Spin dynamics in a weakly itinerant magnet from ^{29}Si NMR in MnSi

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(Received 15 December 2006; revised manuscript received 2 February 2007; published 9 March 2007)

^{29}Si NMR spectra and nuclear spin-lattice relaxation rate measurements in MnSi paramagnetic phase are presented. The experimental results are analyzed in the framework of the self-consistent renormalization theory for spin fluctuations, and detailed estimates of microscopic parameters describing the $\vec{q}$ and frequency dependence of the dynamical spin susceptibility are obtained. It is shown, in the light of a comparison with neutron scattering results, that some early determined parameters need to be revised. Accordingly, also the derivation of Curie-Weiss law within this model should be critically reconsidered.

DOI: 10.1103/PhysRevB.75.115111 PACS number(s): 76.60.Es, 71.27.+a, 75.40.Gb

I. INTRODUCTION

In the past, MnSi has been considered one of the best examples of weakly itinerant magnet and one of the demonstrations for the validity of the self-consistent renormalization (SCR) theory[1] developed by Moriya. It is characterized by a low ordering temperature $T_c=29.5$ K, a reduced low temperature (T) magnetic moment, a Curie-Weiss static uniform susceptibility, and a nuclear spin-lattice relaxation rate ($1/T_1$) which at high temperature resembles the one of a Heisenberg paramagnet.[2] More recently this compound has triggered a lot of interest owing to the possibility to drive it through a quantum critical point (QCP) under moderate pressures.[3] The vicinity to a QCP and the fact that the validity of the SCR theory has been questioned by recent μSR measurements[4] have triggered a renewed interest on MnSi.

In the past the spin dynamics in MnSi paramagnetic phase has been studied by means of ^{55}Mn NMR,[2] but just few $1/T_1$ data have been obtained and only for $T>200$ K. The reason is that one must work on powders to allow a suitable irradiation by the radio-frequency (RF) field and ^{55}Mn NMR spectra become very broad at low T due to the sizeable anisotropy in the hyperfine coupling.[2] Then the measured relaxation rates strongly depend on which part of the spectrum is irradiated, preventing reliable estimates of $1/T_1$. Eventually below 200 K the measurement of ^{55}Mn $1/T_1$ is extremely difficult. Both ^{55}Mn NMR as well as μSR $1/T_1$ data for $T\rightarrow T_c$,[5] could be suitably explained in the light of SCR theory. Nevertheless, a broad temperature range ($200\ \text{K}\geq T\geq 50$ K) was left unexplored, so that it is not clear which is the range of validity of the SCR model, also in view of recent μSR results which seriously question the validity of the SCR theory below T_c.[4]

In order to verify the validity of the SCR theory over a broad temperature range and to provide detailed estimates of the microscopic parameters describing the frequency and $\vec{q}$ dependence of the dynamical spin susceptibility, ^{29}Si NMR measurements were performed for $50\ \text{K}\leq T\leq 300$ K. In MnSi, owing to the dominant isotropic hyperfine coupling, ^{29}Si NMR powder spectra are narrow at high T and an accurate determination of $1/T_1$ is possible. Only upon decreasing T the marked increase in the spin susceptibility yields a line broadening and eventually causes the disappearance of the signal. In the following we present a study of the temperature dependence of the local static uniform spin susceptibility and of the low-energy excitations in MnSi, by means of ^{29}Si NMR spectra and nuclear spin-lattice relaxation rate measurements. These experiments allow to determine with a good accuracy some important microscopic parameters, such as ^{29}Si hyperfine coupling, the magnetic moment in the ordered phase, and the characteristic temperatures T_A and T_0 which describe the spin fluctuations in the SCR theory, also in the light of a fruitful comparison with inelastic neutron scattering (INS) results. It is pointed out that although SCR theory provides a satisfactory framework to describe the qualitative aspects of the spin fluctuations in weakly itinerant ferromagnets, some parameters and assumptions should be revised in order to achieve a quantitative description of MnSi results. The hyperfine coupling was also compared to local density approximation (LDA) calculations and some discrepancies were found, confirming the differences recently found between theoretical[6] and experimental studies[7] of the electronic band structure.

II. TECHNICAL ASPECTS AND EXPERIMENTAL RESULTS

NMR measurements were performed by using standard RF pulse sequences on the same crystals used for XAS experiments,[7] which were crushed and ground into powders in order to allow a better RF penetration. ^{29}Si NMR powder spectra were obtained from the Fourier transform of one-half of the echo signal after a $\pi/2$-τ-π pulse sequence. Only at low temperature, when the line broadening prevented the full irradiation, the spectra had to be derived by recording the echo amplitude upon sweeping the irradiation frequency. The spectra were observed to be nearly Gaussian and to sizeably shift to lower frequencies on cooling, indicating a strong and negative hyperfine coupling (Fig. 1). Also a sizeable increase in the linewidth was detected on decreasing temperature (Fig. 1), suggesting a non-negligible anisotropy in the hyperfine coupling. Eventually, below 50 K the broadening is so strong to prevent the observation of the NMR signal. As the broadening is associated with the paramagnetic shift aniso-

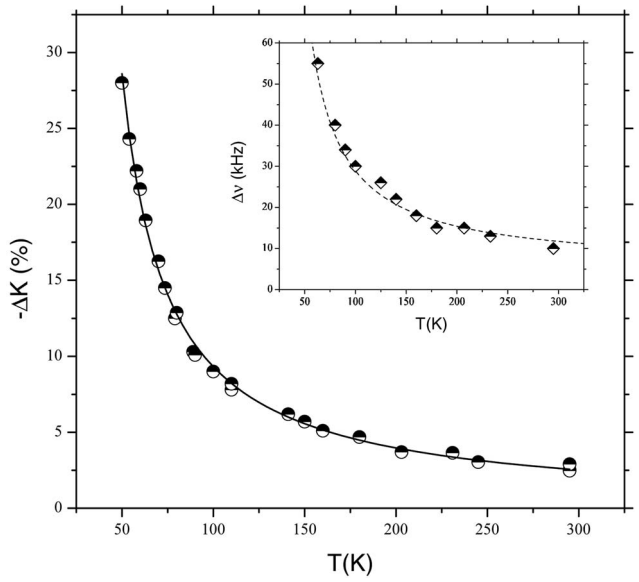

FIG. 1. Temperature dependence of ^{29}Si NMR paramagnetic shift in MnSi powders for $H=1.57$ Tesla. In the inset the temperature dependence of ^{29}Si NMR linewidth is shown.

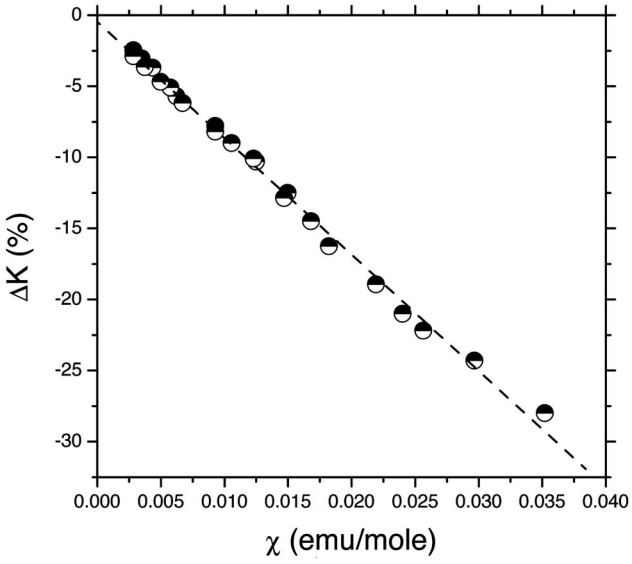

FIG. 3. ^{29}Si paramagnetic shift is plotted versus the macroscopic susceptibility, with T as an implicit parameter. The slope directly yields the hyperfine coupling.

tropy it is convenient not to work at high fields. In fact, all measurements were performed at $H=1.57$ Tesla. It is noted that both the shift and the linewidth follow the same temperature dependence of the static uniform magnetization, measured with a MPMS-XL7 SQUID (see Figs. 2 and 3). The macroscopic susceptibility $\chi_0=M/H$, with M the magnetization, was observed to follow a Curie-Weiss law above the ordering temperature, with a $T_c=29.5$ K and a Curie constant consistent with a magnetic moment of $2.46\mu_B$ per Mn atom (Fig. 2).

^{29}Si $1/T_1$ was estimated from the recovery of nuclear magnetization after a saturating RF pulse sequence. The recovery law was a single exponential (Fig. 4), as expected for an ensemble of $I=1/2$ nuclei in a homogeneous system. The corresponding T dependence of $1/T_1$ is reported in Fig. 4. One notices that $1/T_1$ progressively increases upon cooling. Also the characteristic decay rate of the echo amplitude $1/T_2$, after a $\pi/2$-τ-π pulse sequence was observed to be nearly exponential, suggesting that the relevant dephasing processes are associated with fast fluctuations, as the ones involved in nuclear spin-lattice relaxation.

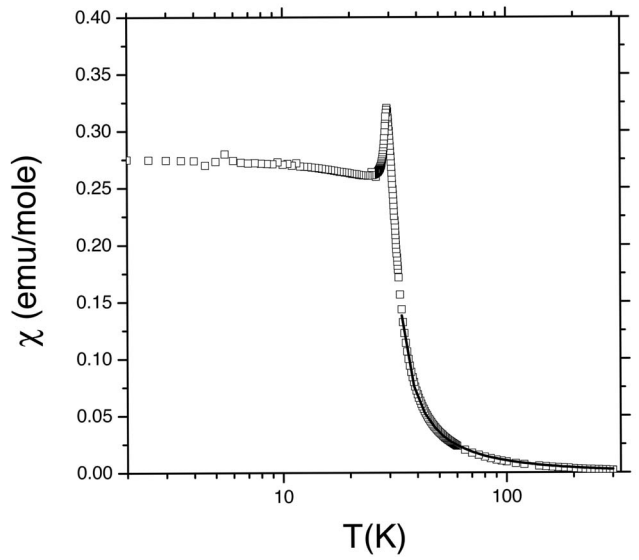

FIG. 2. The T dependence of MnSi static uniform molar susceptibility $\chi_0=M/H$, for $H=50$ Gauss, is shown.

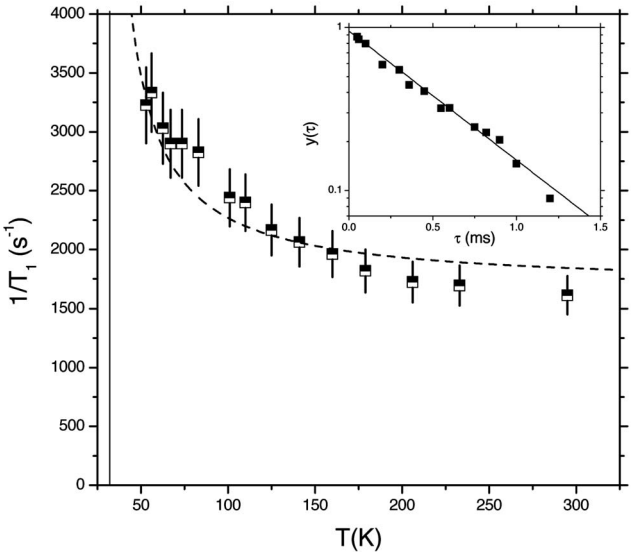

FIG. 4. T dependence of ^{29}Si $1/T_1$ in MnSi, for $H=1.57$ Tesla, is shown. The dashed line is the best fit according to Eq. (5) in the text with the susceptibility derived from magnetization data. The vertical line indicates T_c. In the inset the recovery of nuclear magnetization after a saturating pulse sequence is shown for $T=90$ K.

III. HYPERFINE COUPLING AND LOCAL DENSITY APPROXIMATION CALCULATIONS

^{29}Si Hyperfine Hamiltonian can be written in the form $\mathcal{H}=-\gamma\hbar\vec{I}A\vec{S}$, with I and S dimensionless nuclear and electron spins, respectively. Then one can write the paramagnetic shift of the NMR line $\Delta K=(\omega_R/\omega_L)-1$ (ω_R the resonance frequency and ω_L the reference resonance frequency of the nucleus) in terms of the macroscopic static uniform spin susceptibility χ_0,

$$\Delta K = \frac{A\chi_0}{g\mu_B N_A} + \delta, \tag{1}$$

where A is ^{29}Si hyperfine coupling and δ is the chemical shift, which is expected to be almost negligible. Hence, by plotting ΔK vs χ_0, leaving the temperature as an implicit parameter, it is possible to determine A and δ (see Fig. 3). It was found that, $A=-91.3\pm1.5$ kOe and $\delta=0\pm30$ ppm.[8] Such a hyperfine coupling is quite strong for ^{29}Si and indicates a sizeable hybridization of Si s, p and Mn d orbitals. In the magnetically ordered phase, for $T\to0$ ^{29}Si zero-field resonance frequency is known to reach $\nu_{\text{low}}=20$ MHz.[9,10] Thus, from the hyperfine coupling estimated above it is possible to make a precise estimate of Mn magnetic moment for $T\to0$. One finds $\langle\mu\rangle_{\text{Mn}}=0.518\pm0.009\mu_B$. This value is sizeably reduced with respect to the magnetic moment derived from the Curie constant. Although such a reduction is expected in the framework of SCR theory[1] we point out that it could reveal a relevant role played by geometric frustration of the Mn sublattice, as pointed out in Ref. 7.

The magnitude of A and its negative sign put severe constraints on MnSi electronic band structure. LDA calculations were performed for the basic B20 MnSi (Ref. 11) cell by means of the self-consistent LMTO method. All core states are relativistic and included in the self-consistent relaxation, while the valence states are semirelativistic. The LDA minimum of the total energy was found for a lattice parameter $a=4.42$ Å, which is lower than the experimental value $a=4.55$ Å (this is a typical LDA error for three-dimensional metals). The corresponding magnetic moment at the minimum was estimated to be $0.75\mu_B$ per formula unit. Almost all of the spin polarization is on the Mn ion, while on the Si ion the polarization is of opposite sign. The magnitude of the Si moment is only 2%–3% of the Mn moment. The spin polarization on Si is induced through hybridization between Mn-d states and Si s and p states. Accordingly, also the hyperfine coupling is very sensitive to the degree of hybridization. It is pointed out that a few test calculations with different relative radii of the Wigner-Seitz and smaller basis reveal no sizeable changes of the calculated value of A. The LDA calculations are able to reproduce the experimental value for ^{29}Si hyperfine coupling for a lattice parameter slightly above the experimental one ($a=4.55$ Å) (Fig. 5).

On the other hand, if the real lattice parameter is considered, LDA calculations give a local moment of about $1.2\mu_B$ per MnSi, much larger than the one experimentally determined. Often,[6,11] the lattice parameter is tuned in the calculation in order to match the experimentally determined ordered moment (which in our calculations occurs for $a=4.39$ Å). The dependence of the local moment on the lattice parameter is depicted in Fig. 5. It is evident that this approach leads to inconsistent results between $\langle\mu\rangle_{\text{Mn}}$, the lattice parameter and the hyperfine field.

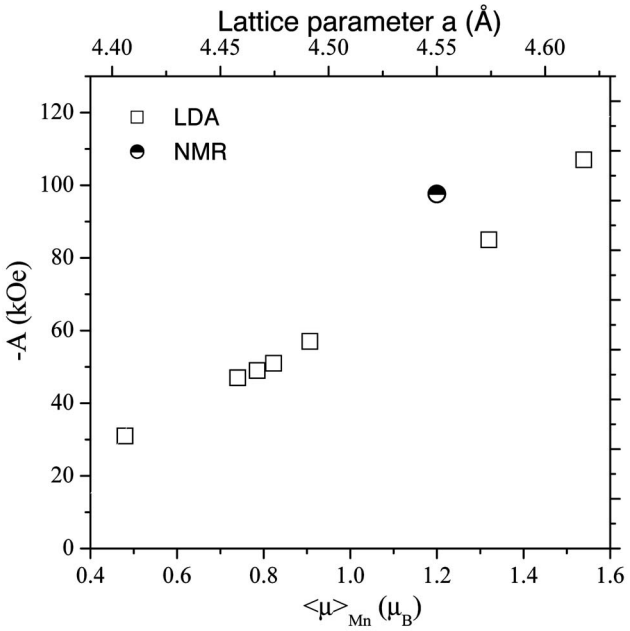

FIG. 5. LDA calculation results for the hyperfine coupling and Mn magnetic moment in MnSi, for different lattice parameters.

At this point, it is interesting to investigate the dependence of the local moment on the external magnetic field. One can do this by applying a magnetic field during the self-consistent calculations. In Fig. 6 we show the magnetic moment per unit cell (4 formula units) as a function of the lattice constant a and of the applied magnetic field H. We notice that at the LDA minimum of the total energy ($a=4.42$ Å) the local moment for increasing lattice parameter and applied field is in a plateau region, where the

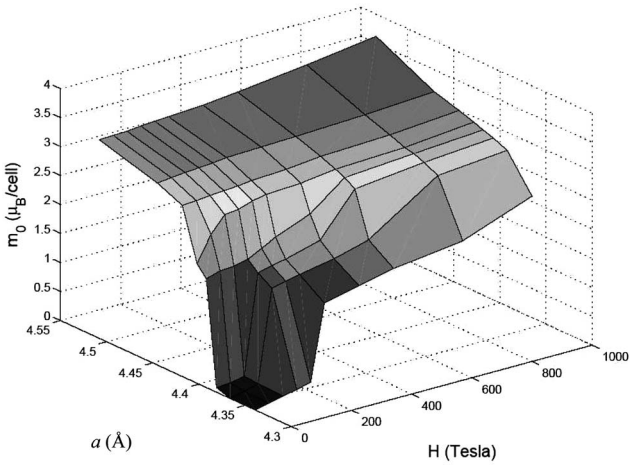

FIG. 6. Dependence of the magnetic moment per unit cell ($m_0=4\langle\mu\rangle_{\text{Mn}}$) on the external magnetic field and on the lattice parameter in MnSi, according to LDA calculations. The region of stability of LDA calculations is approached only at very high fields.

changes are small even for sizeable changes of a and H. On the contrary, when a is reduced below the LDA minimum value, the local moment decreases quite rapidly and depends more strongly on the applied field. This indicates that a state consistent with the experimental local moment (around $2\mu_B$/cell) would be found in a region where a marked dependence on the lattice volume and on the internal fields is present. This observation shows that, if not all correlations are properly considered, severe changes in the estimated values for $\langle\mu\rangle_{\mathrm{Mn}}$ are found in MnSi. Under these circumstances the derivation of the correct local moment from LDA calculations would hardly lead to the correct electronic structure. The thermal expansion yields only a modest increase of $\langle\mu\rangle_{\mathrm{Mn}}$ and of A, which cannot explain the differences between the experimental values and the calculated ones. On the other hand, it should be remarked that a reduced moment on Mn could originate either from disorder or from the geometric frustration.[7] Another possibility is that the spin density on the transition metal ion increases in the paramagnetic state.[12]

Finally we point out that a slight anisotropy in the hyperfine coupling tensor is present. In fact, the broadening of the NMR line on cooling (Fig. 1) is due to the shift anisotropy which yields a broadening proportional to χ_0. Again, by plotting the broadening of the line vs the macroscopic spin susceptibility it is possible to estimate the anisotropic terms of the hyperfine coupling. It is found that $A_{\mathrm{aniso}} \simeq 4.2$ kGauss. This anisotropy suggests an anisotropic transfer of the electron polarization to the nuclei through p electrons.

IV. SPIN DYNAMICS AND SELF-CONSISTENT RENORMALIZATION THEORY

Let us now discuss the low-energy excitations in the light of the results obtained from $1/T_1$ measurements. In the presence of a relaxation mechanism driven by spin fluctuations, taking into account the hyperfine Hamiltonian, one can write ^{29}Si $1/T_1$ in terms of the imaginary part of the spin susceptibility $\chi''(\vec{q},\omega_R)$,

$$\frac{1}{T_1} = \frac{\gamma^2 A^2}{2} k_B T \frac{1}{N} \sum_{\vec{q}} \frac{\chi''(\vec{q},\omega_R)}{\omega_R}. \tag{2}$$

Following Ishikagi and Moriya,[13] it is convenient to write the dynamical spin susceptibility in terms of two characteristic parameters T_0 and T_A which characterize the width of the spin excitations spectrum in frequency and $\vec{q}$, respectively. For nearly ferromagnetic correlations, as in MnSi, one has[13,14]

$$\chi(q,\omega) = \frac{\pi T_0}{\alpha_Q T_A} \left(\frac{x}{k_B 2\pi T_0 x(y+x^2) - i\omega\hbar} \right), \tag{3}$$

where $x = q/q_D$, with q_D a Debye-like cutoff wave vector, α_Q a dimensionless interaction constant close to unity for a strongly correlated system, and $y = 1/2\alpha_Q k_B T_A \chi(0,0)$. Here the susceptibility is per spin and in $4\mu_B^2$ units and has the dimensions of the inverse of an energy, while T_A and T_0 are in Kelvin. From the previous expression one can derive $\chi''(\vec{q},\omega_R)/\omega_R$ by taking the limit $\omega_R \to 0$, since $\hbar\omega_R \ll k_B T$.

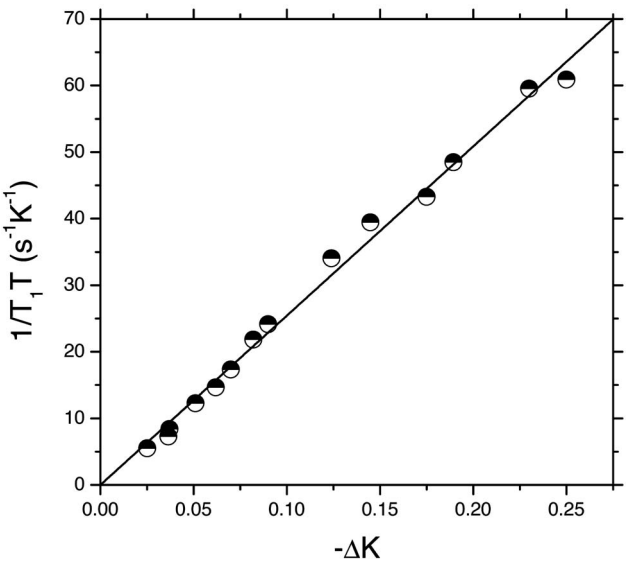

FIG. 7. ^{29}Si $1/T_1T$ is plotted against the paramagnetic shift in order to evidence the validity of Eq. (6).

Then, by integrating $\chi''(\vec{q},\omega_R)/\omega_R$ in $\vec{q}$, over a sphere of radius q_D, one derives

$$\frac{1}{T_1} = \frac{\gamma^2 A^2}{2} T \left(\frac{3\hbar}{4\pi k_B T_A T_0 \alpha_Q} \right) \left(\frac{1}{2y(1+y)} \right). \tag{4}$$

Now, since $T_A \gg T$ in the T range of interest (see T_A estimate later on) $y \ll 1$ (Refs. 13 and 14) and one can simplify the previous expression in the form

$$\frac{1}{T_1} \simeq \gamma^2 A^2 \frac{3\hbar}{8\pi} \left(\frac{T}{T_0} \right) \chi(0,0). \tag{5}$$

This expression corresponds to the one derived by Ishikagi and Moriya,[13,14] provided one takes into account that their hyperfine coupling constants are in kOe/μ_B. It should be noticed that since $\chi_0 = 4\mu_B^2 \chi(0,0) N_A$, one can write $\Delta K = 2\mu_B A \chi(0,0)$ and then

$$\frac{1}{T_1 T} \simeq \gamma^2 A \frac{3\hbar}{16\pi\mu_B} \left(\frac{1}{T_0} \right) \Delta K. \tag{6}$$

Hence by plotting $1/T_1T$ vs ΔK a linear behavior is expected and from the slope it is possible to derive directly T_0, which corresponds to an average over the Brillouin zone of the frequency for the spin fluctuations. Indeed (see Fig. 7) a linear behavior is observed and a value for $T_0 \simeq 71 \pm 3$ K is derived. This value is much smaller than the one estimated by Ishikagi and Moriya in their previous analysis.[13] One should notice that in a magnetic field a flattening and eventually a decrease of $1/T_1$ is expected for $T \ll T_0$.[1,14,15] The absence of this flattening (see Fig. 7) suggests that even at 50 K this temperature limit has not been reached in agreement with our estimate of T_0.

Now, according to SCR theory,[1]

$$T_0 = \Gamma_0 q_D^3 / 2\pi, \tag{7}$$

where Γ_0 characterizes the width in energy of the spin excitations,[12] while $q_D^3 = (6\pi^2/v_0)$ with $v_0 = 23.7$ Å^3 Mn atomic volume.[1] Γ_0 was estimated from the dispersion curve derived from INS experiments[12] $\Gamma_0 = 50$ meV Å^{-3} (recent estimates gave a value of 70 meV Å^{-3}).[16] Given these numbers, T_0 should be around 230 K, much larger than our estimate. Previous estimates of T_0 were based on Eq. (7) with Γ_0 derived from INS,[17] but no independent explicit derivation of T_0 has been carried out on the basis of NMR and μSR results.[2,5] The discrepancy between our estimate for T_0 and the previous estimates based on Eq. (7) could rely on an unappropriate value for v_0 used in the SCR theory. In fact, v_0 should be the primitive cell volume and not Mn atomic volume,[1] with q_D close to the zone boundary. Indeed, based on Eq. (7), one can find a perfect agreement between our estimate for T_0 and the value of Γ_0 estimated by neutron scattering experiments, provided that one takes $v_0 \simeq 91$ Å^3, close to primitive cell volume.[7] It is pointed out that a small value for v_0 would imply a large value for q_D and since SCR model is based on a small q and small ω/q expansion[1] one can expect discrepancies if the appropriate value of q_D is not considered. In particular, in Ref. 1, it is shown how for different choices of the q-integration range different trends of the static uniform susceptibility are derived and Curie-Weiss law is found only for particular values of q_D. It is remarked that both our and earlier results evidence a Curie-Weiss law above T_c in MnSi. However, if we take the proper q_D, departures from Curie-Weiss law must be expected on the basis of the SCR model.

From our estimate of T_0 and $\langle\mu\rangle_{\mathrm{Mn}}$ it is now possible to estimate the parameter T_A. In fact, from the SCR theory[1] one can write for the ordering temperature

$$T_c \simeq 1.419 \left(\frac{\langle\mu\rangle_{\mathrm{Mn}}}{\mu_B}\right)^{3/2} \left(\frac{T_A}{6\pi^2}\right)^{3/4} (2\pi T_0)^{1/4}. \tag{8}$$

By taking $T_c = 29.5$ K one finds $T_A \simeq 1690$ K. This value is lower than the one obtained by previous estimates[13,14] but still much larger than the temperatures of interest in our measurements, thus supporting the approximations made in the derivation of Eqs. (5) and (6).

V. CONCLUSIONS

In conclusion, ^{29}Si NMR spectra and $1/T_1$ measurements in the paramagnetic phase of MnSi were reported. We estimated several microscopic parameters, the hyperfine field, the magnetic moment, and the characteristic temperatures T_0 and T_A describing the spin fluctuations. We show that the observed hyperfine field value cannot be explained within LDA calculations. Although our results are qualitatively consistent with SCR theory, we point out that in order to get a quantitative agreement between different experiments, some of the parameters of the theory must be modified. Accordingly some of the predictions of SCR theory should be reconsidered.[18–21]

ACKNOWLEDGMENTS

The authors acknowledge useful discussions with D. van der Marel, B. Roessli, J. Mesot, and T.G. Perring. NMR measurements in Pavia were supported by PRIN2004 National Project on *Strongly correlated electron systems with competing interactions*.

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