

Disaccommodation in $\text{LaMnO}_{3.075}$

M. Muroi and R. Street

Research Centre for Advanced Mineral and Materials Processing, Department of Physics, The University of Western Australia, Nedlands, WA 6907, Australia

J. W. Cochrane and G. J. Russell

Advanced Electronic Materials Group, School of Physics, The University of New South Wales, Sydney, NSW 2052, Australia
(Received 11 May 2000)

The time dependence of low-field ac susceptibility has been studied on the cation-deficient perovskite manganite $\text{LaMnO}_{3.075}$. It is found that the ac susceptibility $|\chi|$ decreases with time over a wide temperature range below T_c (122 K) and the decay of $|\chi|$ is roughly proportional to the logarithm of time after demagnetization. It is argued that the time dependence of $|\chi|$, or disaccommodation, arises from progressive domain-wall stabilization through induced exchange interaction, as well as induced magnetocrystalline anisotropy.

In some ferromagnetic materials the initial susceptibility decreases with time after demagnetization. It is well established that this phenomenon, commonly referred to as disaccommodation, results from progressive domain-wall stabilization through changes in local atomic arrangement or electron configuration that are coupled with the local magnetization direction within the domain wall.^{1,2} The study of disaccommodation thus provides valuable information not only on domain-wall dynamics but also on the nature of thermally activated processes occurring in the domain wall.² Disaccommodation has been observed in a range of ferromagnetic materials, including amorphous alloys,³⁻⁵ nanocrystalline alloys,^{5,6} intermetallic compounds,^{7,8} spinel ferrites,^{9,10} and garnets,¹¹ and the underlying mechanisms extensively investigated. In the present work, we have carried out ac susceptibility measurements on $\text{LaMnO}_{3.075}$, a ferromagnetic perovskite manganite, and found disaccommodation in this material.

The sample used in this study was a sintered pellet (4.5 mm in diameter and 3.0 mm in thickness) of $\text{LaMnO}_{3+\delta}$ prepared by standard ceramic processing, as described in detail in Ref. 12. The final heat treatment in air at 1000 °C, followed by quench into liquid nitrogen, resulted in a cation-deficient composition, $\text{LaMnO}_{3.075}$.¹² [$\text{La}_{1-\alpha}\text{Mn}_{1-\alpha}\text{O}_3$ with $\alpha = \delta/(3 + \delta)$] is more appropriate for describing cation-deficient composition than $\text{LaMnO}_{3+\delta}$. However, since the conversion is straightforward, we use the latter formula, which is simpler and widely used in the literature.^{13,14} The sample was about 85% dense with the grain size ranging between 2 and 4 μm . X-ray diffraction analysis indicated that the sample was single phase and had a quasicubic perovskite structure with a slight rhombohedral distortion. It had a T_c of 122 K, defined as the inflection point of the magnetization versus temperature curve [Fig. 1(a)], and a low-temperature saturation magnetization (M_s) of $3.70\mu_B/\text{Mn}$ site, a value slightly smaller than, but close to, the spin-only value expected for a mixture of 85% Mn^{3+} and 15% Mn^{4+} , $3.85\mu_B/\text{Mn}$ site.¹²

Measurements of ac susceptibility ($\chi = \chi' + i\chi''$) were carried out using a mutual inductance bridge with a lock-in amplifier for signal detection. The measurements were made at various temperatures in an ac field (H_{ac}) of 350 mOe at a

frequency of 5 kHz. After the temperature was stabilized at each set value, an additional ac field of 50 Oe (100 Hz) was applied for 3 s and then reduced to zero in 1 s. χ was recorded for 180 s after the sample was demagnetized.

Representative results are shown in Fig. 2, where χ_n , the real part of ac susceptibility normalized to the value at $t=180$ s, is plotted as a function of time after demagnetization for various temperatures. [It turned out that the variations of the real part (χ') and the imaginary part (χ'') of the ac susceptibility were always synchronized. The variation of the phase shift, $\theta = \tan^{-1}(\chi''/\chi')$, during the measurement period was less than 0.2° at any temperature. The variations of χ_n observed in Fig. 2 therefore reflect those of $|\chi|$.] It can be seen that for $T \leq 105$ K [Figs. 2(a)–2(c)] χ_n decreases with time and the decay of χ_n is reasonably well described by

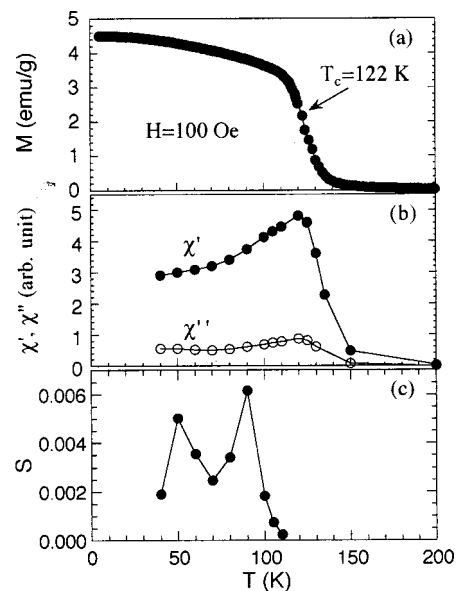


FIG. 1. (a) Temperature dependence of magnetization measured in a field of 100 Oe (field cooled). (b) Temperature dependence of the real part (χ') and the imaginary part (χ'') of ac susceptibility measured in an ac field of 350 mOe at a frequency of 5 kHz. (c) Temperature dependence of S, obtained by fitting Eq. (1) to the data points of the χ_n vs $\ln t$ plot.

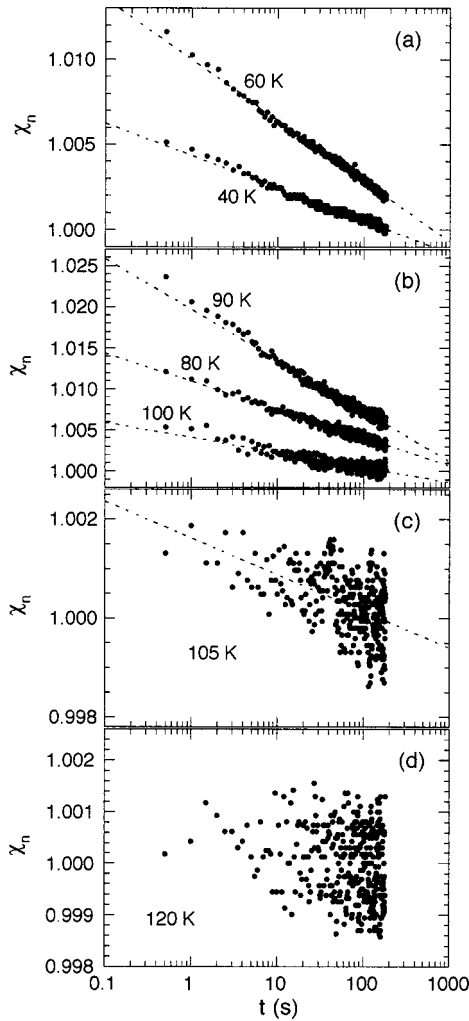


FIG. 2. Time dependence of χ' normalized to the value at $t=180$ s, measured at various temperatures. The plot for 60 K in (a) and the plots for 80 and 90 K in (b) are displaced vertically for clarity. The dashed lines are the best fits of Eq. (1) to the data points.

$$\chi_n = \chi_{n0} - S \ln t. \quad (1)$$

The logarithmic time dependence indicates that the relaxation process consists of transitions having a wide range of activation energies.² The decrease in χ_{n0} with time, or disaccommodation, becomes negligibly small near $T_c=122$ K [Fig. 2(d)], as expected.

In Fig. 1(c) the constant S , which was obtained by fitting Eq. (1) to the data points and is a measure of disaccommodation, is plotted as a function of temperature. Two peaks are observed, one at 50 K and the other at 90 K, but in the range $T \leq 100$ K the variation of S with temperature is relatively small, within a factor of 4. This again indicates that the disaccommodation involves transitions having a wide range of activation energies. Above 100 K, S decreases sharply, while $|\chi|$ continues to increase and exhibits a peak near T_c [Fig. 1(b)], a phenomenon known as the Hopkinson effect.¹⁵ This is ascribed to the increase in the contribution of incoherent rotations of magnetization to the initial magnetization process as the temperature approaches T_c .¹⁵

We discuss the relaxation process leading to domain-wall stabilization, and hence disaccommodation, in terms of in-

trinsic inhomogeneity in electronic structure, found in many mixed-valence manganites including $\text{LaMnO}_{3+\delta}$. Recent NMR studies¹⁶ have shown that in $\text{LaMnO}_{3+\delta}$ Mn ions having distinct oxidation states, namely Mn^{3+} , Mn^{4+} , and $\text{Mn}^{3+/4+}$ (Mn ions in the mixed-valence state), coexist regardless of δ ; and that the fraction of $\text{Mn}^{3+/4+}$ is increased by applying a magnetic field. Considering that our $\text{LaMnO}_{3.075}$ sample, as well as $\text{LaMnO}_{3+\delta}$ samples having similar compositions,^{13,14} are insulating, it is most likely that superexchange (SE) interactions between Mn^{3+} and Mn^{4+} ions dominate double exchange (DE) interactions between $\text{Mn}^{3+/4+}$ ions in these samples. At the same time, the fraction of Mn ions ferromagnetically coupled through either DE or positive SE interactions must be much larger than the fraction of Mn ions antiferromagnetically coupled through negative SE interactions, since the low-temperature M_s is fairly close to the value for fully aligned Mn moments.

It is expected that the fractions of Mn^{3+} and Mn^{4+} ions are greater and that of DE-coupled $\text{Mn}^{3+/4+}$ ions is smaller in a domain wall than in a domain, because the Mn moments are forced to change directions across the domain wall and the resultant larger angles between neighboring Mn moments are unfavorable for the hopping of e_g electrons. The effect of forming a domain wall is opposite to that of applying a magnetic field, which assists e_g -electron hopping by reducing the angle between neighboring Mn moments, and similar to that of reducing the size of the A-site cations,¹⁷ which hinders e_g -electron hopping by decreasing the Mn-O-Mn bond angle.

We consider transitions of the following three types: (i) e_g -electron hopping from a Mn^{3+} ion to a Mn^{4+} ion, which changes the charge distribution; (ii) e_g -electron hopping within a Mn^{3+} ion, which changes the orientation of the occupied e_g orbital; and (iii) localization or delocalization of e_g electrons, which converts $\text{Mn}^{3+/4+}$ ions into Mn^{3+} and Mn^{4+} ions, or vice versa. The interaction of the domain wall with these transitions will induce favorable exchange interactions, as well as magnetocrystalline anisotropy, thereby stabilizing the domain wall.

In perovskite manganites, the magnitude and sign of the exchange constants (J) depend on the oxidation states of neighboring Mn ions and, when Mn^{3+} ions are involved, on the orientation of the occupied e_g orbitals.¹⁸ The above transitions would then take place so as to reduce the exchange energy (E_{ex}) of the domain wall; in other words, the domain wall would stabilize itself by inducing favorable exchange interactions. Note that within a domain wall, where the spins must change directions in one way or another, a large positive J is not necessarily favorable. A smaller J or a negative J enables neighboring Mn moments to make a large angle without a substantial cost in E_{ex} , thus allowing a reduction in the domain-wall thickness, which is favorable in terms of magnetocrystalline anisotropy energy (E_K). The total energy, $E_{ex} + E_K$, could then be lower for a thin domain wall with increased fractions of Mn^{3+} and Mn^{4+} ions than for a thick domain wall with a large fraction of $\text{Mn}^{3+/4+}$ ions,¹⁹ considering that the $\text{Mn}^{3+/4+}$ state and the $\text{Mn}^{3+}/\text{Mn}^{4+}$ state have similar energies. Direct observation of the domain walls in a $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ thin film, recently achieved by transmission electron microscopy,²⁰ indeed shows that the domain-wall thickness (10–20 nm at 120 K) is much smaller than the value expected from a simple double-exchange picture,

~ 100 nm.²¹ The thinning of domain walls, accompanied by an increase in the number of localized e_g electrons, is also consistent with the fact that the domain-wall resistance in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ thin films is four orders of magnitude higher than expected from the double-exchange picture.²¹

Domain-wall stabilization can also occur through induced anisotropy. The three types of transition all result in changes in the symmetry of local atomic arrangements and hence magnetocrystalline anisotropy. The relaxation process would then proceed so as to induce magnetocrystalline anisotropy favorable for the local magnetization, thereby lowering E_K of the domain wall. This mechanism of domain-wall stabilization is the same as the ones proposed to explain disaccommodation in various ferromagnetic materials,^{1,2} except that in $\text{LaMnO}_{3.075}$ electronic transitions, and not atomic rearrangements, are responsible for the relaxation process; the temperature range considered is too low to allow ionic diffusion in $\text{LaMnO}_{3.075}$.

Each transition, involving e_g -electron hopping or localization/delocalization, invariably accompanies local structural changes. This means that the lattice must deform locally, by means of thermal activation, to suit the final electron configuration before the transition takes place. The distribution of the energies required for such deformations, or the activation energies, is expected to be wide because the local atomic arrangement is strongly coupled with the charge distribution and the spin configuration, both of which are inhomogeneous in $\text{LaMnO}_{3.075}$, particularly in the domain

walls. The $\ln t$ dependence of χ and the relatively small temperature dependence of disaccommodation are indications of a wide range of activation energies, as already mentioned.

It is possible that the transitions of the three types play major roles at different temperature ranges. (For instance, the intra-atomic e_g -electron hopping will become more difficult and contribute less to the domain-wall stabilization as the orthorhombic distortion increases with decreasing temperature.¹³) This might be a possible reason for the appearance of two peaks in the S versus T plot [Fig. 1(c)]. A more detailed analysis of disaccommodation spectra^{2,3} would be required to clarify this point.

One of the predictions of the above model is that disaccommodation will be small in metallic, ferromagnetic manganites having high T_c . In these materials most Mn ions are in the mixed-valence state and DE interactions dominate SE interactions; the relaxation process involving localized e_g electrons has therefore little relevance. We have made measurements of χ on a polycrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ sample ($T_c = 365$ K) at 290 K ($T/T_c = 0.79$) and indeed found that the disaccommodation was only about 5% of that in $\text{LaMnO}_{3.075}$ at 100 K ($T/T_c = 0.82$).

In conclusion, we have observed disaccommodation, or decrease in initial susceptibility with time after demagnetization, in the cation-deficient perovskite manganite $\text{LaMnO}_{3.075}$. We argue that the disaccommodation results from progressive domain-wall stabilization through induced exchange interactions and magnetocrystalline anisotropy.

¹D. J. Craik and R. S. Tebble, *Ferromagnetism and Ferromagnetic Domains* (North-Holland Publishing, Amsterdam, 1965), Chaps. 2 and 10.

²H. Kronmüller, *Philos. Mag.* B **48**, 127 (1983).

³H. Kronmüller, N. Moser, and F. Rettenmeier, *IEEE Trans. Magn.* **20**, 1388 (1984).

⁴T. Miyazaki, M. Takahashi, and K. Hisatake, *J. Appl. Phys.* **57**, 3575 (1985).

⁵W. Ciurzynska and J. Zbroszczyk, *J. Magn. Magn. Mater.* **140-144**, 447 (1995).

⁶W. Ciurzynska, J. Zbroazczyk, J. Olszewski, J. Frackowiak, J. Seierczek, B. Wyslocki, and S. Szymura, *J. Magn. Magn. Mater.* **140-144**, 87 (1995).

⁷L. M. García, J. Bartolomé, F. J. Lázaro, C. de Francisco, and J. M. Muñoz, *Phys. Rev. B* **54**, 15 238 (1996).

⁸C. Piquer, M. Artigas, and J. Bartolomé, *J. Magn. Magn. Mater.* **196-197**, 757 (1999).

⁹F. Walz, J. Rivas, J. Iiguez, and H. Kronmüller, *Phys. Status Solidi A* **158**, 217 (1996).

¹⁰Ó. Alejos, C. de Francisco, J. M. Muñoz, P. Hernández, C. Torres, J. I. Níguez, and L. Torres, *J. Magn. Magn. Mater.* **202**, 141 (1999).

¹¹I. Matsubara, K. Hisatake, K. Maeda, Y. Kawai, and K. Uematsu, *J. Magn. Magn. Mater.* **104-107**, 427 (1992).

¹²M. Muroi and R. Street, *Aust. J. Phys.* **52**, 205 (1999).

¹³C. Ritter, M. R. Ibarra, J. M. De Teresa, P. A. Algarabel, C. Marquina, J. Blasco, J. García, S. Oseroff, and S-W. Cheong,

Phys. Rev. B **56**, 8902 (1997).

¹⁴J. Töpfer and J. B. Goodenough, *J. Solid State Chem.* **130**, 117 (1997).

¹⁵S. Chikazumi, *Physics of Magnetism* (John Wiley & Sons, New York, 1964), Chap. 12.

¹⁶Cz. Kapusta and P. C. Riedi, *J. Magn. Magn. Mater.* **196-197**, 446 (1999).

¹⁷J. Blasco, J. García, J. M. de Teresa, M. R. Ibarra, P. A. Algarabel, and C. Marquina, *J. Phys.: Condens. Matter* **8**, 7427 (1996).

¹⁸J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience, New York, 1963), Chap. 3, Sec. B.

¹⁹This is best illustrated by the following example. Consider a case where e_g electrons accumulate in two adjacent MnO_2 layers so that all the Mn ions in these layers are Mn^{3+} . If the occupied e_g orbitals of these Mn^{3+} ions order as in LaMnO_3 , the intralayer and interlayer couplings will be ferromagnetic and antiferromagnetic, respectively. This allows a 180° rotation of ferromagnetically coupled spins across a "domain wall with zero thickness" at no cost in either E_{ex} or E_K . Such an extreme situation is certainly not realized because of the large cost in the Coulomb and elastic energies, but it does indicate that the combination of a large positive J and a thick domain wall is not necessarily favored in manganite.

²⁰S. J. Lloyd *et al.* (unpublished).

²¹N. D. Mathur, P. B. Littlewood, N. K. Todd, S. P. Isaac, B.-S. Teo, D.-J. Kang, E. J. Tarte, Z. H. Barber, J. E. Evetts, and M. G. Blamire, *J. Appl. Phys.* **86**, 6287 (1999).