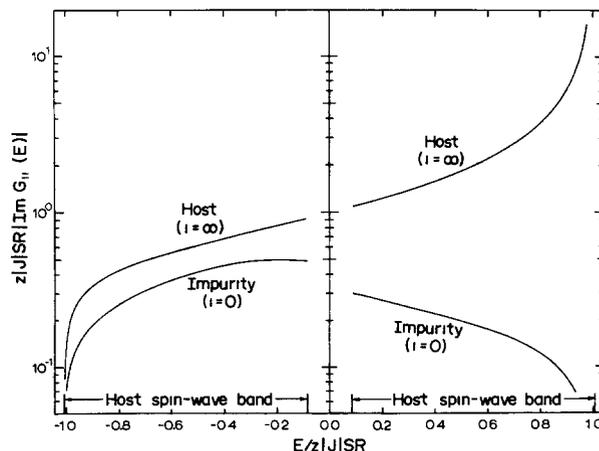


Fig. 3. $Im G_{ii}(E)$ for the Ni impurity site ($i = 0$), and Mn far from the impurity ($i = \infty$, equivalent to the pure system K_2MnF_4) vs energy. The energy is made dimensionless by scaling with $z|J|SR$, with $R = 1.0316$ representing the renormalization, and $z = 4$.

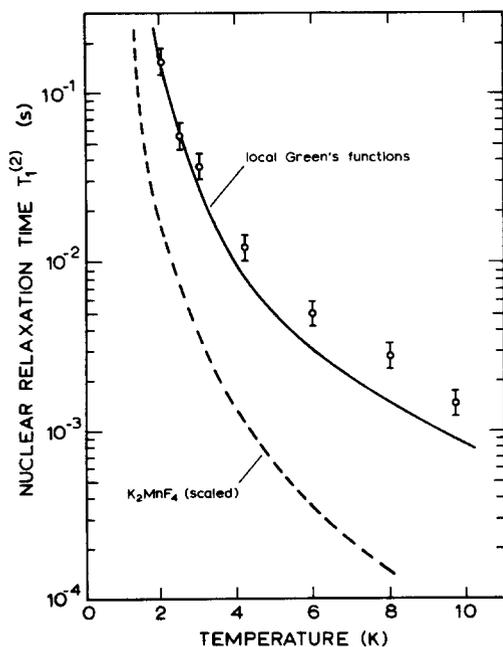


Fig. 2. Nuclear spin-lattice relaxation times $T_1^{(2)}$ of ^{19}F adjacent to Ni impurities in K_2MnF_4 vs temperature (circles), as extracted from sets of data for T_1 vs a transverse magnetic field [cf. Fig. 1]. The solid line is calculated using local Green's functions [cf. equation (6)]. The dashed line represents $T_1^{(2)}$ in pure K_2MnF_4 after scaling of the hyperfine interaction.

field are negligible, at least in the fields used in the present experiments. The results for $1/T_1^{(2)}$ as derived from the slopes of data sets as the one in Fig. 1 are collected in Fig. 2. The rate $1/T_1^{(2)}$ is seen to fall over two decades in the temperature interval from 2 to 10 K.

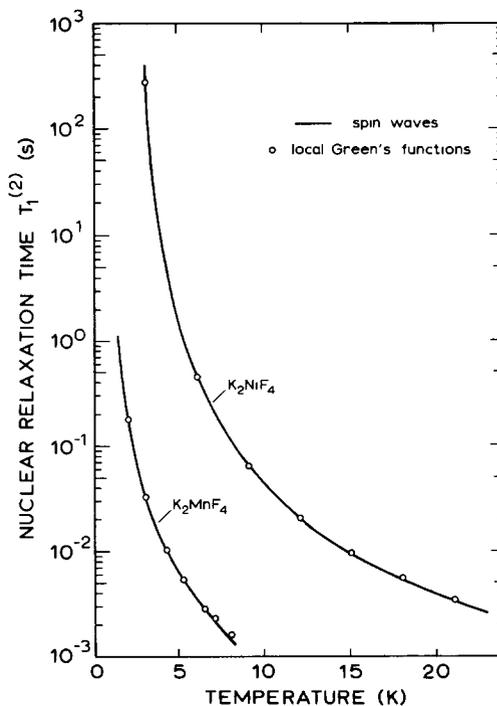


Fig. 4. Calculated $T_1^{(2)}$ of ^{19}F in pure K_2MnF_4 and K_2NiF_4 vs temperature. Circles are calculated from equation (6). They coincide with the result of spin-wave calculations with exact integration over the Brillouin zone [solid line, equation (7)].

As already indicated, $1/T_1^{(2)}$ is a measure for the low-frequency Fourier transform of the spin autocorrelation function [6]. From perturbation theory we have for the present case

$$1/T_1^{(2)} = \frac{1}{2}(A_2/\hbar)^2 \int_{-\infty}^{+\infty} dt \langle \delta S_0^z(t) \delta S_0^z(0) \rangle \cos \omega t, \quad (3)$$

where δ denotes a fluctuation about the thermal average, the subscript 0 as before refers to the impurity site, and ω is the angular Larmor frequency. To allow a comparison of the correlation function of the impurity with that of the host, we have also inserted in Fig. 2 the results for $T_1^{(2)}$ in pure K_2MnF_4 [4] after scaling according to $[T_1^{(2)}]^{(Mn,sc)} = (A_2^{(Mn)}/A_2^{(Ni)})^2 [T_1^{(2)}]^{(Mn)}$. Here, we have used for the hyperfine constants the numerical values of the ordered pure systems, i.e. $A_2^{(Ni)} = 189$ MHz and $A_2^{(Mn)} = 64.4$ MHz (see [4]). The experimental results may therefore be summarized by saying that over the whole temperature range the low-frequency spin correlations at the Ni impurity are smaller relative to the Mn host by an order of magnitude.

For a theoretical calculation of $1/T_1^{(2)}$ one has to evaluate the spin autocorrelation function occurring in equation (3). Since it is not judicious to decompose the excitations associated with the impurity into spin waves, we resort to a local technique, quite similar to the one used in [1] to calculate the local magnetizations. After transformation to local spin-deviation operators according to $S^z = S - a^\dagger a$, etc., the Hamiltonian of the pure system is written in a form quadratic in the local operators. Oguchi renormalization due to higher-order terms is accommodated in the coefficients in an effective way. Further, the anisotropy field is scaled according to the fall of the spin-wave gap with temperature [7]. The perturbative Hamiltonian substituting an impurity spin for a host spin at the origin only modifies the exchange interaction with the first shell of neighbors and, although insignificantly to the results, the anisotropy at the origin. Noting that $\langle a^\dagger(t) a^\dagger(0) \rangle$ vanishes within this framework, we have with $\delta S_0^z = a_0^\dagger a_0 - \langle a_0^\dagger a_0 \rangle$ and decoupling in the random-phase approximation (RPA)

$$\langle \delta S_0^z(t) \delta S_0^z(0) \rangle \rightarrow \langle a_0^\dagger(t) a_0(0) \rangle \langle a_0(t) a_0^\dagger(0) \rangle. \quad (4)$$

After passage to the energy domain, the two-deviation correlations are related according to [8]

$$\langle a_0^\dagger(t) a_0(0) \rangle = \int_{-\infty}^{+\infty} N_0(E) n(E) e^{iEt/\hbar} dE \quad (5)$$

to their spectral density $N_0(E)$, which in turn may be recovered from the Green's function $G_{00}(E) = \langle\langle a_0; a_0^\dagger \rangle\rangle_E$ through $N_0(E) = -\pi^{-1} \text{Im} G_{00}(E)$; $n(E) = (e^{E/\hbar T} - 1)^{-1}$ is the Bose factor. Substitution of equations (4) and (5) in equation (3), and setting $\cos \omega t = 1$, leads to the final result for the relaxation rate,

$$1/T_1^{(2)} = \frac{\pi}{\hbar} A_2^2 \int_{-\infty}^{+\infty} N_0^2(E) n(E) [n(E) + 1] dE, \quad (6)$$

which evidently represents processes involving absorption and emission of a spin deviation.

In evaluating equation (6), we first remark that all relevant parameters are known from other sources. Apart from the dispersion of the pure system, these include the exchange constant between the Ni impurity and its first Mn neighbors J_0 , and the hyperfine constant between the Ni spin and the adjacent out-of-layer ^{19}F . From the earlier analysis of the local magnetizations [1] $|J_0| = 25$ K, and in fact $\text{Im} G_{00}(E)$ as taken from this reference (Fig. 3) was substituted into equation (6). The constant A_2 is derived directly from the measured out-of-layer ^{19}F frequency extrapolated to zero field and temperature, 165.65 ± 0.02 MHz, combined with the theoretical zero-point spin reduction $\Delta_0^{(Ni)} = 0.106$, yielding $A_2 = 185$ MHz. The calculated results of equation (6) are given in Fig. 2 as the solid line. In view of the uncertainty of say 15% in the calculated $T_1^{(2)}$ due to the propagated errors of J_0 and A_2 , and the experimental error of 20%, not including possible systematic errors due to the inherent weakness of the impurity-associated NMR, the agreement should be considered gratifying. In particular, the drop of $T_1^{(2)}$ over two decades in the temperature range from 2 to 10 K is correctly described. It is noted that the systematic error in the theory related to ignoring the shifts of the spin-wave gap towards higher energies at finite concentrations of Ni is in the right direction, but amounts to a few percent only.

A crucial step in the derivation of equation (6) is the application of the RPA, equation (4). In addition to justification by the reasonable agreement between theory and experiment, substantial support for the RPA may also be gained from the observation that in pure 2D systems equation (6) is equivalent to a rigorous spin-wave expression for ^{19}F relaxation by field-induced two-magnon processes. The expression reads [4]

$$1/T_1^{(2)} = \frac{\pi}{\hbar} A_2^2 \frac{1}{N^2} \sum_{\mathbf{k}_1, \mathbf{k}_2} (u_1^2 u_2^2 + v_1^2 v_2^2) n_1 (n_2 + 1) \times \delta(E_1 - E_2), \quad (7)$$

in which u_i, v_i ($i = \mathbf{k}_1, \mathbf{k}_2$) are Bogoliubov coefficients, n_i the Bose occupation numbers, and N the number of magnetic unit cells. As equation (6), equation (7) is based on the effectively renormalized two-magnon Hamiltonian, i.e. damping of the magnons is ignored. Converting the summations over \mathbf{k} to integrals over the energy, noting that the u_i and v_i depend on \mathbf{k} through the energies E_i only, and employing the relation between $N(E)$ and the density of states $D(E)$ appropriate for translationally invariant systems, i.e. $N(E) = u^2(E)D(E)$ for $\epsilon > 0$ and $-v^2(E)D(E)$ for

$\epsilon < 0$, we indeed retrieve equation (6) from equation (7). In Fig. 4, equations (6) and (7) are worked out numerically and compared for both K_2MnF_4 and K_2NiF_4 up to temperatures corresponding to about the spin-wave gaps. Figure 4 incidentally also serves as a test for the computer program evaluating equation (6).

We finally compare the spin autocorrelations $\langle S^z(t)S^z(0) \rangle$ of the Ni impurity and the host. From the measured relaxation times as presented in Fig. 2 we see that these differ by an order of magnitude over the whole temperature range, with the autocorrelation of the Ni impurity being the smaller one. This has also been borne out by the calculations, equation (6), which related $T_1^{(2)}$ to an integral over the squared spectral density $N(E)$, yet it is of interest to note that the Bose factors put the weight on the low-energy part of $N(E)$, or for that matter $\text{Im } G(E)$. The ratio $[N_{Ni}(E)/N_{host}(E)]^2$ at low energies indeed amounts to about 0.1, only weakly dependent on E . The physical rationale why $\langle S^z(t)S^z(0) \rangle$ of the Ni impurity is so much smaller is that the major contribution ($\approx 87\%$) of $N(E)$ is

contained, to the detriment of $N(E)$ at low E , in a localized s mode lying far above the band ($E/z|J|SR = 2.87$), and therefore does not contribute to $\langle S^z(t)S^z(0) \rangle$ at the temperatures considered.

REFERENCES

1. J.A. van Luijk, A.F.M. Arts & H.W. de Wijn, *Phys. Rev.* **B21**, 1963 (1980).
2. W. Lehmann & R. Weber, *J. Phys.* **C10**, 97 (1977).
3. D. Beeman & P. Pincus, *Phys. Rev.* **166**, 359 (1968).
4. A.J. van der Wal & H.W. de Wijn, *Phys. Rev.* **B20**, 3712 (1979).
5. Relaxation involving three spin excitations is considered in more detail in: H. van der Vlist, W.C.M. Claassen, A.F.M. Arts & H.W. de Wijn, *J. Magn. Magn. Mat.* **31–34**, 1183 (1983), and H. van der Vlist, A.F.M. Arts & H.W. de Wijn (to be published).
6. T. Moriya, *Prog. Theor. Phys.* **16**, 23 (1956); *Prog. Theor. Phys.* **16**, 641 (1956).
7. H.W. de Wijn, L.R. Walker & R.E. Walstedt, *Phys. Rev.* **B8**, 285 (1973); *Phys. Rev.* **B9**, 2419 (1974).
8. D.N. Zubarev, *Sov. Phys. Usp.* **3**, 320 (1960).