Nuclear spin-lattice relaxation in the randomly diluted magnetic system $KNi_xMg_{1-x}F_3$

M. Engelsberg, J. Albino O. de Aguiar, and A. Franco, Jr.
Departamento de Física, Universidade Federal de Pernambuco, 50 000 Recife, Pernambuco, Brazil

Claudio José Magon
Instituto de Física e Química de São Carlos, Departamento de Física e Ciência dos Materiais, Universidade de São Paulo 13 560 São Carlos, São Paulo, Brazil
(Received 21 May 1986)

We present the result of measurements of ^{19}F nuclear spin-lattice relaxation (NSLR) rates in single crystals of the randomly diluted magnetic system $KNi_xMg_{1-x}F_3$. The data correspond to fluorine nuclei missing both of its magnetic nearest neighbors and were obtained at various frequencies and temperatures for samples with concentrations in the range $0.2 \leq x \leq 0.9$. For $x \approx 1$ the data basically confirm the correctness of a relaxation mechanism proposed earlier. For lower concentrations our results suggest that a second exchange constant, much smaller than the large nearest-neighbor exchange coupling but still large compared with electronic magnetic dipole-dipole interactions, may play a dominant role in the NSLR mechanisms of $KNi_xMg_{1-x}F_3$ and also of $KMn_xMg_{1-x}F_3$. For this last system the suggestion of a nonvanishing next-nearest-neighbor exchange coupling appears to contradict earlier conclusions inferred from an analysis of NSLR data but agrees with predictions based upon other experimental techniques.

I. INTRODUCTION

Considerable effort has been dedicated in recent years to the study of randomly diluted magnetic systems. The main objective has been to understand the effects of disorder upon the magnetic properties and the critical behavior of these materials. Nuclear magnetic resonance has been extensively employed to probe the spin dynamics of the magnetic ions and to better understand the nature of the processes that take place when random dilution is introduced in a magnetic crystal.

Among the systems that proved to be most fruitful for testing various theoretical predictions were the diluted paramagnetic crystals of the perovskite type of composition, $KMn_xMg_{1-x}F_3$,[1–4] and those with the rutile structure[5–7] of compositions $Mn_xZn_{1-x}F_2$ and $Fe_xZn_{1-x}F_2$. Nuclear spin-lattice relaxation of the ^{19}F nuclei in these systems is especially sensitive to changes in the spectral density of the magnetic-ion spin fluctuations. Magnetic ions which are members of large exchange-coupled clusters for example, can be expected to contribute fluctuations of a quite different spectral composition than magnetic ions which are exchange isolated.

In the paramagnetic phase, two sources of spin fluctuations can be regarded as predominant: Mutual spin flips induced by the exchange interaction, independent of temperature but strongly dependent upon magnetic concentration and temperature-dependent spin-lattice relaxation flips of the magnetic ions themselves. As the magnetic ordering temperature is approached with concentrations of magnetic ions higher than the percolation threshold x_p, the spectrum of fluctuations can be expected to drastically change shifting toward lower frequencies. This can strongly affect the nuclear spin-lattice relaxation (NSLR) rate.

^{19}F spin-lattice relaxation data in the randomly diluted paramagnetic systems $KMn_xMg_{1-x}F_3$ were first reported as a function of concentration of magnetic ions by Borsa and Jaccarino.[1] Their measurements were carried out at 300 K on a ^{19}F NMR line ($F^{(0)}$) which was identified as corresponding to fluorine nuclei having no magnetic nearest neighbors. These authors further proposed a simplified model to explain the steep variation of the ^{19}F spin-lattice relaxation rate $1/T_1$ with concentration. In this model, the dominant contribution to the nuclear relaxation rate originates in magnetic-ion spin fluctuations associated with large exchange-coupled clusters for $x \approx 1$. For smaller values of x the fluctuations originating from single exchange-isolated magnetic ions would become predominant. The basic correctness of this model was later confirmed by the results of Thayamballi and Hone[3] (TH), who developed a microscopic theory and performed more realistic computer calculations involving clusters of various sizes. These calculations were also aimed at describing the peculiar nonexponential recovery of the ^{19}F magnetization observed in $KMn_xMg_{1-x}F_3$ after saturation. In order to obtain quantitative agreement with the experimental decays, the value of the second-neighbor exchange constant J_2 in $KMnF_3$ was estimated[3] to be considerably smaller than values that had been determined earlier using other techniques. Although good agreement was found by setting $J_2 \approx 0$ this result was considered[3] as partially fortuitous and the role of J_2 in the ^{19}F spin-lattice relaxation rate could not be accurately ascertained.

In this paper we report the results of our measurements of the ^{19}F spin-lattice relaxation rates in single crystals of the randomly diluted paramagnetic system $KNi_xMg_{1-x}F_3$. The data correspond to the relaxation rate of ^{19}F nuclei of type $F^{(0)}$ and covers the range of concentrations $0.2 \leq x \leq 0.9$, with crystals above and also

 ©1987 The American Physical Society

below the percolation threshold.

The comparison of our data with earlier results[1,4] on the isostructural system $KMn_xMg_{1-x}F_3$ are rather revealing enabling one to establish a meaningful test of the range of validity of the various relaxation mechanisms that have been proposed for these diluted paramagnets. One important difference between these two isostructural system resides in the fact that, unlike Mn^{2+} which has a half-filled $3d$ shell and $L=0$, the ground state of Ni^{2+} is ^3F with an incompletely quenched orbital angular momentum ($g=2.3$). Orbital effects are therefore expected to play some role in the interpretation of the differences observed between the behavior of $1/T_1$ in both systems. An earlier comparison between the behavior of $Mn_xZn_{1-x}F_2$ and $Fe_xZn_{1-x}F_2$ (Ref. 5) also displayed significant differences in the temperature dependence of $1/T_1$ attributable to orbital effects associated with the Fe^{2+} ion. In our present case however, we can draw additional conclusions from the fact that the exchange frequency in $KNiF_3$ is almost an order of magnitude larger than in $KMnF_3$. By contrast the exchange frequencies in MnF_2 and FeF_2 are almost equal.

Another more subtle difference between $KMn_xMg_{1-x}F_3$ and $KNi_xMg_{1-x}Fe_3$, which is also believed to originate in orbital effects, has been recently observed[8] in the dependence with x of the ordering temperature $T_N(x)$. The critical curve $[T_N(x)/T_N(1)$ versus $x]$ for $KNi_xMg_{1-x}F_3$ displays a faster initial slope near $x=1$ than for $KMn_xMg_{1-x}F_3$. Such a behavior as well as the absence of some NMR lines[8,9] present in $KMn_xMg_{1-x}F_3$ could be understood if one postulates that for the Ni^{2+} ion the exchange interaction between two nearest neighbors may also be somewhat dependent upon the occupancy of other neighboring sites.[10]

II. BASIC NSLR MECHANISMS IN RANDOMLY DILUTED PARAMAGNETS

A rigorous treatment of NSLR in randomly diluted paramagnetic systems valid for a large range of concentrations of magnetic ions is a quite difficult problem. Computer simulations can be of considerable help but even then some approximations seem unavoidable. On the other hand, very simple models based upon drastic simplifications seem to yield apparently useful results[1,5] with the advantage of furnishing analytical expressions that easily permit comparisons.

Restricting the discussion to $F^{(0)}$ nuclei in the cubic perovskite paramagnetic crystals one notices that a range of relaxation rates for $F^{(0)}$ nuclei with different environments is possible. If the condition of rapid nuclear spin diffusion[11] were satisfied among these $F^{(0)}$ nuclei one could expect a common nuclear spin temperature to be established, leading to an exponential[12] recovery of the nuclear magnetization after saturation. The overall NSLR rate $1/T_1$ could be computed in this case by averaging over the relaxation rates of all individual nuclei.

The problem can be simplified enormously if instead of averaging over all nuclei one averages over all possible configurations of magnetic environments around a single nucleus. In this case one could write the NSLR rate as

$$1/T_1=\sum_k\sum_j P_k\alpha_{jk} \ , \tag{1}$$

where k classifies the type of cluster to which the magnetic ion belongs ($k=A$ for a large cluster, $k=B$ for an exchange-isolated ion, $k=C$ for an exchange-coupled pair, etc.). The probability that an ion of type k occupies any given site j is denoted by p_k and satisfies the condition $\sum_k p_k=x$. Furthermore the contribution to the relaxation rate from an ion of type k at site j relative to a $F^{(0)}$ nucleus at the origin is denoted by α_{jk} in Eq. (1) and the dominant electron-nucleus interaction for $F^{(0)}$ nuclei can be considered to be of magnetic dipole-dipole origin with next-nearest neighbors and beyond.

On the opposite extreme one could have a situation of negligible diffusion.[13] In this case the recovery of the nuclear magnetization after saturation should be computed by a weighted average of the individual decays associated with each configuration. This usually results in a nonexponential decay but with an initial slope of its logarithmic derivative still given by Eq. (1).[3] From an experimental point of view it could be rather difficult to distinguish this situation of negligible diffusion from one in which a common spin temperature is eventually established asymptotically leading to an exponential decay for long times. This may explain the variety of apparently contradictory ways of analyzing NSLR data in these systems that can be found in the literature.[1,3,4,14] A more detailed discussion of this important aspect of the problem will be presented in Sec. III.

First-order time-dependent perturbation theory can be used to calculate the relaxation rates α_{jk} corresponding to the various configurations. The general form of the result[1,3] is

$$\alpha_{jk}=(\Omega_{\rm en})^2_{jk}\tau_{ek} \ , \tag{2}$$

where $(\Omega_{\rm en})_{jk}$ is a frequency associated with the magnetic dipole-dipole interaction between a nuclear spin at the origin and an electron spin at position $\mathbf{r}_j$. The fluctuations of the electronic dipolar field at the nucleus affect the relaxation rate of Eq. (2) through the characteristic time τ_{ek}. These fluctuations of electronic origin have appreciable spectral weight only for frequencies close to $1/\tau_{ek}$ much larger than the nuclear Larmor frequency $\gamma_n H_0/2\pi$. As a consequence no dependence of the NSLR rate with magnetic field H_0 is expected.

In computing the configurational average of Eq. (1) some simplifications are useful.

A. High-concentration regime

For $x\approx 1$, the theory of Ref. 3 predicts an exponential recovery of the nuclear magnetization even with no diffusion. In this limit, the sum over k in Eq. (1) can be restricted to a single value ($k=A$) representing the predominant type of environment (an infinite cluster) surrounding any given electronic spin j. For the cubic perovskite structure the value of P_A is given in this high-concentration regime to a good approximation by

$$P_A=x(1-(1-x)^6) \ , \tag{3}$$

where we have required that the site j be occupied and at least one of its six first neighbors also be occupied.

The term $\sum_j \alpha_{jA}$ in Eq. (1) can be calculated along the lines of Ref. 3. Assuming a Gaussian decay for the electron-spin autocorrelation function one finds [Eq. (3.4) of Ref. 3]

$$\tau_{eA} = \tfrac{1}{3} S(S+1) \frac{\sqrt{2\pi}}{\langle \omega_{e1} \rangle} , \tag{4a}$$

where

$$\langle \omega_{e1} \rangle = [\tfrac{2}{3} S(S+1) Z_1 x]^{1/2} J_1 . \tag{4b}$$

In Eqs. (4), S denotes the electronic spin of the magnetic ion, $Z_1 = 6$ is the number of nearest neighbors of a given ion in the cubic perovskite structure and J_1 is the exchange coupling between magnetic ions who are nearest neighbors. An explicit form for the electron-nucleus dipolar term $(\Omega_{\text{en}})^2_{jA}$ in Eq. (2) can also be obtained following the procedure outlines in Ref. 3. For a polycrystalline sample, the final result[15] for the nuclear spin-lattice relaxation rate in the high-concentration regime can be expressed in the following form:

$$(1/T_1)_A = \tfrac{2}{3} (\gamma_e \gamma_n \hbar)^2 S(S+1) \times \sqrt{2\pi} \frac{D_1^2}{\omega_{e1}^A} x^{1/2} (1-(1-x)^6) , \tag{5}$$

where we have introduced $\omega_{e1}^A = [\tfrac{2}{3} S(S+1)(Z_1 - 1)]^{1/2} J_1$ instead of $\langle \omega_{\text{el}} \rangle_{x=1}$ of Eq. (4b), to account for the fact that at most $Z-1$ of the nearest-neighbors of the central ion can be magnetic of this ion is next-nearest neighbor to an $F^{(0)}$ nucleus. D_1^2 in Eq. (5) denotes the dipolar sum

$$D_1^2 = \sum_j{}' \, 1/r_j^6 , \tag{6}$$

where $\mathbf{r}_j$ are the position vectors of all magnetic-ion sites relative to a $F^{(0)}$ nucleus at the origin. The sum extends over all sites (occupied or empty) excluding the two first nearest neighbors of the nucleus $F^{(0)}$. Finally γ_e and γ_n in Eq. (5), denote electronic and nuclear gyromagnetic ratios, respectively.

B. Intermediate regime: Effect of exchange-isolated ions

It has been quite firmly established[1,3] that magnetic ions which are exchange isolated can have a dominant role in the nuclear spin-lattice relaxation process for $x \lesssim 0.7$ although their abundance may be quite low. The reason for this is the large spectral weight of the fluctuations associated with these ions at the nuclear Larmor frequency. We denote by $k = B$, a configuration where the central ion is exchange isolated from its six nearest neighbors, but at least one of the twelve next-nearest neighbors belongs to a large exchange-coupled cluster. One can show[1,3] that τ_{eB} in Eq. (2) may be close to two orders of magnitude larger than τ_{eA} discussed earlier. The probability p_B associated with an exchange isolated ion can be represented to a good approximation by

$$p_B = x(1-x)^6 [1-(1-x)^{12}] , \tag{7}$$

where we have required that the central ion and at least one of its 12 next-nearest neighbors be magnetic but all six nearest neighbors be nonmagnetic.

Using the procedure outlined in Ref. 3 [Eqs. (3.6) and (3.9)], one can compute the explicit form of $\alpha_{jB} = (\Omega_{\text{en}})^2_{jB} \tau_{eB}$ in Eq. (2). The final result[15] for the contribution $(1/T_1)_B$ from exchange-isolated spins to the configurational average of Eq. (1) for a polycrystalline sample is

$$(1/T_1)_B = \frac{2}{3} (\gamma_e \gamma_n \hbar)^2 \frac{S(S+1)}{\sqrt{2\pi}} \times D_2^2 \frac{\omega_{e1}^B}{\omega_{e2}^2 + \omega_{d2}^2} x^{1/2} (1-x)^6 [1-(1-x)^{12}] , \tag{8}$$

where ω_{e1}^B is defined in analogy with ω_{e1}^A of Eq. (5) as $\omega_{e1}^B = [\tfrac{2}{3} S(S+1)(Z_1 - 2)]^{1/2} J_1$. The term Z_1-2 corresponds to the fact that an ion which is next-nearest neighbor to an exchange-isolated central ion must have at least two nonmagnetic nearest neighbors.

The electron-nucleus dipolar sum D_2^2 in Eq. (8) is now defined as

$$D_2^2 = \sum_j{}' \frac{\frac{2}{3} + 2\gamma_j^2}{r_j^6} , \tag{9}$$

where γ_j a direction cosine of the electron-nucleus vector $\mathbf{r}_j$ relative to the crystal axes,[3] and the other terms of Eq. (9) have the same meaning as in Eq. (6). Furthermore, ω_{e2} represents a next-nearest-neighbor exchange frequency

$$\omega_{e2}^2 = \tfrac{2}{3} S(S+1) Z_2 J_2^2 \tag{10}$$

and ω_{d2}^2 an electron-electron dipolar sum extending to all ionic sites $\mathbf{r}_\alpha$ beyond the first $Z_1 = 6$ nearest neighbors (NN):

$$\omega_{d2}^2 = \tfrac{4}{3} \gamma_e^4 \hbar^2 S(S+1) \sum_{\alpha > \text{NN}} 1/r_\alpha^6 . \tag{11}$$

III. EXPERIMENTAL RESULTS AND DISCUSSION

Using conventional pulsed NMR we have performed ^{19}F NSLR rate measurements in single crystals of the randomly diluted magnetic system $KNi_xMg_{1-x}F_3$. The concentrations of Ni and Mg in the samples were determined separately yielding independent values of x which agree to within 3% with the corresponding average values. The data refer to the $F^{(0)}$ resonance line and were obtained at temperatures ranging from 4.2 to 300 K in the paramagnetic region of the crystals. A train of saturating $\pi/2$ pulses followed by a measuring $\pi/2$ pulse was employed for the determination of the magnetization recoveries at three operating frequencies (54, 32, and 22 MHz). The data were found to be independent of frequency as expected from the arguments of Sec. II. Also the dependence of the relaxation rates with the orientation of the crystal axes with respect to the external magnetic field was found to be negligible ($\sim 10\%$ variation).

From the discussion of the previous section it is clear

that any attempt of interpreting NSLR data in these systems should address the question of how to handle the magnetization recovery decays. Figure 1(a) shows several such decays at 300 K for sample with x above the percolation threshold while Fig. 1(b) shows data for values of x below the nominal percolation threshold $x_c = 0.31$. It is clear from Fig. 1 that the most concentrated sample ($x = 0.81$) exhibits a very fast initial recovery of about 30% of the decay followed by a much slower recovery which is well characterized by an exponential function. The initial fast decay is less pronounced for $x = 0.57$ and is not observed for $x = 0.28$ at $T = 300$ K or for $x = 0.2$ and $x = 0.015$ at any temperature.

The behavior observed in Fig. 1 is exactly opposite to what would be expected from a naive application of the theory of Thayamballi and Hone.[3] For the regime described in Ref. 3 one would expect an exponential decay at high concentrations turning into a decay of type $e^{-\sqrt{t/\tau}}$ for $x \ll 1$. Instead we observe in $KNi_xMg_{1-x}F_3$ an exponential decay for $x \ll 1$.

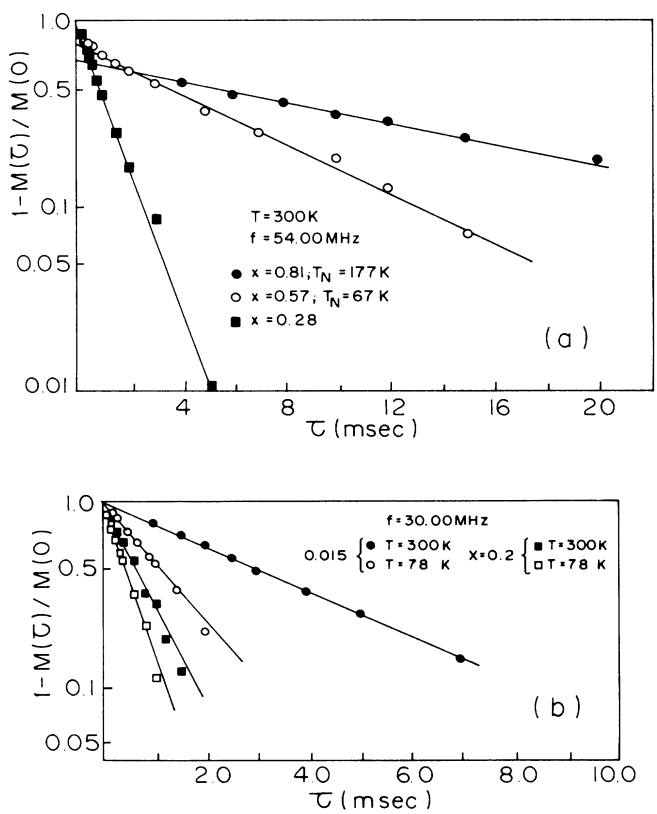

FIG. 1. (a) ^{19}F Nuclear magnetization recoveries in $KNi_xMg_{1-x}F_3$ samples with x above or close to the nominal percolation concentration at $T = 300$ K. (●), $x = 0.81$ (magnetic ordering temperature $T_N = 177$ K); (○), $x = 0.57$ ($T_N = 67$ K); and (■), $x = 0.28$. (b) Magnetization recoveries for $KNi_xMg_{1-x}F_3$ samples with x below the nominal percolation concentration. (●), $x = 0.015$, $T = 300$ K; (○), $x = 0.015$, $T = 78$ K; (■), $x = 0.2$, $T = 300$ K; (□), $x = 0.2$, $T = 78$ K.

A detailed comparison between the predictions of the theory of Thayamballi and Hone and the nuclear magnetization recoveries observed in $Fe_xZn_{1-x}F_2$ and in $Mn_xZn_{n-1}F_2$ has been recently published.[16] Since the arguments[3] leading to the $e^{-\sqrt{t/\tau}}$ result for $x \ll 1$ are of quite general nature independing upon the details of the magnetic ion spin fluctuations it is worth inquiring about the origin of the discrepancy in $KNi_xMg_{1-x}F_3$. One possible explanation is nuclear spin-diffusion to fast-relaxing (exchange-isolated) $F^{(0)}$ nuclei. Although the influence of nuclear spin-diffusion is much less amenable to a quantitative analysis than in the usual very dilute limit[11] one can nevertheless attempt a very rough estimate. The rapid diffusion regime in the present case would be attained when spin-lattice flips of $F^{(0)}$ nuclei induced by exchange-isolated ions occur less frequently than mutual diffusive flips among pairs of $F^{(0)}$ nuclei induced by their magnetic dipole-dipole interaction. Denoting by $\tau_D \approx (\bar{b})^2/6\bar{D}$ the diffusion flip time,[17] where $\bar{D}$ is an average diffusion constant and $\bar{b}$ is an average distance between $F^{(0)}$ nuclei, the above condition can be stated as $\tau_D < \tau_e$. Here, $\tau_e = 1/\sum_j \alpha_{jB}$ has been defined in Eq. (2) and Eq. (8) and represents the characteristic time of a direct nuclear spin-lattice flip induced by an exchange-isolated ion. Making the further assumption that the diffusion constant is reduced in relation to its $x = 0$ value D_0 according to $\bar{D} = D_0 a/2\bar{b}$, where a is the lattice constant and that $(\bar{b})^3 \approx a^3/3(1-x)^2$, where $(1-x)^2$ denotes the probability of finding an $F^{(0)}$ nucleus, one can arrive at a condition for rapid diffusion. In terms of the above quantities the condition can be expressed as $(1-x)^2 > (\sum_j \alpha_{jB})(2a)^{1/2}/18D_0$. The direct relaxation rate can be estimated from our $KNi_xMg_{1-x}F_3$ data $\sum_j \alpha_{jB} \approx 1.8 \times 10^4/x^{1/2}$ sec^{-1}. The ^{19}F diffusion constant in $KMgF_3$ can be estimated from its value in CaF_2 (Ref. 18) by correcting for the large number of nearest neighbors and slightly different interatomic distances. A value $D_0 \sim 8 \times 10^{-12}$ cm^2/sec was adopted. Thus the condition for rapid diffusion in $KNi_xMg_{1-x}F_3$ can be stated as $x^{1/2}(1-x)^2 > 0.28$ which is approximately satisfied for values of x in the range 0.35—0.1 but which is violated for values $x = 0.65$ and higher. It is also interesting to notice that in $KMn_xMg_{1-x}F_3$ the term $\sum_j \alpha_{jB}$ should be about ten times larger than in $KNi_xMg_{1-x}F_3$ and the criterion established above could be violated. These results suggest that nuclear spin diffusion may be playing an important role in $KNi_xMg_{1-x}F_3$, leading to an exponential recovery of the nuclear magnetization except in the high-concentration limit. Since the diffusion may be very rapid, the diffusion constant need not affect the relaxation rate.[11] The process would merely establish a common spin temperature and an exponential recovery whose decay rate could be calculated using Eq. (1).

In $KMn_xMg_{1-x}F_3$ the situation appears to be somewhat different and nonexponential decays may be expected as predicted by the theory of Thayamballi and Hone[3] and are actually observed experimentally.[1] Whether an asymptotic exponential recovery should still be detectable in the long-time behavior of the data is rather difficult to assess but the consequences of such an assumption will be examined.

A. High-concentration regime

Since for $x=1$, spin-diffusion is not effective we expect the theory of Ref. 3 to be applicable. An exponential decay should be observed in this regime even without diffusion. Although this is the case for $KMn_xMg_{1-x}F_3$, in $KNi_xMg_{1-x}F_3$ there exists also a fast initial decay. The prediction of a single exponential decay in this regime[3] is based upon the assumption that a single configuration (the infinite cluster, with $k=A$) is important. It is also assumed that this single configuration leads to a single relaxation rate α_{jA} associated with it. However at temperatures not too high above the ordering temperature one can expect regions within this cluster where incipient short-range order effects may considerably slow down electronic fluctuations. $F^{(0)}$ nuclei within this region will therefore relax at a much faster rate than α_{jA} corresponding to other $F^{(0)}$ nuclei. Since nuclear spin diffusion is ineffective in this concentration range one expects to observe a fast initial decay followed by a slow exponential recovery associated with α_{jA}. For the sample $KNi_{0.81}Mg_{0.19}F_3$ whose ordering temperature is 177 K, it appears that the fast initial decay still present at $T=300$ K is caused by incipient short-range order effects which should become more pronounced at lower temperature in agreement with our observations.

From the previous remarks it appears that a comparison between the long-time exponential behavior of the magnetization recovery in $KNi_xMg_{1-x}F_3$ for $x\approx 1$ with the exponential decay in $KMn_xMg_{1-x}F_3$ may be meaningful. Figure 2 shows the results of our measurements of NSLR rates in $KNi_xMg_{1-x}F_3$ as a function of x at various temperatures and frequencies. The higher concentration data in Fig. 2 correspond to the rate associated with the slow exponential decays observed in Fig. 1(a). For comparison Fig. 2 also shows NSLR rates in $KMn_xMg_{1-x}F_3$ at $T=300$ K obtained from magnetization-recovery decays using the same procedure.[1,4] The predicted relaxation rate for $x\approx 1$ from Eq. (5) is given by

$$(1/T_1)_A=\tfrac{2}{3}(\gamma_e\gamma_n\hbar)^2S(S+1)\sqrt{2\pi}D_1^2/\omega_{e1}^A\ . \qquad (12)$$

Substituting into Eq. (12) the numerical values[3] $\omega_{e1}^A=[\frac{2}{3}S(S+1)(Z_1-1)]^{1/2}J_1\approx 5.4\times 10^{12}\ \mathrm{sec}^{-1}$, $S=\frac{5}{2}$, and $D_1^2=0.9\times 10^{45}\ \mathrm{cm}^{-6}$ corresponding to $KMnF_3$ one obtains $(1/T_1)_A\approx 0.55\times 10^3\ \mathrm{sec}^{-1}$. This result is approximately a factor of 2 smaller than the experimental value obtained by Borsa and Jaccarino[1] and shown in Fig. 2 for $x=1$. Although the disagreement casts some doubts about the validity of the relaxation model, Thayamballi and Hone[3] have argued that the origin of the discrepancy may reside in the assumption of a pure Gaussian decay of the electronic spin autocorrelation function which neglects the low-frequency diffusive behavior. Consequently a smaller value of ω_{e1}^A, more representative of the low frequency spectral weight should be employed in Eq. (12) leading to a larger $(1/T_1)_A$ rate.

Our results in $KNi_xMg_{1-x}F_3$ unambiguously confirm the basic correctness of the relaxation mechanism implied by Eq. (12). Although the exact value of ω_{e1}^A may require a more detailed knowledge of the long-time behavior of the electronic spin autocorrelation function one can inquire about the scaling of Eq. (12) when one goes from $KMnF_3$ to $KNiF_3$. Using the numerical values[19,20] $J_1(KNiF_3)/J_1(KMnF_3)=100.1\ \mathrm{K}/7.6\ \mathrm{K}=13.2$, $D_1^2(KMnF_3)/D_1^2(KNiF_3)=(4.012/4.182)^6=0.78$, $S(KNiF_3)=1$ and $\gamma_e^2(KMnF_3)/\gamma_e^2(KNiF_3)=(2.0/2.3)^2=0.76$ (Ref. 21), one obtains

$$(1/T_1)_A^{KMnF_3}/(1/T_1)_A^{KNiF_3}=16.4\ . \qquad (13)$$

The above result agrees almost exactly with the experimental value of this ratio obtained from the data of Fig. 2 for $x\approx 1$. It strongly supports the validity of the relaxation mechanism in the high-concentration regime in spite of some uncertainty in the numerical value of ω_{e1}^A.

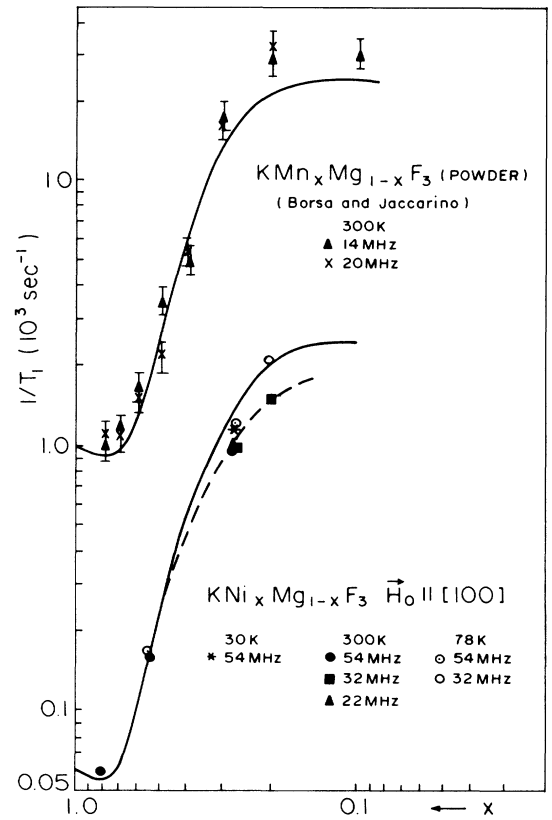

FIG. 2. (Upper) ^{19}F NSLR rates $KMn_xMg_{1-x}F_3$ from Ref. 1. The solid line is a theoretical fit based upon Eq. (5) and Eq. (8) of the text. (Lower) ^{19}F NSLR rates in single crystals of $KNi_xMg_{1-x}F_3$ at various temperatures and frequencies. $T=300$ K, (●), 54 MHz (■); 32 MHz (▲); 22 MHz; $T=30$ K, (*), 54 MHz; $T=78$ K, (⊙), 54 MHz, (○), 32 MHz. The solid line is a fit based upon Eq. (5) and Eq. (8). The dashed line is only to aid the eye.

B. Intermediate regime

In $KMn_xMg_{1-x}F_3$ this regime is characterized by magnetization recoveries which cannot be described by a single exponential decay. Thayamballi and Hone[3] have cal-

culated the shape of these decays using a theory that completely neglects spin diffusion. Although nuclear spin diffusion in $KMn_xMg_{1-x}F_3$ appears to be much less important than in $KNi_xMg_{1-x}F_3$ for the relevant range of concentrations, an agreement between the magnetization recoveries predicted by TH (Ref. 3) and the decays observed experimentally in $KMn_xMg_{1-x}F_3$ required values of the next-nearest neighbor exchange coupling J_2 close to zero.[3] This result is in disagreement with values of J_2 determined by other methods. An alternative procedure has been adopted by Borsa and Jaccarino[1] who applied Eq. (2) to describe the decay rate of the slow final portion of the magnetization recoveries fitting it by an exponential.[4] It is interesting to reproduce this analysis using Eq. (8). This equation is slightly different from Eq. (4) of Ref. 1. The $x^{1/2}$ term which appears in Eq. (8) and not in Ref. 1 arises from a treatment of $\langle \omega_{e1} \rangle$ consistent with what was used to derive $(1/T_1)_A$ in Eq. (5). The other additional term in Eq. (8) is $[1-(1-x)^{12}]$ but this is of little consequence for the range of concentrations of interest. Furthermore, most parameters entering Eq. (8) have well defined meanings and can be determined independently of the NLSR data. The value of ω_{e1}^B must be chosen in a way that brings the relaxation rate $(1/T_1)_A$ in Eq. (5) in agreement with its experimental value of $x \approx 1$. The appropriate values of the parameters for $KMn_xMg_{1-x}F_3$ are: $\omega_{e1}^B = 2.96 \times 10^{12}$ sec^{-1}, $D_2^2 = 1.3 \times 10^{45}$ cm^{-6} and $\omega_{d2} = 2 \times 10^{10}$ sec^{-1}. The next-nearest neighbor exchange constant J_2 has been the cause of some controversy.[3] We believe that the most reliable value for the present problem is $J_2 = (0.01 \pm 0.006) J_1$ determined from studies of pairs of Mn^{2+} ions in $KMgF_3$.[22]

Figure 2 also shows the best fit of the data corresponding to NSLR in $KMn_xMg_{1-x}F_3$ with $1/T_1 = (1/T_1)_A + (1/T_1)_B$ given by Eq. (5) and Eq. (8). The value of the next-nearest-neighbor exchange constants that yielded the best agreement was $J_2 = 0.013 J_1$ corresponding to a value $\omega_{e2} = 0.11 \times 10^{12}$ sec^{-1} much larger than the next-nearest-neighbor dipolar frequency ω_{d2}. Although the applicability of Eq. (5) and Eq. (8) to the long-time behavior of the recoveries in $KMn_xMg_{1-x}F_3$ may be somewhat questionable, the very good agreement obtained using realistic values of all parameters leads us to believe that this agreement may not be merely fortuitous.

In $KNi_xMg_{1-x}F_3$ the conditions for the applicability of Eq. (1) should be much better satisfied as discussed earlier. Rapid nuclear spin diffusion may be prevalent in the intermediate concentration range and exponential magnetization recoveries are actually observed. The term $(1/T_1)_A$ for $x = 1$ nicely yields the correct relaxation rate by scaling the exchange coupling constant, lattice parameter, spin and gyromagnetic ratio corresponding to $KMn_xMg_{1-x}F_3$.

The data shown in Fig. 2 for NSLR rates in $KNi_xMg_{1-x}F_3$ exhibit a clear temperature dependence for $x \lesssim 0.3$. In this range the relaxation rate increases as the temperature decreases in contrast with the behavior observed in $KMn_xMg_{1-x}F_3$ where the variation[4] appears to be less pronounced. A similar difference has been observed in the temperature dependences of the ^{19}F NSLR rates in $Fe_xZn_{1-x}F_2$ and $Mn_xZn_{1-x}F_2$ and attributed[5] to electronic fluctuations of spin-lattice origin becoming prevalent for the Fe^{2+} ion. The behavior exhibited by $KNi_xMg_{1-x}F_3$ can be understood along the same arguments. As the temperature is increased by $x \lesssim 0.3$ in $KNi_xMg_{1-x}F_3$ the relevant electronic flip rate $1/\tau_e$ in Eq. (2) appears to become mainly of spin-lattice origin and dominates the NSLR process. Since we are here mainly concerned with fluctuations of spin-spin origin, only the lower-temperature data in the region $x \lesssim 0.3$ should be compared with $KMn_xMg_{1-x}F_3$.

When one attempts to apply Eq. (5) and Eq. (8) to our $KNi_xMg_{1-x}F_3$ NSLR rate measurements, one immediately notices that it is impossible to fit the data in the intermediate range unless the next-nearest-neighbor exchange frequency ω_{e2} is assumed to have a much larger value than the dipolar frequency ω_{d2} in Eq. (8). In fact if one sets $\omega_{e2} = 0$ as proposed in Ref. 3 for $KMnF_3$, the relaxation rate $(1/T_1)_B$ predicted by Eq. (8) would become larger in $KNi_xMg_{1-x}F_3$ than in $KMn_xMg_{1-x}F_3$. Since the latter can be seen from data of Fig. 2 to be actually one order of magnitude larger than the former we conclude that ω_{e2} cannot be neglected in $KNi_xMg_{1-x}F_3$ within the framework of the present theory. Using in Eq. (8) the numerical values $\omega_{e1}^B = 1.86 \times 10^{13}$ sec^{-1}, $D_2^2 = 1.64 \times 10^{45}$ cm^{-6}, and $\omega_{d2} = 1.43 \times 10^{10}$ sec^{-1} appropriate for $KNiF_3$, the best fit to the data shown as the dashed line of Fig. 2, is obtained for $J_2 \approx 0.01 J_1$ which corresponds to $\omega_{e2} = 5.36 \times 10^{11}$ sec^{-1}. The general agreement between this theoretical curve and our $KNi_xMg_{1-x}F_3$ data appears to be good with quite realistic values of the parameters involved. Subtler differences between $KMn_xMg_{1-x}F_3$ and $KNi_xMg_{1-x}F_3$, of the type observed in the ^{19}F line shape and in the critical curve,[8,9] should also affect the spin-lattice relaxation data. This however cannot be clearly confirmed by our T_1 measurements since more experimental data and a more sophisticated analysis would be needed for a conclusive statement.

IV. CONCLUSIONS

The result of our NSLR measurements in $KNi_xMg_{1-x}F_3$ are employed for a meaningful comparison with earlier data on the isostructural system $KMn_xMg_{1-x}F_3$. The correctness of the relaxation mechanism for randomly diluted magnets proposed by Borsa and Jaccarino[1] and Thayamballi and Hone[3] in the high-concentration regime ($x \approx 1$) is unambiguously confirmed by our data. In the intermediate concentration regime an improved version of the model introduced earlier by Borsa and Jaccarino[1] for their $KMn_xMg_{1-x}F_3$ NSLR measurements yields a good fit of these data with a value $J_2 \approx 0.013 J_1$ of the next-nearest-neighbor exchange constant. This result is in agreement with an independently determined value[21] but disagrees with the value $J_2 \approx 0$ suggested in Ref. 3.

For $KNi_xMg_{1-x}F_3$ in the intermediate region an application of the above model also requires a next-nearest-neighbor exchange coupling much larger than the corresponding electronic magnetic dipole-dipole interaction. From a fit to our data a value $J_2 \approx 0.01 J_1$ was obtained.

ACKNOWLEDGMENTS

We wish to thank H. J. Guggenheim for making available and analyzing the crystals used in this investigation. We are also indebted to Professor Francisco C. Alcaraz for helpful comments. This work has been supported by the Brazilian agencies Financiadora de Estudos e Projetos, Conselho Nacional de Desenvolvimento Científico e Tecnológico and Coodenação de Aperfeiçoamento de Pessoal do Ensino Superior.

[1]F. Borsa and V. Jaccarino, Solid State Commun. **19**, 1229 (1976).

[2]D. J. Breed, K. Gilijamse, J. W. Sterkenburg, and A. R. Miedema, J. Appl. Phys. **41**, 1267 (1970).

[3]P. Thayamballi and D. Hone, Phys. Rev. B **21**, 1766 (1980).

[4]G. D. Ariano and F. Borsa, Phys. Rev. B **26**, 6215 (1982).

[5]H. Yasuoka, S. P. Vernon, and V. Jaccarino, J. Appl. Phys. **53**, 2707 (1982).

[6]H. Yasuoka, C. J. Magon, and V. Jaccarino, J. Phys. Soc. Jpn. **51**, 1039 (1982).

[7]C. J. Magon, J. Sartorelli, A. R. King, V. Jaccarino, M. Itoh, H. Yasuoka, and P. Heller, J. Magn. Magn. Mater. **54-57**, 49 (1986).

[8]J. Albino O. de Aguiar, M. Engelsberg, and H. J. Guggenheim, J. Magn. Magn. Mater. **54-57**, 107(1986).

[9]M. Engelsberg, J. Albino O. de Aguiar, Osiel F. de Alcântara Bonfim, and A. Franco, Jr., Phys. Rev. B **32**, 7143 (1985).

[10]J. Albino O. de Aguiar, F. G. Brady Moreira, and M. Engelsberg, Phys. Rev. B **33**, 652 (1986).

[11]I. J. Lowe and D. Tse, Phys. Rev. **166**, 279 (1968).

[12]C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1980), Chap. V.

[13]W. E. Blumberg, Phys. Rev. **119**, 79 (1960).

[14]G. D. Ariano, R. L. Lecander, C. Marchetti, and F. Borsa, J. Magn. Magn. Mater. **15-18**, 681 (1980).

[15]C. J. Magon, Doctoral thesis, Instituto de Fisica e Química de São Carlos, Universidade de São, Brasil, 1986 (unpublished).

[16]M. Itoh, H. Yasuoka, A. R. King, and V. Jaccarino, J. Phys. Soc. Jpn. **55**, 964 (1986).

[17]A. B. Lidiard, in *Encyclopedia of Physics,* edited by S. Fluge (Springer, Berlin, 1957), p. 374.

[18]D. Tse and I. J. Lowe, Phys. Rev. **166**, 292 (1968).

[19]J. E. Gulley, Daniel Hone, D. J. Scalapino, and B. G. Silbernegel, Phys. Rev. B **1**, 1020 (1970).

[20]S. R. Chinn, H. J. Zeiger, and J. R. O'Connor, Phys. Rev. B **3**, 1709 (1971).

[21]F. Ganott, C. Dugatier, P. Moch, and J. Nouet, J. Phys. C **15**, 801 (1982).

[22]C. G. Windsor, Ph.D. thesis, Oxford, 1963 (unpublished), referred to in M. B. Walker, Proc. Phys. Soc., London **87**, 45 (1966).