Effect of disorder on the thermodynamic phase transition in $La_{0.70}Ca_{0.30}MnO_3$

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Thermodynamic analysis of the ferromagnetic phase transition at T_C of Y-doped $La_{0.70}Ca_{0.30}MnO_3$ reveals that the broad anomaly in the specific heat is consistent with a large pressure effect on T_C. This is discussed in terms of random local strain fields originating from a distribution of rare-earth ionic sizes that cause competition between double-exchange and superexchange interactions.

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INTRODUCTION

The colossal magnetoresistance (CMR) effect in perovskite manganese oxides results from the strong interplay between lattice, charge, and spin degrees of freedom.[1] In the canonical compound $La_{0.70}A_{0.30}MnO_3$, smaller A ions reduce the average Mn-O-Mn bond angle, which weakens the ferromagnetic double-exchange (DE) interaction.[2] A similar effect occurs when small rare-earth ions such as Y are substituted for La.[3] $YMnO_3$ is a superexchange (SE) antiferromagnet (T_N=70 K) with hexagonal crystal structure, ferroelectric behavior (below 900 K), and frustrated magnetism.[4] Y (ionic radius[5] of 1.019 Å) substitution for La (ionic radius of 1.160 Å) in $La_{0.70}A_{0.30}MnO_3$ will lead to significant local distortions and competition between DE and SE interactions, which might also promote disorder and frustration within the magnetic lattice. In some cases a spin-glass-like state may result or the level of frustration could be high enough to prevent the establishment of long-range magnetic order.[6] Indeed, several studies indicate that the ferromagnetic (FM) transition in manganese oxides can be suppressed through doping of Y, Ga, Gd, or Dy leading to a cluster-glass state.[7–9]

Although the magnetic and transport properties of Y-substituted $La_{0.70}Ca_{0.30}MnO_3$ have been well studied, heat capacity at constant pressure C_P and thermal expansion have received less attention. Herein we show that substitution of 15% Y for La suppresses the anomaly in C_P at the ferromagnetic transition temperature T_C. In contrast with the C_P data, high-resolution thermal-expansion measurements reveal a distinct anomaly in the volume at T_C. Careful comparison of C_P of the undoped and doped samples reveals a very broad feature in $La_{0.55}Y_{0.15}Ca_{0.30}MnO_3$. Furthermore, thermodynamic analysis indicates that the peak in C_P at T_C should be small and broad; this analysis *correctly* predicts an extremely large pressure effect on T_C as well. The results are discussed in terms of local strain fields induced by the smaller Y ions, and the resulting competition between DE and SE interactions, which leads to an inhomogeneous ferromagnetic state composed of FM and canted-FM regions.

Polycrystalline samples of $La_{0.70-x}Y_xCa_{0.30}MnO_3$ (x=0.0 and 0.15) were prepared through a sol-gel method, which provides better chemical homogeneity, smaller particle size, and higher density (90% of theoretical density) than a standard solid-state reaction. The dried gel was heat treated at 1000 °C and 1100 °C in air for 30 h, subsequently pressed into pellets, and subjected to a final heat treatment at 1200 °C in air for 30 h. Rietveld refinement (space group *Pnma*) of x-ray powder-diffraction data confirmed the single-phase nature. Heat capacity was measured using a Quantum Design PPMS. A fused quartz capacitive dilatometer was used to measure the linear thermal expansion with a sensitivity in Δl of 0.1 Å. ac and dc magnetization $M(T,H,P)$ under zero-field cooling (ZFC) and field cooling (FC), was measured in a SQUID magnetometer. For hydrostatic pressure measurements, a Cu-Be clamp-type cell was placed in the magnetometer with n-pentane-isoamyl alcohol (50:50 mixture) as a pressure medium. Pressure was determined with a superconducting tin manometer placed in the cell with the sample.

The dc magnetization (ZFC and FC) versus temperature of the samples with x=0.0 and 0.15 is shown in Fig. 1. The saturated magnetic moments, determined from the curves at 5 T and 5 K, were found to be ~3.6 and 3.3μ_B for x=0 and 0.15, respectively. These are slightly smaller than expected (3.7μ_B for a 70:30 ratio of Mn^{3+}/Mn^{4+} ions) but indicate that both samples display ferromagnetic order. The sample with x=0.15 has a smaller magnetic moment, which suggests a canted FM alignment. For x=0, T_C=250 K at H=0.1 T. Yttrium doping causes a *strong* decrease of T_C to 90 K and 100 K upon cooling and warming, respectively; the hysteresis disappears at 5 T. This large thermal hysteresis was not observed for x=0. $La_{0.55}Y_{0.15}Ca_{0.30}MnO_3$ is known to exhibit

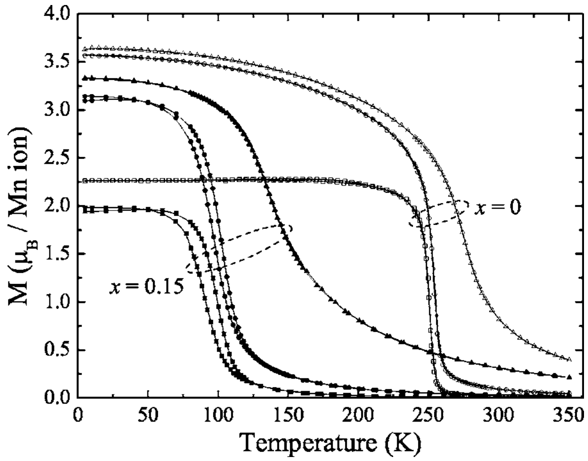

FIG. 1. Magnetization for x=0 and 0.15 upon ZFC (warming) and FC (cooling) in magnetic fields 0.1, 0.5, and 5 T.

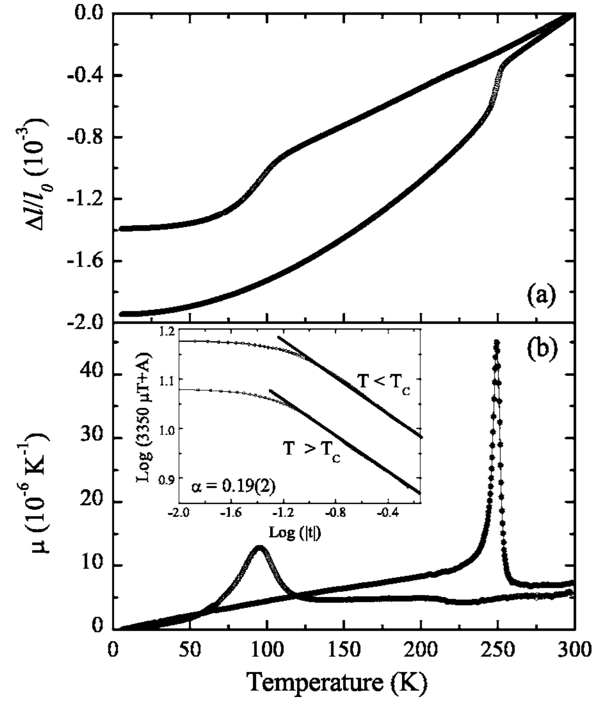

FIG. 2. (a) Linear thermal expansion $\Delta l/l_0$ and (b) linear thermal-expansion coefficient $\mu(T)$. The inset reveals the critical behavior above and below T_C for the doped sample (see the text).

cluster-glass behavior with a freezing temperature[9] close to T_f=30 K. Similar behavior occurs[10] in our sample although the magnetic transition near 100 K was frequency *independent* which suggests that it is not a glasslike transition. Simultaneously to the magnetic-phase transition, a crossover in the electrical resistivity from localized (insulating) to itinerant (metallic) behavior occurs[11] at T_{MI}=263 K, for x=0 and T_{MI}=103 and 109 K, during cooling and warming, respectively, for x=0.15. This hysteresis, in agreement with magnetic results, stems from an inhomogeneous electronic state due to the presence of both canted-FM (insulating character) and FM (itinerant character) regions.

Clearly, the smaller Y ion must lead to variations of Mn-O bond lengths and Mn-O-Mn bond angles in its vicinity, which can be thought of as the introduction of random local strain fields. The shift of T_C to lower temperatures in the Y-doped specimen clearly indicates weakening of the FM interaction. However, it is significant that this reduction in T_C is accompanied by hysteresis that vanishes at high magnetic fields. We believe this suggests the coexistence of both FM and canted-FM regions at low magnetic field, with pure FM predominant at high field. From a theoretical standpoint,[12] the introduction of a random field is *not* expected to induce first-order behavior. This supports our assertion that Y doping leads to competition between DE and SE interactions, which results in an inhomogeneous FM state in low magnetic fields.[1]

The linear thermal expansion $\Delta l/l_0$ versus T for both samples is illustrated in Fig. 2(a). Contraction of the volume sets in at T_C for both specimens, which leads to a diverging behavior in the linear thermal-expansion coefficient $\mu(T)$ near T_C [Fig. 2(b)]; $\mu(T)$ is obtained by differentiating the

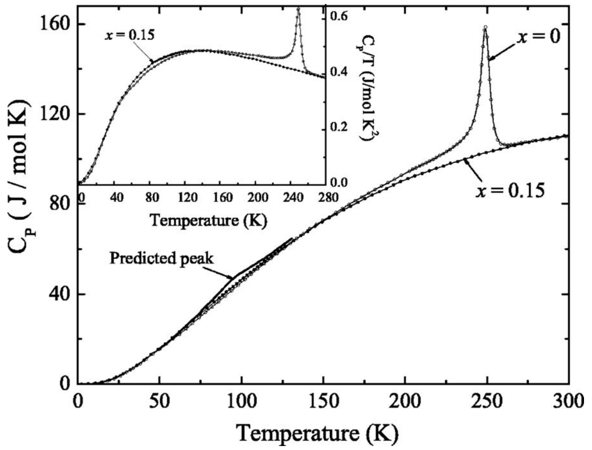

FIG. 3. Specific heat C_P for both samples. The solid line depicts the predicted peak for x=0.15. The inset displays C_P/T.

data in Fig. 2(a). The volume change near the FM transition (from 225 to 260 K) for x=0 is ΔV=0.104(6)% and 0.089(7)% (50 to 130 K) for x=0.15. The sample with x=0 shrinks about 0.58% in the whole temperature range while the doped sample shrinks by 0.42%. Furthermore, the data in Fig. 2(b) reveal that the phase transition for x=0.15 is about 3 times broader than the transition for x=0.

The molar heat capacity at constant pressure C_P versus T for $La_{0.70}Ca_{0.30}MnO_3$ is displayed in Fig. 3. A sharp peak in C_P is observed at T_C=250 K. The results for the doped sample differ significantly from those of $La_{0.70}Ca_{0.30}MnO_3$. The most prominent difference is an absence of a distinct peak at T_C in C_P. Careful inspection of the inset in Fig. 3 reveals that the C_P/T curve of the x=0.15 specimen lies slightly above the curve for x=0 in the region near T_C. Thus, a peak is evident in these data although it is significantly broadened. The data in Fig. 1 also reveal that the magnetic transition of the doped sample is broader than in the pristine compound. Note that canted-FM ordering should also remove most of the system's magnetic entropy. Theoretically, *all* Mn localized spins should be ordered at T=0 resulting in zero magnetic entropy. The entropy change resulting from total randomization of the Mn spins is $\Delta S=R[0.7\ln 5+0.3\ln 4]=12.7$ J/mol K, where R=8.318 J/mol K and ln 5 and ln 4 are due to spin S=2 and S=3/2 of Mn^{3+} and Mn^{4+} ions, respectively.[13] The magnetic contribution to the heat capacity is difficult to separate from nonmagnetic contributions[14] even for the undoped sample, which displays a pronounced peak.[15] The total entropy change for both samples in the temperature range $2<T<325$ K is obtained by integrating $S(T)=\int(C/T)dT$ (see the inset of Fig. 2). The total entropies are 127.1(7) and 125.3(7) J/mol K for x=0 and 0.15, respectively. Thus, the total entropy changes are almost identical (within our uncertainty) further indicating that the peak of the doped sample is severely smeared out by disorder. Our observations up to this point reveal that distinct features in the magnetization and thermal expansion occur in $La_{0.70}Y_{0.15}Ca_{0.30}MnO_3$, but C_P exhibits substantial broadening of the feature at T_C.

It is well known that C_P and μT for a continuous phase transition should scale such that their ratio is proportional to

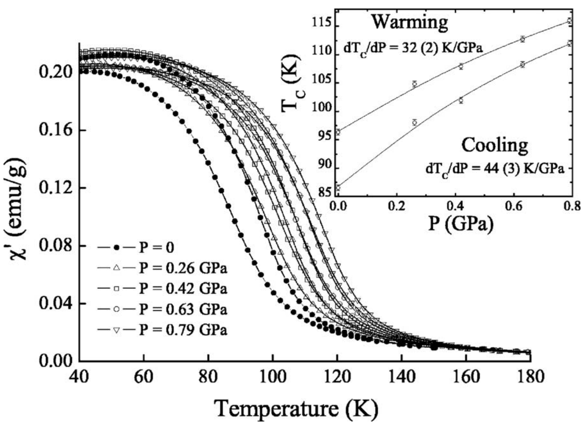

FIG. 4. Temperature dependence of the real component of the magnetic susceptibility of $x=0.15$ (upon warming and cooling) at 100 Oe for several pressures. The inset shows the pressure dependence of T_C; lines are a polynomial fit.

the pressure derivative of T_C.[17,18] This relationship is given by[18]

$$\frac{dT_C}{dP}=\frac{3v\mu T}{C_P^*}, \tag{1}$$

where $v=3.57\times10^{-5}$ m^3/mol is the molar volume and C_P^* is the specific heat after subtraction[17,18] of a term linear in T. Equation (1) is applicable to continuous transitions; the phase coexistence, suggested by the presence of hysteresis shown in Fig. 1 in the doped sample, indicates that the Clausius-Clapeyron equation should be used. However, there is neither latent heat nor discontinuities in S or $\Delta l/l_0$ as revealed in Figs. 2 and 3 for this sample. Furthermore, critical behavior has been observed through thermal-expansion data in our doped sample with $\alpha=0.19(2)$ (see the inset of Fig. 2), suggesting that the phase transition is continuous (i.e., second order); this observation agrees with other reports.[19] As a result, we believe that Eq. (1) can be applied with confidence to this phase transition.

The ratio $\mu T/C_P^*$ in Eq. (1) is determined through measurements of C_P and μ, here this ratio is referred to as λ. In previous work,[18] we found λ=7000 J/mol K for the sample with $x=0$ using the scaling behavior between μT and C_P^*, which yields $dT_C/dP=15.3(7)$ K/GPa, in agreement with the experimental value found in La$_{0.70}$Ca$_{0.30}$MnO$_3$. Since the peak in C_P of the doped sample has been completely suppressed, it is impossible[15] to subtract a polynomial to obtain C_P^*, and then to apply the scaling relationship between C_P^* and μT. On the other hand, the scaling factor can be estimated by using the experimental value of dT_C/dP. In order to perform this analysis, we measured ac magnetic susceptibility as a function of both temperature and pressure for the doped sample.

The real part of the magnetic susceptibility as a function of temperature (warming and cooling) at several pressures and under an applied magnetic field of 100 Oe is shown in Fig. 4. Increasing pressure results in an increase of T_C. A large thermal hysteresis between cooling and warming is observed. The width of the thermal hysteresis decreases as the applied pressure increases, in a similar fashion to the effect of applying magnetic fields (see Fig. 1). The pressure dependence of T_C is displayed in the inset of Fig. 4. The $dT_C/dP=44(3)$ K/GPa value obtained on cooling is higher than that obtained during warming $dT_C/dP=32(2)$ K/GPa, a consequence of the inhomogeneous magnetic state mentioned above.

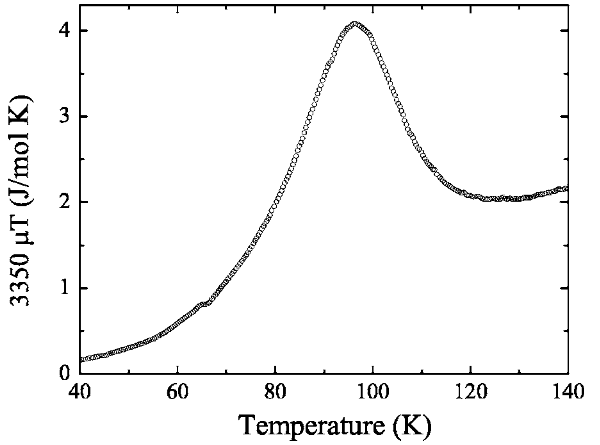

FIG. 5. μT multiplied by the scaling factor λ=3350 as a function of temperature for $x=0.15$.

Equation (1), dT_C/dP, and μT are now used to estimate the peak in C_P for La$_{0.55}$Y$_{0.15}$Ca$_{0.30}$MnO$_3$. To obtain C_P^* for the doped sample, the scaling factor is estimated by using the experimental value of $dT_C/dP=32(2)$ K/GPa through Eq. (1), yielding $C_P^*/\mu T=(3v)/(dT_C/dP)=3350\pm210$ J/mol K. This result is displayed in Fig. 5 where $3350\mu T$ is plotted against T. The estimated height of the peak is found to be ~4 J/mol K in the vicinity of the transition temperature near 100 K, which is very small when compared with ~80 J/mol K for the sample with $x=0$ (not shown). The peak predicted by our scaling argument is superimposed on the C_P data in Fig. 3. If the experimental value of dT_C/dP =44(3) K/GPa (upon cooling) were used, the predicted peak shown in Fig. 3 will reduce by 25%. Given a possible variation in the predicted peak's height due to differences in dT_C/dP (whether the warming or cooling value is used), uncertainties as to the correct background for the predicted peak, as well as differences[18] in peak height between C_P and μT that are typically observed, we feel that this agreement is very good.

Let us begin the discussion by summarizing our observations. Yttrium substitution for lanthanum in La$_{0.70}$Ca$_{0.30}$MnO$_3$ leads to a magnetic transition that reflects competition between DE and SE magnetic interactions resulting in an inhomogeneous FM state. The magnetic transition is broadened such that no distinct peak appears in the heat-capacity data. Thermodynamic scaling using the thermal-expansion coefficient μ suggests that a broadened peak in C_P is consistent with the very large *observed* pressure dependence of T_C.

We believe a qualitative understanding of the data can be developed by considering random local strain fields, which can lead to a distribution of Mn-O-Mn bond angles that, in turn, promote competition between DE and SE interactions.

These random local strain fields arise through the existence of two distinct ionic sizes for the rare-earth ions. Small ions like Y promote local canting of the FM moments with insulating character in the electrical resistivity. Large ionic sizes, like La or Ca, lead to Mn-O-Mn bond angles closer to 180° and FM/itinerant behavior.[20] The influence of pressure on T_C of the Y-doped sample is exceptionally large since it drives the average Mn-O-Mn angle closer to 180°, thereby reducing the canted FM regions, the local strain fields, and DE/SE competition. This idea also encompasses the possibility of FM and canted-FM clusters that are strongly temperature, magnetic field, and strain (or pressure) dependent leading to frustrated magnetism. Furthermore, the critical behavior of C_P in frustrated systems is known to be broadened and the entropy changes attributed to their phase transitions are much smaller than theoretically predicted.[21,22] Besides quenched disorder, dynamic fluctuations of this inhomogeneous state, which have different electronic character due to different magnetic or orbital structure (localized versus itinerant), may play a role in these systems.[23] If the explanation suggested above is correct, pressure will sharpen the peak in C_P at T_C in $\mathrm{La}_{0.55}\mathrm{Y}_{0.15}\mathrm{Ca}_{0.30}\mathrm{MnO}_3$.

To summarize, the suppression of the peak in C_P at T_C in the compound $\mathrm{La}_{0.55}\mathrm{Y}_{0.15}\mathrm{Ca}_{0.30}\mathrm{MnO}_3$ is actually a broadening resulting from local strain fields associated with a distribution of Mn-O-Mn bond angles that causes inhomogeneous ferromagnetism. The results indicate that the small peak observed in C_P in this magnetically frustrated system is thermodynamically related [through Eq. (1)] to high sensitivity of T_C to pressure.

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[1] E. Dagoto, T. Hotta, and A. Moreo, Phys. Rep. **344**, 1 (2001).

[2] H. Y. Hwang, T. T. M. Palstra, S.-W. Cheong, and B. Batlogg, Phys. Rev. B **52**, 15046 (1995).

[3] J. Fontcuberta, B. Martínez, A. Seffar, S. Piñol, J. L. García-Munõz, and X. Obradors, Phys. Rev. Lett. **76**, 1122 (1996).

[4] J. Park, J.-G. Park, G. S. Jeon, H.-Y. Choi, C. Lee, W. Jo, R. Bewley, K. A. McEwen, and T. G. Perring, Phys. Rev. B **68**, 104426 (2003).

[5] R. D. Shannon, Acta Crystallogr. 32, 751 (1976).

[6] B. D. Gaulin, in *Magnetic Systems with Competing Interactions (Frustrated Spin Systems)*, edited by H. T. Diep (World Scientific, Singapore, 1994).

[7] S. C. Bhargava, H. Kunkel, Sher Singh, S. K. Malik, D. D. Buddhikot, and A. H. Morrish, Phys. Rev. B **71**, 104419 (2005).

[8] S. M. Yusuf, M. Sahana, K. Dörr, U. K. Röbler, and K.-H. Müller, Phys. Rev. B **66**, 064414 (2002); Y. Sun, M. B. Salamon, W. Tong, and Y. Zhang, *ibid.* **66**, 094414 (2002).

[9] R. S. Freitas, L. Ghivelder, F. Damay, F. Dias, and L. F. Cohen, Phys. Rev. B **64**, 144404 (2001).

[10] We measured ZFC and FC magnetization at low field and thermoremanent magnetization relaxation. These measurements exhibit features found in systems comprised of random magnetic clusters with frustrated interactions (Ref. 9).

[11] J. A. Souza and R. F. Jardim, Phys. Rev. B **71**, 054404 (2005).

[12] D. Nicolaides and A. A. Lisyansky, Phys. Rev. B **70**, 054401 (2004).

[13] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1996), p. 431.

[14] R. M. Bozorth, *Ferromagnetism* (IEEE Press, New York, 1993), p. 735.

[15] The nonmagnetic background was subtracted using several fitting procedures. For the undoped sample, all methods gave values near 3.29 J/mol K for the magnetic entropy change. This is far smaller than expected, but in agreement with literature values (Ref. 16). For the doped sample near T_C, the difference between the background fits and the data was less than 1 J/mol K.

[16] J. Y. Gu, S. D. Bader, H. Zheng, J. F. Mitchell, and J. E. Gordon, Phys. Rev. B **70**, 054418 (2004).

[17] J. A. Souza, Yi-Kuo Yu, J. J. Neumeier, H. Terashita, and R. F. Jardim, Phys. Rev. Lett. **94**, 207209 (2005).

[18] A. B. Pippard, *The Elements of Classical Thermodynamics* (Cambridge University Press, New York, 1957).

[19] P. Mandal, P. Choudhury, S. K. Biswas, and B. Ghosh, Phys. Rev. B **70**, 104407 (2004).

[20] H. Y. Hwang, S.-W. Cheong, P. G. Radaelli, M. Marezio, and B. Batlogg, Phys. Rev. Lett. **75**, 914 (1995).

[21] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).

[22] Z. Slanic, D. P. Belanger, J. Wang, and D. R. Taylor, Phys. Rev. B **53**, 97 (1996).

[23] J. B. Goodenough, J. Phys.: Condens. Matter **15**, R257 (2003).