NMR in manganese perovskites: Detection of spatially varying electron states in domain walls

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^{55}Mn and ^{139}La NMR line shape and spin-spin relaxation time T_2 measurements on polycrystalline $La_{0.67}Ca_{0.33}MnO_3$ were carried out as a function of temperature. For $T<80$ K the ^{55}Mn NMR line shapes have been attributed to spatial encoding of the NMR frequency due to variation of the charge-carrier (hole) density across domain walls. For $T>80$ K walls are effectively transparent to hole motion and by using ^{55}Mn and ^{139}La $1/T_2$ measurements hole scattering is shown to be governed solely by spin-wave excitations. [S0163-1829(98)00241-0]

INTRODUCTION

In recent years, there is a growing interest in the magnetotransport properties of the $La_{1-x}Ca_xMnO_3$ family, mainly due to the development of the magnetic read-write technology. The central role in the theory of these systems is played by the double-exchange model proposed by Zener in 1951,[1] and advanced by de Gennes in the early 1960s.[2] According to this model, mobile carriers in the e_g orbitals of the Mn ions and the Hund's coupling interaction between e_g and the localized t_{2g} spins are responsible for the transition from a high-temperature insulating paramagnetic (PM) phase to a low-temperature conducting ferromagnetic (FM) phase for dopant concentrations $0.2\leqslant x\leqslant 0.45$. The amplitude of the electron hopping integral $\tilde{t}$ between two neighboring sites, modeling a hole in a real system, has been considered to depend on the relative orientation $\Delta\theta$ of the corresponding localized t_{2g} spins, i.e., $\tilde{t}=b\cos(\Delta\theta/2)$.[2] As a consequence, deviation of the spins from a perfect parallel alignment should lead to a strong reduction of conductivity, whereas the application of an external magnetic field, which restores spin alignment, should increase conductivity considerably. However, it is unclear whether spin fluctuations or domain walls (DW's) are the main source of spin misalignment. Resistivity data in Ca- and Sr-doped $LaMnO_3$ polycrystalline samples[3–5] indicate that at high temperatures spin fluctuations dominate charge-carrier scattering, whereas at low temperatures DW scattering becomes equally important.

In this work we try to investigate the effect of DW's on the electronic properties of manganese perovskites, by using NMR techniques. For this reason an extensive series of ^{55}Mn and ^{139}La NMR line-shape and T_2^{-1} spin-spin relaxation-rate measurements have been performed on polycrystalline $La_{0.67}Ca_{0.33}MnO_3$ as a function of temperature. A model is then proposed, based on a continuous charge-density variation across DW's, which explains nicely both NMR lineshape and relaxation results.

EXPERIMENTAL RESULTS

In contrast to bulk experimental techniques that measure macroscopic properties, zero-field NMR probes the local magnetic environment of the resonating nuclei through the hyperfine field, $B_{\rm hf}=(1/\gamma\hbar)A\langle S\rangle$, A and $\langle S\rangle$ being the hyperfine coupling constant and the average electronic spin, respectively. According to this formula, ^{55}Mn NMR probes the spin state of the individual Mn^{+3}/Mn^{+4} ions, whereas the nucleus of the spinless La^{3+} ion probes the average spin state of the surrounding Mn octant spin cell.[6] Besides, under certain circumstances NMR can distinguish signals coming from domains and DW's. In FM materials strong NMR signals are produced by weak external rf fields due to the rf enhancement created by the oscillating (at the rf frequency) electron magnetic moments.[7] In single-domain materials the rf enhancement is of the order of $n\approx 10-10^2$, and it arises from the coherent precession of the electronic magnetization. On the other hand, in multidomain systems the response involves domain-wall displacements and the enhancement factor lies in the range[7] $n\approx 10^2-10^4$. Another difference between DW's and domains is that in most cases nuclei in DW's are shown to have much shorter T_1 spin-lattice and T_2 spin-spin relaxation times than domain nuclei.[7] Furthermore, NMR signals from DW's have lower Larmor frequency than the corresponding NMR signals from domains due to the stronger frequency pulling effect.[8]

Figure 1 demonstrates ^{55}Mn NMR spectra of $La_{0.67}Ca_{0.33}MnO_3$ in a zero external magnetic field at selected temperatures. Spectra were obtained by using an untuned probe head and a 2-μsec$-\tau-$2-μsec spin-echo sequence with rf field H_1 of the order of 0.1 G. At $T=9$ K a distorted doubly peaked spectrum is observed with peaks at frequencies $\nu\approx 380$ MHz (peak A) and $\nu\approx 395$ MHz (peak B). At higher temperatures, the overall signal decreases considerably, disappearing at $T\approx 160$ K. For $T>80$ K measurable spectra could be recorded only after increasing the pulse width to 6 μsec while keeping H_1 constant, which indicates that the rf enhancement factor is reduced by increasing temperature. Furthermore, it is observed that by increasing temperature, peak B decreases faster than peak A, and it shifts to lower frequencies until it merges with peak A at $T\approx 80$ K. For $T>120$ K a third sufficiently smaller signal at $\nu\approx 360$ MHz was detected, which decreases slowly by increasing temperature.

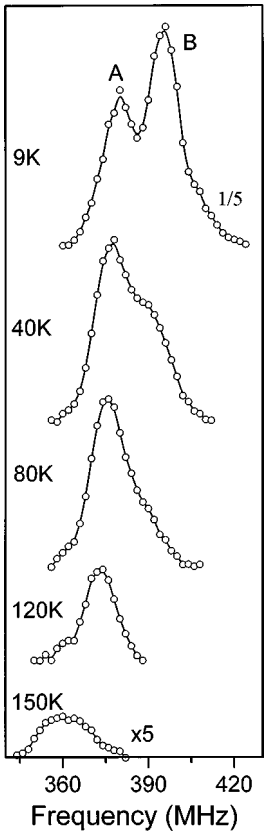

FIG. 1. ^{55}Mn zero-external-field NMR spectra at various temperatures. Spectra at 9 (150) K are reduced (increased) by a factor of 5. The Boltzmann correction factor (multiplication by T) was taken into consideration.

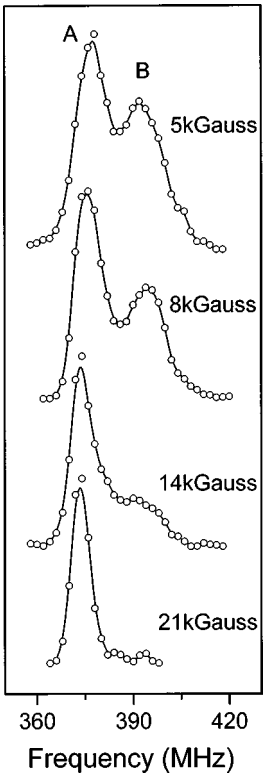

FIG. 2. ^{55}Mn spectra at 9 K and various external magnetic fields. For clarity spectra are not scaled. The spectrum at 21 kG is an order of magnitude smaller than the spectrum at 5 kG.

The influence of an external magnetic field on the line shape is shown in Fig. 2. It is observed that the application of a field $H_{\text{ext}} \approx 21$ kG is enough to remove completely peak *B*, while it reduces considerably peak *A*. From a point of view, this may be considered as a proof that peak *B* arises from wall nuclei, while peak *A* arises from domain nuclei. On the other hand, both peaks have similar rf enhancement factors and according to Fig. 3 similar T_2 values. These results imply that both peaks are coming from topologically equivalent regions. Besides, peak *B* has a higher frequency than peak *A*.

Another important observation is that at 9 K T_2^{-1} varies symmetrically across the line profile with a maximum value $T_2^{-1} \approx 67 \times 10^3$ sec^{-1} at the center of the line shape $\nu \approx 385$ MHz (Fig. 3). This indicates the presence of a continuous Larmor frequency distribution confined between the two-edge peaks. By increasing temperature, the T_2^{-1} maximum becomes broader, and for $T > 80$ K T_2^{-1} is almost frequency independent. According to Hone *et al.*[9] the frequency dependence of T_2^{-1} in FM systems originates from Suhl-Nakamura interactions in the presence of very broad inhomogeneous spectra. In such a case $1/T_2 = f(\nu)/(T_2)_{S-N}$, where $f(\nu)$ is the line-shape function. The observation of a single T_2^{-1} maximum instead of two, as implied by this relation, indicates that Suhl-Nakamura interactions are not the main spin-spin relaxation mechanism at low temperatures.

In addition to the ^{55}Mn NMR measurements, ^{139}La zero external magnetic-field NMR line-shape measurements in $La_{0.67}Ca_{0.33}MnO_3$ have been performed in the temperature range 5–250 K. For $T < 60$ K ^{139}La NMR spectra are quite asymmetric, and by increasing temperature they remain almost invariant (Fig. 4). Recently, ^{139}La NMR measurements in $La_{1-x}Ca_xMnO_3$ for $0.1 < x < 0.75$ illustrate that at low temperatures the signal frequency and line-shape asymmetry as a function of x depend strongly on the presence of local Jahn-Teller distortion σ_{JT}.[10] In addition, pulsed neutron-diffraction experiments on $La_{1-x}Sr_xMnO_3$ demonstrate marked differences in the number of short ⟨Mn-O⟩ bonds between room temperature and 10 K.[11] A question thus arises whether the temperature dependence of σ_{JT} is responsible for the observed ^{55}Mn NMR line shape versus T variation. From the ^{139}La NMR data in Fig. 4, it is concluded that σ_{JT} for $T < 60$ K does not vary considerably with temperature. This is in accordance with recent neutron-scattering results in $La_{1-x}Ca_xMnO_3$, that indicate that at low temperatures σ_{JT}, as well as the unit-cell volume V_c, remain almost invariant with temperature.[12] Most probably, Jahn-Teller distortions create a ^{55}Mn line-shape asymmetry like the one observed in the ^{139}La NMR spectra, which at low temperatures is masked by the strong doubly peaked line shape.

In Fig. 5(a) the ^{139}La NMR signal amplitude A_s (corrected by the Boltzmann factor) at the peak of the line shape, is shown as a function of the rf field H_1. It is observed that at low temperatures the maximum ^{139}La signal intensity is obtained at rf level $H_1 \approx 0.5$ G. By increasing temperature this maximum reduces rapidly, and in correspondence with the ^{55}Mn NMR signals, it disappears at $T = 160$ K. This is clearly observed in Fig. 5(b), where the ^{55}Mn signal intensity of peak *A* is compared with the ^{139}La signal intensity measured at rf level $H_1 \approx 0.5$ G. For $T > 160$ K the maximum

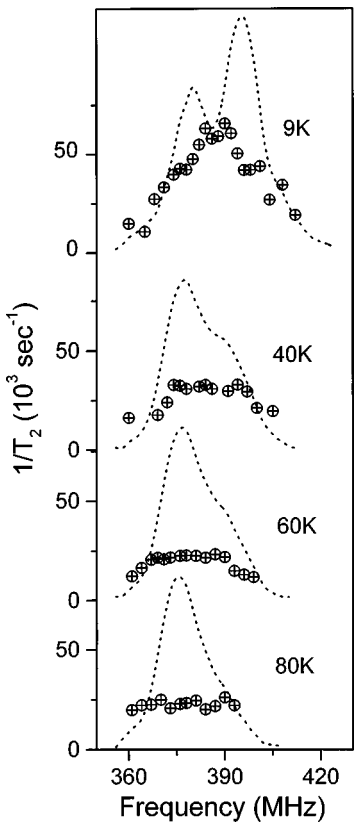

FIG. 3. ^{55}Mn spin-spin relaxation rate $1/T_2$ (⊕) in zero external magnetic field as a function of frequency, at various temperatures. Dashed lines are the corresponding ^{55}Mn NMR line shapes.

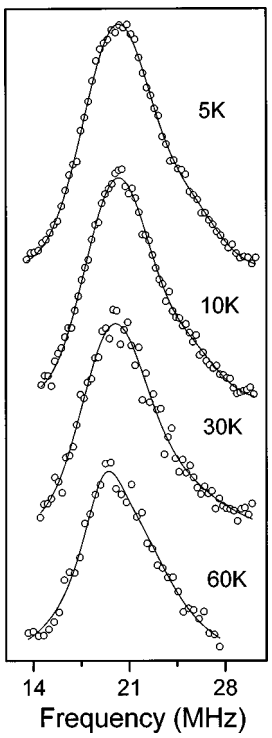

FIG. 4. ^{139}La zero-external-field NMR spectra at various temperatures. The Boltzmann correction factor (multiplication by T) was taken into consideration.

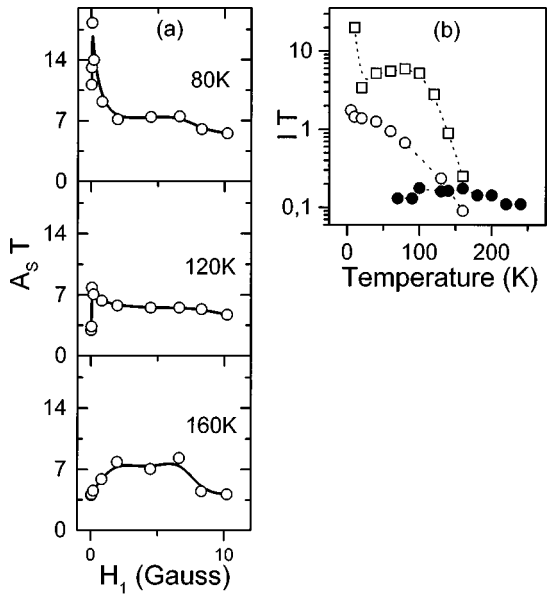

FIG. 5. (a) The ^{139}La signal amplitude A_S at the peak of the line shape vs H_1. (b) The ^{55}Mn NMR signal intensity I of peak A (spectral area) vs T at $H_1 \approx 0.1$ G (□), and the ^{139}La NMR signal intensity I vs T at $H_1 \approx 0.5$ G (○) and 3.5 G (●). In all cases the Boltzmann correction factor (multiplication by T) was taken into consideration.

^{139}La signal intensity is obtained at $H_1 \approx 3.5$ G. Furthermore, ^{139}La T_2 values measured at $H_1 \approx 0.5$ G are found to be sufficiently shorter than T_2 values measured at $H_1 \approx 3.5$ G. An analogous effect has been observed in $La_{0.5}Ca_{0.5}MnO_3$.[6] In view of these results, it is concluded that both peaks (A and B) of the ^{55}Mn NMR signals, as well as the ^{139}La NMR signals at $H_1 \approx 0.5$ G, are produced in DW's. This explains the similar rf enhancement factors and the similar T_2 values measured on peaks A and B of the ^{55}Mn NMR spectra.

THEORETICAL MODEL AND DISCUSSION

A working hypothesis, which explains the—apparently strange—^{55}Mn NMR line shape and T_2 versus frequency results, is based on the assumption that the charge-carrier (hole) density in DW's is reduced by a factor Δn in comparison to the charge-carrier density in domains. As a consequence, the effective charge state in DW's is not $Mn^{3.33+}$, as in a FM domain, but $Mn^{(3+0.33\Delta n)+}$ with $0 \leqslant \Delta n \leqslant 1$. The tendency of holes to keep apart from DW's is explainable if we consider that despite Coulomb repulsion, holes have a lower energy and larger hopping integral in FM domains than in DW's. This problem seems to be relevant with phase separation in charge-carrier-rich and charge-carrier-poor phases, occurring in degenerate antiferromagnetic semiconductors,[13] as well as in lightly hole-doped antiferromagnetic systems.[14]

The prediction of the exact spatial dependence of the hole density in DW's is not an easy task. Roughly, one may consider that at finite temperatures hole motion through DW's is thermally enhanced and the hole-density reduction in DW's varies with temperature as $\Delta n = \exp(-\Delta U/kT)$. Here, $\Delta U \propto 1-\cos\{\frac{1}{2}[d\theta(z)/dz]\}$ is the potential barrier experienced by holes crossing a DW,[15] and $\theta(z)$ the electron-spin angle de-

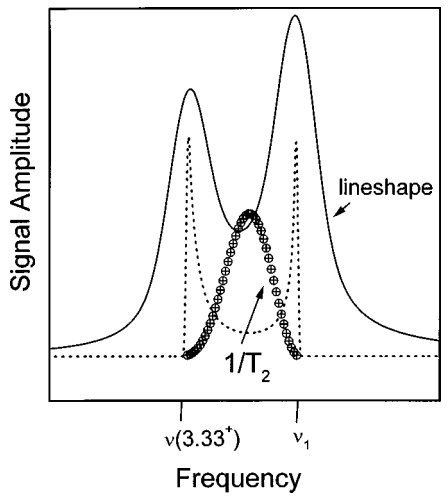

FIG. 6. Theoretical simulation of the ^{55}Mn inhomogeneous frequency distribution (dashed line) according to relation (2). The solid line is the convolution of relation (2) with a Gaussian. Theoretical simulation of the ^{55}Mn $1/T_2$ across the line shape ($\oplus$) according to relation (3b) is also presented.

viation from FM ordering in DW's. In FM domains $\Delta U = 0$ and consequently $\Delta n = 1$, while in the middle of DW's Δn becomes minimum. Besides, at high temperatures holes can move freely through DW's, and for $T \to \infty$ $\Delta n \to 1$.

In a number of papers it has been shown that localized Mn^{3+} and Mn^{4+} states produce NMR signals at frequencies $\nu^{3+} \approx 420$ MHz and $\nu^{4+} \approx 330$ MHz, while delocalized $Mn^{3.33+}$ states produce a signal at frequency $\nu^{3.33+} \approx 390$ MHz.[16–20] The dependence of the NMR frequency on the Mn charge reflects the linear relation between the average electron spin $\langle S \rangle$, and the average e_g electron-state occupancy. It is thus straightforward to show that the spatial variation of the NMR frequency in DW's is given by relation

$$\nu = \nu^{3.33+} + \frac{\alpha}{kT}\left[1 - \cos\left(\frac{1}{2}\frac{d\theta(z)}{dz}\right)\right]. \tag{1a}$$

In the simple case of uniaxial anisotropy[21]

$$\frac{d\theta(z)}{dz} = \sqrt{K/J}\,\sin\,\theta(z), \tag{1b}$$

K and J being the anisotropy and the exchange-interaction constants, respectively. Assuming a uniform Mn density ρ_0 over the sample, the inhomogeneous NMR frequency distribution $f(\nu)$ across a DW is given by

$$f(\nu) = \frac{\rho_0}{d\nu(z)/dz} \propto \left[\frac{a}{kT}\sin\left(\frac{1}{2}\frac{d\theta(z)}{dz}\right)\sin[2\theta(z)]\right]^{-1}. \tag{2}$$

This formula represents a doubly peaked line shape with peaks at frequencies $\nu^{3.33+}$ and

$$\nu^1 = \nu^{3.33+} + \frac{\alpha}{kT}\,[1 - \cos(0.5\sqrt{K/J})]$$

as shown in Fig. 6. The peak at $\nu^{3.33+}$ corresponds to the wall boundaries, while the higher frequency peak at ν^1 corresponds to the center of the walls. For $T \to \infty$ the two peaks coalesce to a single one located at $\nu^{3.33+}$ due to the enhancement of hole motion through DW's.

In the framework of this model, the faster decrease of peak B in comparison to peak A by increasing temperature indicates that DW width, and consequently the number of resonating Mn nuclei at the center of the wall, decrease rapidly on heating. A possible origin of this effect could be reduction of the FM coupling at elevated temperatures.[22] Louca *et al.* have shown that in Jahn-Teller–distorted $La_{1-x}Sr_xMnO_3$ the number of short Mn-O bonds, and thus FM coupling, decreases by increasing temperature.[11] It seems that even at low temperatures, where according to Fig. 4 σ_{JT} varies slowly, FM coupling decreases considerably by increasing temperature. Similarly, it may be argued that the application of an external magnetic field reduces DW thickness, thus explaining the faster decrease of peak B by increasing magnetic-field intensity. On the other hand, the ^{139}La line shape appears to be insensitive to the average occupancy of the e_g electron state. This is expected as the hyperfine field at the La sites arises indirectly from π-type overlapping of the Mn t_{2g} $|3d_{xy}\rangle$, $|3d_{yz}\rangle$, $|3d_{zx}\rangle$, and the ligant $|2p_\pi\rangle$ wave functions.[6]

Under the same scheme, the T_2^{-1} frequency dependence is explainable by using the ''Gaussian-phase approximation'' formalism based on the approach of Kubo and Tomita, and Anderson.[23] We postulate that thermal fluctuations of the DW's produce Larmor frequency fluctuations $\Delta\nu$, which are described statistically by the correlation function $\langle \Delta\nu(0)\Delta\nu(t)\rangle = \langle \Delta\nu^2\rangle \exp(-t/\tau_c)$. In the limit of fast fluctuations ($\gamma^2\langle\Delta\nu^2\rangle 2\tau_c^2 \ll 1$ and $\tau_c \ll T_2$), the spin-echo decay is shown to be given by the formula[24]

$$M_{\text{spin-echo}} \approx M_0 \exp[-(4\pi^2\gamma^2\langle\Delta\nu^2\rangle\tau_c 2t)], \tag{3a}$$

where

$$4\pi^2\gamma^2\langle\Delta\nu^2\rangle\tau_c = \frac{1}{T_{2,\text{eff}}} \propto \left(\frac{\alpha\,\sin\{\frac{1}{2}[d\theta(z)/dz]\}\sin[2\theta(z)]}{kT}\right)^2. \tag{3b}$$

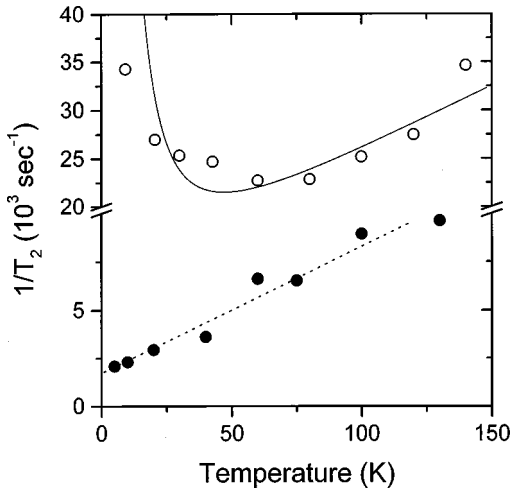

FIG. 7. ^{55}Mn $1/T_2$ (○) and ^{139}La $1/T_2$ (●) as a function of temperature. The solid line is theoretical fit of relation (4) on the experimental data.

According to formula (3b) the highest T_2^{-1} rate is obtained at the center of the line shape (Fig. 6) in agreement with the experimental results shown in Fig. 3. On the other hand, the shortest T_2^{-1} rate is obtained at the boundaries and at the center of the DW's, i.e., at positions where the amplitude of the Larmor frequency fluctuations is minimum.

The validity of the proposed model is further supported by ^{55}Mn and ^{139}La T_2^{-1} vs T measurements as shown in Fig. 7. All T_2^{-1} measurements have been performed at the center of the corresponding line shapes. Since T_2^{-1} depends strongly on the experimental settings, the pulse widths in all measurements shown in Fig. 7 were set to 6 μsec (the different parameter settings are the cause of the different ^{55}Mn T_2^{-1} values presented in Figs. 3 and 7). The dependence of T_2^{-1} on the rf level H_1 and the pulse width is common in all FM systems, and it can be explained by an appropriate model of DW motion.[25] However, it has been observed that for low H_1 and relatively short pulses the shape of the T_2^{-1} vs T curve is independent of the experimental settings. According to Fig. 7, at low temperatures ^{55}Mn T_2^{-1} decreases rapidly by increasing temperature, reaches a shallow minimum at $\approx$70 K, and subsequently increases almost linearly. This is explainable if we consider that a spin-wave relaxation mechanism is superimposed on the Larmor frequency fluctuations. In such a case,

$$\frac{1}{T_2} = \frac{1}{T_{2,SW}} + 4\pi^2\gamma^2\langle\Delta\nu^2\rangle\tau_c . \tag{4}$$

At low temperatures the Larmor frequency-fluctuation term dominates, while at higher temperatures T_2^{-1} follows the characteristic for one-magnon relaxation processes temperature dependence,[25] $1/T_{2,SW} \propto T$. A fit of formula (4) on the ^{55}Mn T_2^{-1} experimental data is shown as a solid line in Fig. 7. On the other hand, the ^{139}La T_2^{-1} rates vary linearly with temperature in the whole temperature range. This is expected as ^{139}La nuclei are insensitive to the occupancy fluctuations of the e_g states.

In summary, ^{55}Mn and ^{139}La zero-field NMR results in $La_{0.67}Ca_{0.33}MnO_3$ provide evidence about the presence of a uniformly varying hole density across DW's for $T<80$ K. Apparently, charge variation in DW's is responsible for the observed strong magnetoresistivity at low temperatures. At higher temperatures DW's are transparent to hole motion, and scattering is overruled by spin-wave excitations.

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