

Disorder-Induced Polaron Formation in the Magnetoresistive Perovskite $\text{La}_{0.54}\text{Ba}_{0.46}\text{MnO}_3$ T. J. Sato,^{1,*} J. W. Lynn,¹ and B. Dabrowski²¹NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8562, USA²Department of Physics, Northern Illinois University, DeKalb, Illinois 60115, USA

(Received 9 January 2004; published 27 December 2004)

Neutron studies of the effect of A-site chemical disorder on the ferromagnetic transition and spin dynamics for the magnetoresistive perovskite $\text{La}_{0.54}\text{Ba}_{0.46}\text{MnO}_3$ are reported. The low temperature spin waves reveal that disorder reduces exchange interactions by only 9%. The development of a quasielastic peak in the spectrum below T_C and long-time relaxation of the order parameter indicate that the transition is discontinuous in the disordered sample, while it appears continuous for the ordered sample. These results strongly suggest that chemical disorder lowers the energy for polaron formation in manganese perovskites, and is the origin of the dramatic 50 K reduction in T_C .

DOI: 10.1103/PhysRevLett.93.267204

PACS numbers: 75.47.Lx, 75.30.Ds, 75.30.Kz, 75.47.Gk

The discovery of colossal magnetoresistance in $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A} = \text{Ca}, \text{Sr}, \text{and Ba}$) [1,2] evoked tremendous interest in the manganese oxide class of materials. By changing the doping concentration, temperature, external magnetic field, and/or A-site cation tolerance factor, these manganites exhibit a surprisingly wide variety of magnetically, structurally, and electronically ordered (or disordered) phases, such as metallic ferromagnet, charge or orbital-ordered insulating antiferromagnet, and polaronic insulating paramagnet [3]. Coexistence of these phases at phase boundaries and the appearance of spatial charge inhomogeneities in some phases make the phase diagram rather intriguing. This complex behavior is believed to be due to a delicate balance of interactions between charge, spin, and lattice degrees of freedom, and understanding their interplay is one of the fundamental issues in current condensed matter physics [4–6].

It has been realized that disorder is a key factor determining the phase stabilization in such a delicately balanced system. For instance, phase stability is strongly influenced by changing the A-site size variance $\sigma^2 = \langle r_A^2 \rangle - \langle r_A \rangle^2$ [7], or by impurity doping as seen in Cr-doped $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ [8]. However, the samples are solid solutions where intrinsic disorder exists due to random alloying. Recently, Millange *et al.* succeeded in synthesizing A-site ordered $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$, where LaO and BaO planes alternately stack along the c axis to form a tetragonal ($P_{4/mmm}$) structure [9], allowing a direct comparison of the physical properties to the more common cubic (P_{m3m}) A-site disordered sample. To date, only a few studies have been performed on A-site ordered materials [9–14]. Among the results, most notable is the enhanced stability of the ferromagnetic phase, by as much as 80 K [T_C increasing from 240 K (disordered) to 320 K (ordered)] [12]. The dramatic enhancement of T_C is of particular importance for understanding the effect of the disorder on the phase stability, but the origin of this enhancement has not yet been elucidated. In this study we have performed neutron scattering experiments using both A-site

disordered and ordered $\text{La}_{0.54}\text{Ba}_{0.46}\text{MnO}_3$ [15]. In the disordered sample we observe time relaxation effects in the ferromagnetic order parameter and a central quasielastic component in the spin excitation spectrum below T_C , indicative of polaron formation in the ferromagnetic phase [16–20], while for the A-site ordered sample the magnetic transition appears continuous. This strikingly different behavior suggests that chemical disorder enables polarons to form at lower temperatures, truncating the ferromagnetic phase.

Polycrystalline samples (~ 2 g) of A-site ordered and disordered $\text{La}_{0.54}\text{Ba}_{0.46}\text{MnO}_3$ were prepared by the solid state reaction technique. This composition was chosen to be away from the $x = 1/2$ compound where additional structural and magnetic transitions are present, but where a well-ordered structure could still be formed [12,21]. Neutron experiments were performed at the NIST Center for Neutron Research using the BT-2 and BT-9 thermal-neutron triple-axis spectrometers. Pyrolytic graphite (PG) 002 was used for the analyzer, whereas either Ge 311 or (filtered) PG 002 was employed for the monochromator. A standard closed-cycle refrigerator (CCR) was used for the disordered sample, whereas the higher T_C of the ordered sample required a high-temperature CCR, which has a longer time constant for temperature stabilization. Inelastic measurements were performed in the forward direction (000 reciprocal lattice point) with tight horizontal collimations 10° - 10° - 10° - 10° or 20° - 10° - 10° - 20° , where for isotropic ferromagnets long-wavelength spin-wave excitations can be observed using powder samples without loss of generality [22]. The lowest temperature data, typically taken around 10 K, were used as an estimate of nonmagnetic background. Elastic measurements were performed using rather coarse collimations such as 60° - 40° - 40° - 110° to improve the intensities.

Magnetization measurements reveal ferromagnetic order at $T_C = 350$ and 300 K for these ordered and disordered $\text{La}_{0.54}\text{Ba}_{0.46}\text{MnO}_3$ samples, respectively. Neutron measurements of the ferromagnetic order parameters were

taken at the 100 reflection [23]. For the disordered sample [Fig. 1(a)] the 100 intensity decreases on heating and becomes constant around 300 K. The temperature dependence can be approximated by power-law behavior [$I \propto (1 - T/T_C)^{2\beta}$] with $T_{C(\text{heat})} = 297.9(7)$ K [and $\beta = 0.37(2)$], suggesting a second order transition. However, the ferromagnetic order parameter exhibits definite thermal irreversibility, with $T_{C(\text{cool})} = 296.6(4)$, indicating the transition is inherently discontinuous. We note that x-ray diffraction measurements do not indicate any structural anomaly associated with the ferromagnetic phase transition [21]. To investigate this thermal irreversibility we measured the time relaxation of the 100 intensity. Shown in the inset is the relaxation taken at $T = 280$ K, after heating from $T = 250$ K (open circle) or cooling from $T = 310$ K (filled circle). The time origin ($t = 0$) was defined when the temperature reading became within 1° of the set point. These relaxation curves can be fit to the usual exponential form $I(t) = I_0 \exp(-t/\tau) + C$, and reveal a relaxation time of $\tau \approx 5$ min. Note, in particular, that

eventually the relaxation curves merge asymptotically, indicating the absence of significant genuine thermal hysteresis in the long-time limit. This behavior is identical to that found in optimally doped $(\text{La}-\text{Ca})\text{MnO}_3$, where irreversibilities were found initially and were interpreted as a two-phase discontinuous transition [19], but the time dependence and clear first-order nature of the transition have been identified only recently [17,24].

For the chemically ordered sample [Fig. 1(b)] we find a transition temperature of $T_C = 348.7(5)$ K (and $\beta = 0.39$, in good agreement with the bicritical value predicted recently [25]). Note that the ordering temperatures in both samples are sharp and well defined, indicating that there is no significant smearing of the ferromagnetic transitions. For the ordered sample no thermal irreversibility was observed within the experimental uncertainties of the measurements, in sharp contrast to the behavior for the chemically disordered system.

The above order parameter data strongly suggest that the phase transition is discontinuous for the chemically disordered sample, and to explore the nature of the spin dynamics in these two cases we undertook inelastic measurements. Figure 2 shows representative inelastic spectra in the disordered sample, observed at a momentum transfer of $q = 0.07 \text{ \AA}^{-1}$. Well below T_C two spin-wave peaks are observed in neutron energy gain ($E < 0$) and energy loss ($E > 0$) [Fig. 2(d)], with a negligible intensity at the quasielastic ($E = 0$) position confirming the validity of our background subtraction procedure. As temperature is increased toward T_C the spin-wave excitations renormalize, and simultaneously a quasielastic component appears. This central peak can be most prominently seen at $T = 282.5 \text{ K} \approx 0.94T_C$ [Fig. 2(b)] and dominates the spectra at higher temperatures. Energies and integrated intensities were determined by fitting the spectra to inelastic and quasielastic Lorentzians convoluted with the instrumental resolution function (solid curves), which reproduces the observed spectra very well. At low temperatures the central-peak intensity I_q [Fig. 2(e)] is negligible, whereas above 250 K the intensity develops gradually, while the spin-wave intensities begin to decrease. This is now known to be a characteristic of two-phase coexistence, one ferromagnetic (and metallic) and one paramagnetic and insulating [16–20,26].

A set of inelastic spectra is shown in Fig. 3 for the ordered sample. Two spin-wave peaks and their renormalization for $T \rightarrow T_C$ are clearly seen in the figure, as were observed in the disordered sample. However, an important difference is that the central peak is absent; even at $T = 337.5 \text{ K} \approx 0.96T_C$ the scattering intensity at the elastic position is quite small [Fig. 3(b)]. Indeed, the spectra can be well accounted for in the entire temperature region below T_C using only the spin-wave part of the cross section. At T_C , the two spin-wave peaks merge, becoming a central peak [Fig. 3(a)]. The absence of the central peak

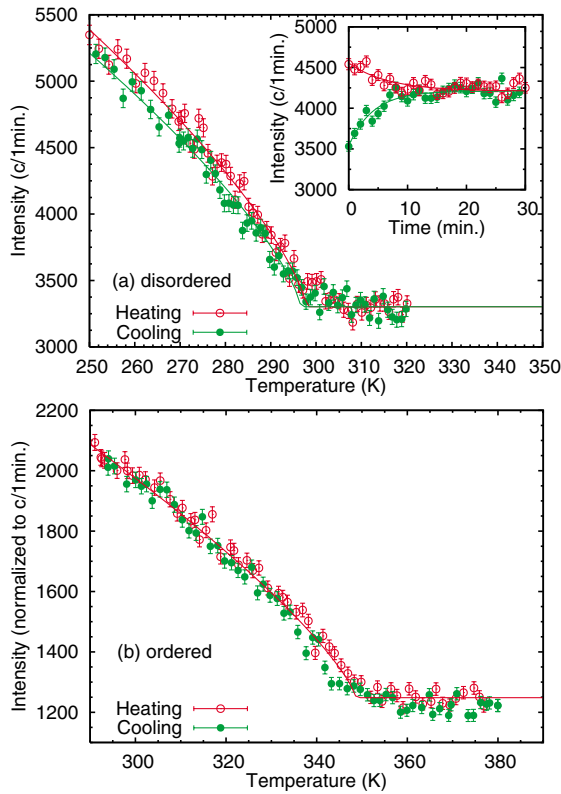


FIG. 1 (color online). (a) Temperature dependence of the 100 intensity in disordered $\text{La}_{0.54}\text{Ba}_{0.46}\text{MnO}_3$ [23]. Open and filled circles stand for heating and cooling runs, respectively. Inset: Time relaxation of the 100 intensity observed at $T = 280$ K. Open and filled circles represent relaxations after heating from 250 K, and after cooling from 310 K, respectively. Lines represent fits to $I(t) = I_0 \exp(-t/\tau) + C$, with $\tau_{\text{cool}} = 4.1 \pm 0.7$ and $\tau_{\text{heat}} = 6.7 \pm 1.3$ min. (b) Temperature dependence of the 100 intensity in the ordered $\text{La}_{0.54}\text{Ba}_{0.46}\text{MnO}_3$.

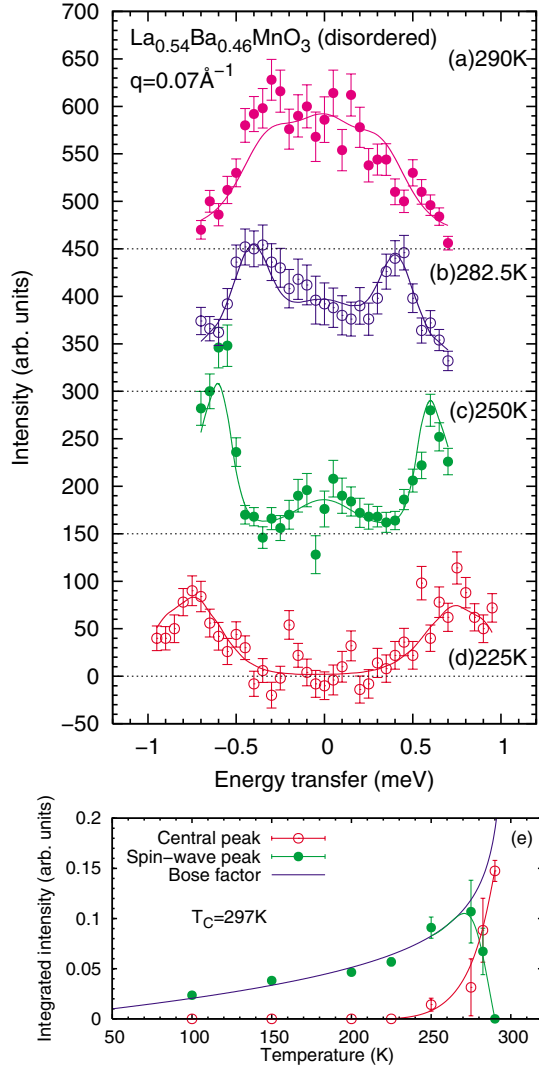


FIG. 2 (color online). (a)–(d) Inelastic spectra observed in disordered $\text{La}_{0.54}\text{Ba}_{0.46}\text{MnO}_3$ at $q = 0.07 \text{ \AA}^{-1}$, and fits to the model scattering function convoluted with the instrumental resolution (lines). (e) Temperature dependence of the spin-wave-peak and central-peak intensity, obtained from the fitting.

below T_C is also evident in Fig. 3(e), where each intensity is shown versus temperature; the central-peak intensity is always negligible below T_C .

One of the dramatic differences between these two cases is the difference of almost 50 K in T_C , and one obvious question to address is whether disorder has decreased the exchange by an amount to explain the decrease in T_C . The q dependence of the spin-wave energy E_q is shown in Figs. 4(a) and 4(b) for the disordered and the ordered samples, respectively, for several temperatures. In both the samples the spin-wave dispersions are well explained by the usual quadratic form with negligible gap, $E_q = D(T)q^2$, shown by the lines. This demonstrates that both the systems are excellent isotropic ferromagnets, as commonly seen in the metallic $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ferromagnets.

Shown in Fig. 4(c) is the temperature dependence of the stiffness $D(T/T_C)$, scaled by T_C for comparison. The stiffness parameters show almost the same temperature dependence for both samples. They are well expressed by the power law $D(T) = D_0(1 - T/T_C)^\beta$, with $D_0^{\text{do}} = 208(6) \text{ meV \AA}^2$ for the disordered sample and $D_0^{\text{o}} = 227(9) \text{ (meV \AA}^2)$ for the ordered one [and $\beta = 0.36(2)$ for both] [27]. The ratio of spin-wave stiffness parameters is $D_0^{\text{o}}/D_0^{\text{do}} \approx 1.09$, only half of that needed to explain the ratio of 1.18 for the observed Curie temperatures.

There must therefore be another origin for the large decrease in T_C . For the chemically disordered sample we found irreversibility and long relaxation times for thermal equilibration of the order parameter, together with the quasielastic component below the nominal T_C which has

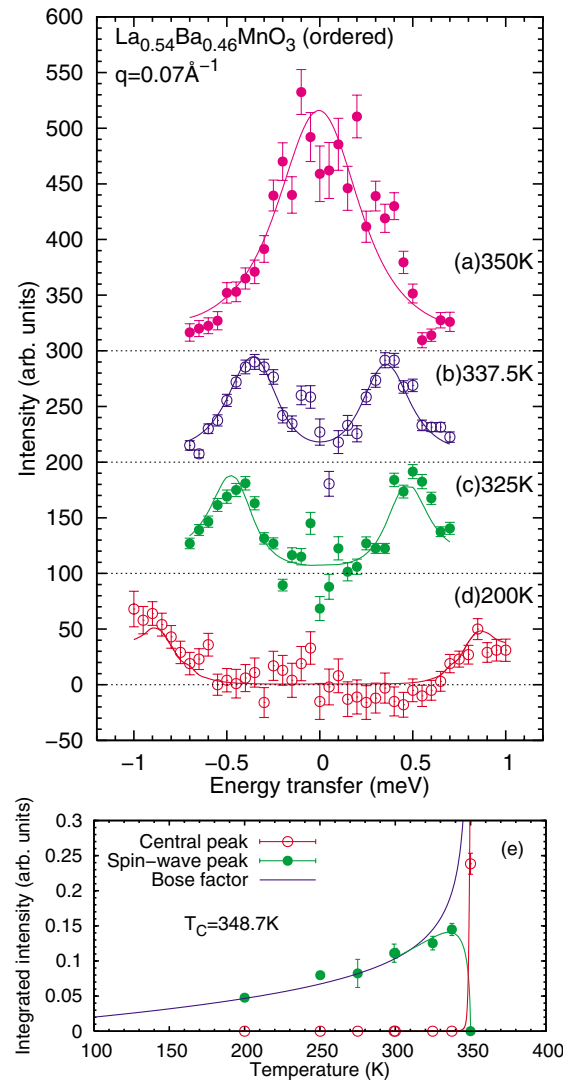


FIG. 3 (color online). (a)–(d) Inelastic spectra observed in ordered $\text{La}_{0.54}\text{Ba}_{0.46}\text{MnO}_3$ at $q = 0.07 \text{ \AA}^{-1}$, and fits to the model scattering function convoluted with the instrumental resolution (lines). (e) Temperature dependence of the spin-wave-peak and central-peak intensity, obtained from the fitting.

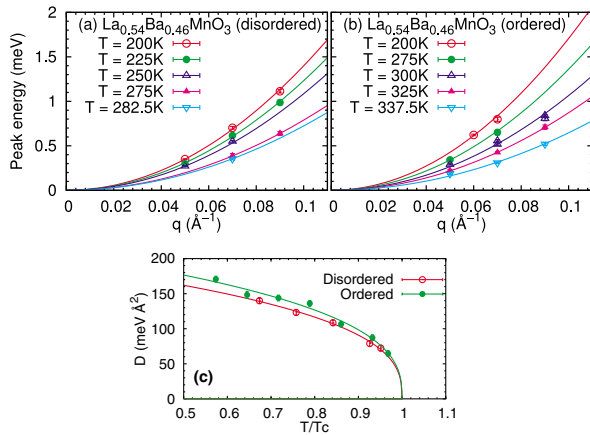


FIG. 4 (color online). (a) Spin-wave dispersions measured at several temperatures for disordered $\text{La}_{0.54}\text{Ba}_{0.46}\text{MnO}_3$. (b) Spin-wave dispersions measured at several temperatures for ordered $\text{La}_{0.54}\text{Ba}_{0.46}\text{MnO}_3$. Lines are fits to the quadratic dispersion relation $E_q = D(T)q^2$, where $D(T)$ is the spin-wave stiffness. (c) Temperature dependence of the spin-wave stiffness $D(T)$.

been directly linked to the two-phase behavior associated with the formation of polarons in perovskite manganites near optimal doping [16,17,19,26,28]. These results argue convincingly that the transition is discontinuous for the chemically disordered system. Since the samples are identical except for the A-site chemical order, we conclude that the formation energy for lattice polarons is lowered in the presence of chemical disorder, and when these polarons form in the ferromagnetic state the ferromagnetism is truncated, rendering the transition (weakly) first order. Chemical disorder then plays the dual role of disrupting the exchange interaction and aiding the formation of lattice polarons, both of which are detrimental to ferromagnetic order.

The work at NIU was supported by the NSF-DMR-0302617. T.J.S. was partly supported by the Atomic Energy Division, MEXT, Japan.

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