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μSR evidence of low frequency spin fluctuations in the AF phase of hole-doped NiO

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Abstract. μSR measurements in the antiferromagnetic (AF) phase of $Ni_{1-x}Li_xO$ for $0 \leq x \leq 0.10$ are reported. While in pure NiO the muon longitudinal depolarization rate λ_μ is found almost temperature independent, in the Li-doped compounds broad maxima around 130 K are observed. These maxima are associated with the progressive freezing of the spin fluctuations of $S = 1/2$ defects induced by the localization of the extra-holes. From the temperature dependence of λ_μ and the stretched exponential form of the depolarization, insights on the distribution of correlation times for the fluctuating field at the muon site are derived.

PACS. 75.30.Hx Magnetic impurity interactions – 75.40.Gb Dynamic properties (dynamic susceptibility, spin waves, spin diffusion, dynamic scaling, etc.) – 76.75.+i Muon spin rotation and relaxation

1 Introduction

During the last decade a renewed interest on the effects of heterovalent substitutions on the magnetic and electronic properties of AF insulator has emerged. Most of the attention has been addressed to the study of the modifications of the electron correlation on approaching the metal-insulator transition in metal oxides and to the problem of the disorder induced by localized holes in the AF background [1]. Lithium doped NiO appears as a suitable system to investigate these problematics. $Ni_{1-x}Li_xO$ in fact, preserves the original pseudocubic cell of the pure compound up to $x \approx 0.25$ and due to the three-dimensional (3D) character of the magnetic interaction, it maintains an AF ordered phase in all this doping range. The heterovalent substitution of Li^+ for Ni^{2+} introduces in the AF matrix a hole that at low temperature is localized on the O_{2p} orbitals around the Li^+ impurity [2,3]. When the temperature is increased, a diffusion-like motion of the hole between different oxygen sites is expected, similarly to what observed in others transition metal oxides [4]. A theoretical approach describing this phenomenon as an effective low-energy transition from a $S = 1/2$ to a $S = 1$ state of the Ni ion, has been proposed by Dagotto *et al.* for one-dimensional nickelates [5]. Recently through ^{7}Li NMR [6], the AF phase of lightly doped NiO was investigated and the diffusional motion of the holes have been clearly evidenced in the temperature range $T \geq 250$ K. Moreover ^{7}Li spin-lattice relaxation rates ($1/T_1$) revealed another low-frequency process at low temperatures ($T \leq 200$ K), which has been attributed to local fluctuations of the effective magnetic moments generated by holes localization. However, the fast ^{7}Li spin-spin relaxation hampered an accurate study of this process.

Muon spin relaxation (μ^+SR) has been successfully used in the study of the collective dynamics of disordered compounds as classical spin-glasses [7–9]. Here we apply this technique to investigate Li doped NiO in the regime of hole localization, which shows many similarities to a spin-glass state. Since no external field is necessary in μ^+SR experiment and quadrupolar contributions to the μ^+ relaxation are absent (whereby they can in principle contribute to ^{7}Li NMR relaxation), by measuring the longitudinal depolarization rate one can probe the unperturbed spin-spin correlation function. Moreover μ^+SR allows a direct comparison between the pure NiO (where no reliable NMR probe is present) and the doped samples. Thus the doping-related part of the spin dynamics can be isolated and investigated.

In this paper it is shown that while in the pure NiO the muon depolarization rate is nearly temperature-independent, in the Li-doped samples one detects maxima around 130 K which are related to the freezing of the spin fluctuations around $S = 1/2$ defects. The distribution of defects in the AF background gives rise to a distribution of correlation times for these fluctuations.

2 Experimental aspects and results

$Ni_{1-x}Li_xO$ powder samples, with $0 \leq x \leq 0.10$, have been prepared by solid state synthesis starting from the reactive system NiO/Li_2CO_3 [10]. The composition and structure have been controlled by X-ray diffraction. Li^+ substitutes

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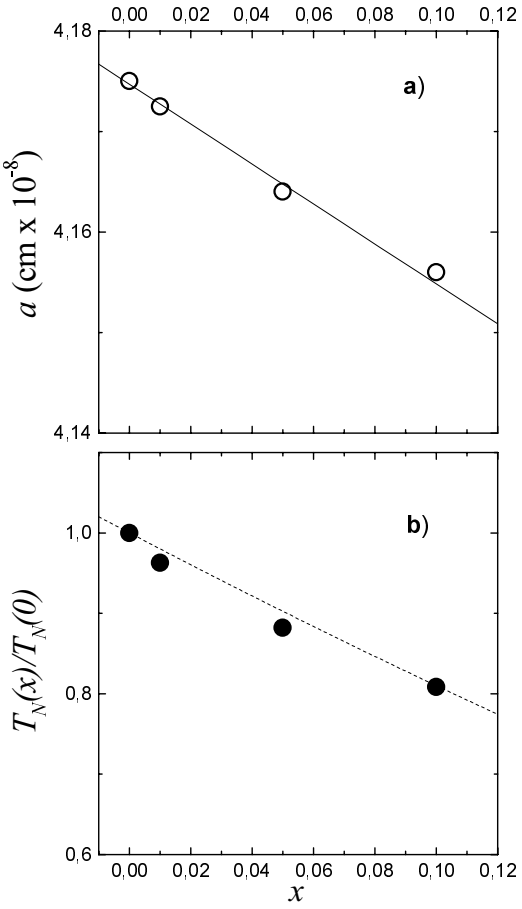

Fig. 1. (a) Lattice parameter of the pseudocubic cell of $Ni_{1-x}Li_xO$ as a function of the Li content. The solid line is the best-fit for a linear decrease of a with increasing x. (b) Reduction of the Néel temperature $T_N(x)$ with x in $Ni_{1-x}Li_xO$ as deduced by ^{7}Li NMR (Ref. [6]). The dashed line is the theoretical behavior resulting from a dilution model, for $T_N(0) = 524.5$ K.

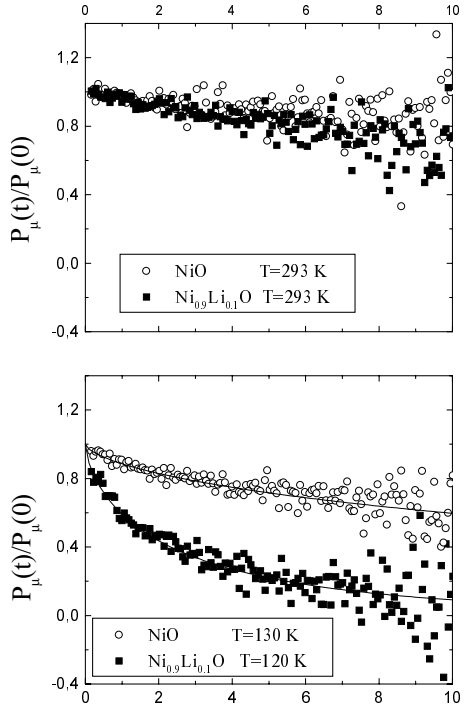

Fig. 2. Decay of the μ^+ longitudinal polarization in $Ni_{1-x}Li_xO$ (after subtracting the constant background amplitude of ≈ 0.02) at room temperature and at $T \approx T^+$, where the difference between pure and doped samples is more evident. In all the samples $P_\mu(0) \approx 0.07$. The solid lines are the best fit of the data according with equation (2) in the text.

Ni^{2+} in equivalent position and the lattice parameter a of the face-centered pseudocubic cell is only slightly modified (Fig. 1a). In NiO, the superexchange interaction between Ni^{2+} ($S = 1$) ions *via* the O^{2-} gives rise to an ordered AF state below $T_N = 524.5$ K [11]. The disorder introduced by doping competes with the long-range order, inducing a sizeable reduction of T_N [6] (Fig. 1b).

Zero-field μ^+SR measurements were performed at ISIS pulsed source on EMU beamline using spin-polarized 29 MeV/c muons. The time evolution of the muon polarization $P_\mu(t)$ was detected over an interval of 16 μs. Typical behaviors for $P_\mu(t)$, after subtraction of the spurious signal (of the order of $0.2 \div 0.3 P_\mu(0)$) due to cryostat walls and silver shielding, are shown in Figure 2. The amplitude of the spurious signal was determined either from the constant background of the total signal in presence of a fast depolarization and by looking at the precessional signal in presence of a 100 G transverse field. A general form which describes the time evolution of the longitudinal muon polarization in magnetic powder samples, with all-equivalent muon sites, is [12]:

$$P_\mu(t) = A_1 e^{-\sigma t} \cos(\gamma_\mu \langle B_\mu \rangle t + \phi) + A_2 e^{-\lambda t} \qquad (1)$$

where $\gamma_\mu/2\pi = 135.5$ MHz/T is the muon gyromagnetic ratio, $\langle B_\mu \rangle$ the mean local field at the muon site, σ and λ the transverse and longitudinal decay rates, respectively.

In our measurements no oscillating fraction A_1 have been detected over all the explored temperature range. At the same time A_2 turned out $\cong 1/3$ of the expected total asymmetry. Because of the finite width of the muon pulses at ISIS, precession signals at frequencies higher than $\cong 10$ MHz are filtered out. Therefore, the fact that $A_1 \cong 0$ is an indication that, in all samples, the hyperfine field at the muon $\langle B_\mu \rangle \geq 1000$ G. Moreover, while above 220 K an exponential decay of the μ^+ polarization is observed, at low temperature one has a progressive changeover towards a non-exponential behavior. This feature is typical of systems with a distribution of magnetic inequivalent muon sites, characterized by different relaxation rates. A form commonly used in these cases to describe the decay of $P_\mu(t)$ (Fig. 2) is the stretched exponential

$$P_\mu(t) = A e^{-(\lambda_\mu t)^\beta} \qquad (2)$$

with temperature dependent β.

In Figure 3 we show the temperature-dependence of the effective depolarization rates λ_μ for $x = 0$, $x = 0.05$

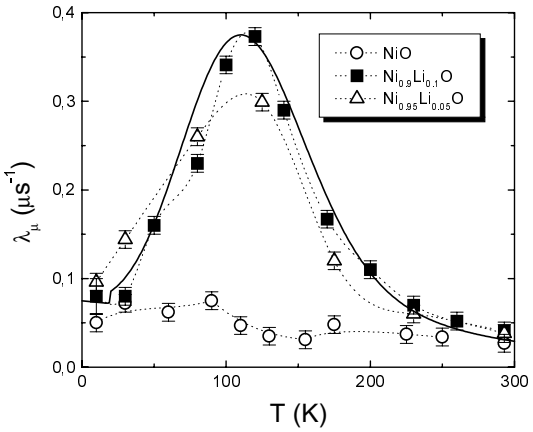

Fig. 3. μ^+ decay rate in $Ni_{1-x}Li_xO$ as a function of temperature, extracted by means of equation (2). The solid line is the plot of equation (5), with the parameters given in the text for $Ni_{0.90}Li_{0.1}O$. The dashed lines are guide to the eye.

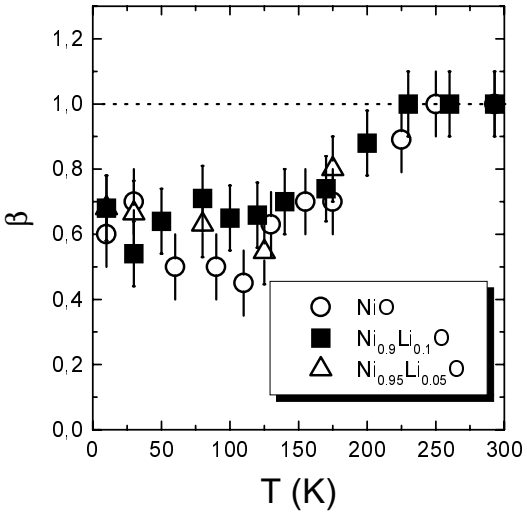

Fig. 4. Temperature behavior of the exponent β deduced from the decay of $P_\mu(t)$ in the light of equation (2).

and $x = 0.10$ samples extracted by means of equation (2). The correspondent behavior for the exponent β is shown in Figure 4. One observes that while for pure NiO λ_μ is practically constant, the Li-substituted samples show broad maxima around $T^+ \approx 130$ K, which indicates the presence of a doping-related contribution to the muon relaxation mechanism. Analogous peaks have been observed in other Heisenberg AF's with heterovalent substitutions [13]. The temperature dependence of λ_μ and the fact that it was not observed to decrease after the application of a longitudinal field, evidence the dynamical origin of the peak at T^+. One can observe that due to the small natural abundance of ^{17}O and ^{61}Ni nuclei, the contribution from nuclear magnetic moments to the decay of the polarization is negligible.

3 Analysis of the results and discussion

Before approaching the problem of the electronic spin dynamics generating the time fluctuations of the local field B_μ, it is worthy to discuss briefly the issue of the muon equilibrium position. On the basis of a point-charge model, with virtual charges $+2e$ for Ni, e for Li, $-2e/-e$ for O, depending if the hole is or not localized on it, the muons are expected to localize close to the oxygen site. However, a reasonable estimate of the O^{2-}–μ^+ distance cannot be done on the basis of this point-charge model alone, since its validity breaks down for distances $d \ll a$ where the correct symmetry and amplitude of the ionic orbitals must be taken into account. On the other hand, from the experimental evidence that $\langle B_\mu \rangle \geq 1000$ G (see Sect. 2), by using a dipolar approximation, one can estimate a distance of the μ^+ from the oxygen which must be at least $\approx 0.05a$. In fact, the magnetic field at the O^{2-} site cancels out because of the symmetry of the magnetic lattice in type II antiferromagnets [14].

The dynamical contribution to the μ^+ longitudinal depolarization is related to the fluctuating part of the hyperfine field at the muon site $\delta\mathbf{B}_\mu(t) = \mathbf{B}_\mu(t) - \langle \mathbf{B}_\mu \rangle$. For equivalent sites ($\beta = 1$ in Eq. (2)) the decay rate can be written

$$\lambda = \frac{\gamma_\mu^2}{2} \int \langle \{\delta B_\mu^+(t)\delta B_\mu^-(0)\}\rangle e^{-i\omega_\mu t} dt \qquad (3)$$

where $\delta B_\mu^\pm = \delta B_\mu^x \pm \delta B_\mu^y$ are the transverse components of the fluctuating field at the muon with respect to the direction z of the average field $\langle \mathbf{B}_\mu \rangle$, $\{AB\} = (AB + BA)/2$, while $\langle\ \rangle$ denotes the statistical average.

In the case of a site-dependent correlation time one has a distribution of depolarization rates and the relaxation is no longer exponential. An average value for the decay rate can be defined as

$$\lambda_A = \int f(\lambda_i)\lambda_i di \qquad (4)$$

where $f(\lambda_i)$ is the distribution function for λ_i. At least in two cases equation (2) can be obtained as analytical Laplace transformation of a given $f(\lambda_i)$. For $f(\lambda_i) \equiv \delta(\lambda_A)$ one has clearly a simple exponential decay ($\beta = 1$), while for $f(\lambda_i) \equiv (\lambda_A^2/2\sqrt{\pi\lambda_i^3}) \exp(-\lambda_A^4/4\lambda_i)$ one obtains $P_\mu(t) = Ae^{-(\lambda_A t)^{1/2}}$. Then, at least for $0.5 \leq \beta \leq 1$, the values of λ_μ extracted by using equation (2) are close to λ_A, the average depolarization rate defined by equation (4). The temperature dependence of the exponent β directly reflects the temperature dependence of the shape of the distribution $f(\lambda_i)$.

In pure AF the low-energy ($\omega \approx \omega_\mu \to 0$) spin dynamics controlling the muon relaxation is dominated by indirect two-magnon Raman processes [15]. Its contribution to the decay rate is usually small and it decreases fast on decreasing temperature, due to the reduction in the statistical population of the magnons states. In the NiO ($x = 0$) powder sample, however, we find λ_μ nearly temperature independent and the recovery law is not single exponential at low temperature. These observations suggest that even in nominally pure NiO, a small amount of

impurities is present and causes a non-negligible increase in the low-energy spectral density. A sizeable effect on the low-frequency spectral density related to a small number of impurities has been already evidenced in Li-doped CuO [4], where the low-temperature ^{7}Li NMR relaxation rate was observed to increase significantly by introducing less than 1% of Li^+. Being interested on the modifications induced by Li-doping on the correlated spin dynamics in the AF phase, we will assume $\lambda_\mu(x=0,T)$ as a background and focus the attention on the differences between the nominally pure sample and the doped ones. The peak in λ_μ observed, even for small Li-doping, can not be related to μ^+ diffusion, otherwise it should be present also in pure NiO.

Although Li-doping is observed to reduce the transport activation energy, $Ni_{1-x}Li_xO$ for $x \leq 0.10$ remains insulating and the extra-holes can be considered as localized for $T \leq 250$ K [6]. Extending to $Ni_{1-x}Li_xO$ the model presented in reference [5], the holes should localize on the O_{2p} orbitals [2] and form a singlet with one of the $3d$-holes of a nearest neighbor Ni^{2+}. Thus, Li-doping generates an ensemble of $S=1/2$ defects in the AF matrix of NiO. We will attribute the observed differences in λ_μ between pure and doped samples to the relaxation processes related to the cooperative spin dynamics of these defects.

Several functional forms have been used to describe the time correlation function of disordered magnetic systems, ranging from stretched exponential [16,17] to power laws [16,18,19]. Here we start from the simple physical picture in which the fluctuating hyperfine field at the muon $(\delta \mathbf{B}_\mu(i,t))_h$, reflecting the dynamics of the $S=1/2$ defects close to the ith muon, is described by an exponentially decaying correlation function with a thermally activated characteristic time $\tau(\Delta_i,T)=\tau_0\exp(\Delta_i/T)$. The effects of disorder is taken into account by assuming a distribution for the activation energies, depending on the distance among defects. We will consider a Gaussian distribution $G_{\langle\Delta\rangle,\sigma}(\Delta_i)$, centered at $\langle\Delta\rangle$ with variance σ. Then one can write the Li-induced contribution to the depolarization rate as

$$\begin{aligned}(\lambda_\mu(T))_h &= \frac{\gamma_\mu^2}{2}\iint G_{\langle\Delta\rangle,\sigma}(\Delta_i)\langle(\delta B_\mu^+)_h^2\rangle \\ &\quad\times\exp[t/\tau(\Delta_i,T)]e^{-i\omega_\mu t}dtd\Delta_i \\ &= \frac{\gamma_\mu^2}{2}\langle(\delta B_\mu^+)_h^2\rangle\int G_{\langle\Delta\rangle,\sigma}(\Delta_i)\frac{\tau(\Delta_i,T)}{1+\omega_\mu^2[\tau(\Delta_i,T)]^2}d\Delta_i.\end{aligned} \tag{5}$$

From equation (5), by taking $\omega_\mu = 85\times10^6$ rad/s (correspondent to $\langle B_\mu\rangle = 1000$ G), $\tau_0 = 3\times10^{-13}$ s, $\langle\Delta\rangle = 1000$ K, $\sigma = 900$ K, one can reproduce the experimental results for $Ni_{0.9}Li_{0.1}O$ (solid line in Fig. 3) with $\sqrt{\langle\left(\delta B_\mu^+(t)\right)_h^2\rangle} = 230$ G and for $Ni_{0.95}Li_{0.05}$ with $\sqrt{\langle\left(\delta B_\mu^+(t)\right)_h^2\rangle} = 200$ G. The values of τ_0 and $\langle\Delta\rangle$ are close to the ones extracted in the analysis of ^{7}Li nuclear relaxation [6] around $T^* \approx 130$ K. Thus it can be concluded that the dynamical process evidenced by NMR in the low temperature AF phase is the same originating the observed behavior of $(\lambda_\mu(T))_h$, and that it is related to the cooperative freezing of the $S=1/2$ defects introduced with doping. Moreover μ^+SR results evidenced the occurrence of a distribution of electronic spin-spin correlation times, which could not be observed by means of ^{7}Li NMR, because below T^* the measurements were prevented by the short transverse relaxation rates.

An estimate of the mean-square amplitude of the transverse components of the fluctuating field can be carried out by considering the μ^+ randomly distributed around the O^{2-} ions. Then one has

$$(\delta B_\mu^+)_h \cong \frac{1}{3}\left(\frac{p_1(x)}{r_1^3}+\frac{p_2(x)}{r_2^3}\right)\mu_B \tag{6}$$

where $p_1(x)$ and $p_2(x)$ are the probability to find a "free" $S=1/2$ (and hence a Bohr magneton μ_B) respectively on one of the six nearest neighbors Ni^{2+} (at distance r_1) and on one of the eight next nearest neighbors Ni^{2+} (at distance r_2) of a given oxygen. The probability to find more than one defect in one of these cluster is negligible for $x \leq 0.10$. By estimating $p_1(x)$ and $p_2(x)$ from the binomial distribution one finds $(\delta B_\mu^+)_h \cong 180$ G for $x=0.10$ and $(\delta B_\mu^+)_h \cong 120$ G for $x=0.05$, in satisfactory agreement with the values used to reproduce the experimental findings.

4 Conclusions

From the comparison of the longitudinal μSR depolarization rates in pure and Li doped NiO, the spin fluctuations effects induced by Li^+ for Ni^{2+} substitution on the AF background have been studied. When the extra-holes localize, they cause the formation of $S=1/2$ defects. The progressive slowing down, on cooling, of the spin dynamics of the randomly distributed impurities gives rise to maxima in λ_μ around 130 K. The temperature dependence of λ_μ and the stretched exponential behavior of $P_\mu(t)$ can be satisfactory accounted for by considering a distribution of correlation times for the spin fluctuations, as expected in disordered systems or spin-glasses. Quantitative information on this distribution have been extracted.

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