Charge Modulation in $La_{1.67}Sr_{0.33}NiO_4$: A Bulk Thermodynamic Study

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We present ultrasonic (ν) and specific heat (c_p) measurements performed on $La_{1.67}Sr_{0.33}NiO_4$ to confirm and characterize the nature of the thermodynamic transition observed at $T_c = 240$ K in this material. The behavior of $\nu(T \sim T_c)$ suggests that this transition is *not* due to the long-range ordering of the uncompensated nickel spins. The possibility of *independent* hole-spin behavior is consistent with the observed entropy and measured anomalies in the resistivity, susceptibility, and ultrasound. A comparison of $\nu(T)$ and $c_p(T)$ suggests that the sound couples primarily to the order parameter energy.

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Neutron studies [1] of superconducting $La_{2-x}Sr_xCuO_4$ have stimulated much interest in incommensurate spin correlations in doped Mott insulators. Several theoretical treatments [2–7] yield system energies per unit area $[E_A(x)]$ that decrease *superlinearly* with increasing hole concentration (x); there is thus an instability to phase separation into undoped spin domains separated by hole-rich walls. This scenario has not been realized in $La_{2-x}Sr_xCuO_4$ where only *dynamical* incommensurate spin structures have been observed [8]. However, there is substantial evidence for such *static* spin and charge modulations [9–11] in the related nickel system, $La_{2-x}Sr_xNiO_{4+\delta}$. It appears that holes in the doped nickelates are less destructive to the antiferromagnetic background than in the isostructural cuprates, possibly due to the higher value of S and to a larger electron-phonon coupling. Thus careful studies of the nickelates provide a useful check on our understanding of the interplay between spin and charge fluctuations in a limit where current theories should be applicable.

Stoichiometric La_2NiO_4 is an antiferromagnetic insulator [12] which, in contrast to its isostructural cuprate analog, remains insulating [13] to very high Sr dopant levels. Neutron scattering measurements have detected short-range incommensurate spin fluctuations [9] in $La_{2-x}Sr_xNiO_4$ [LSNO(x)] for $x = 0.20$. Electron diffraction studies of LSNO(x) indicate the presence of charge modulations [11,14] for $0.075 \leq x \leq 0.50$. More recent neutron scattering results have confirmed the coexistence of spin and charge modulations in the $x = 0.135$ and 0.20 systems [10]. Magnetic and transport anomalies were then observed in the $x = 0.33$ nickelate at the same temperature where the superlattice peaks became visible; these results were robust to the choice of divalent ion (Sr, Ba, Ca) substituted for lanthanum [14,15]. These measurements suggest that a continuous thermodynamic transition occurs in the $x = 0.33$ nickelate that is both electronic and structural in character; its determining parameter appears to be the hole concentration. In this paper we present ultrasonic and specific heat measurements performed on $La_{1.67}Sr_{0.33}NiO_4$ [LSNO($\frac{1}{3}$)] to confirm and characterize the structural, magnetic, and electronic nature of this phase transition, thereby providing the first bulk thermodynamic study of microscopic hole segregation in a doped Mott insulator.

The polycrystalline samples used for the experiments described here were pellets prepared by conventional solid-state reaction in air as described elsewhere [14]; no annealing was performed to ensure sharp critical behavior. $\chi(T)$ and $\rho(T)$ measurements for $T < 300$ K performed on these samples were in good agreement with previously published results [14]. For the ultrasonic studies, transducers of $LiNbO_3$ with a fundamental frequency 5 MHz were oriented for longitudinal sound and epoxied onto flat, smooth, parallel faces of each pellet. Frequency shifts in the second and third echoes were measured using a standard homodyne technique. $\Delta L(T)$, where L is the sample length, was measured independently to ensure that the observed frequency changes could be reliably converted into shifts in the sound velocity; this experiment was performed using Micro-Measurements precision strain gauges [16] with the LSNO($\frac{1}{3}$) sample referenced to copper. Finally the specific heat was measured using a standard semiadiabatic heat pulse technique with a high sensitivity ($d \ln R/dT \approx -10$) thermistor. The sintered sample was powdered and mixed with Ag powder (50:50 by weight) to ensure good internal thermal response.

The measured sound velocity data for the three samples of LSNO(x) with $x = 0.25,\ 0.33,$ and 0.40 are shown in Fig. 1. The measured length change from 100 to 300 K is 0.3% which is 10% of the frequency change over the same interval; hence, measured frequency shifts are effectively proportional to velocity shifts. We note that the data from the $x = 0.25$ and 0.40 samples increase uniformly with decreasing temperature; by contrast the

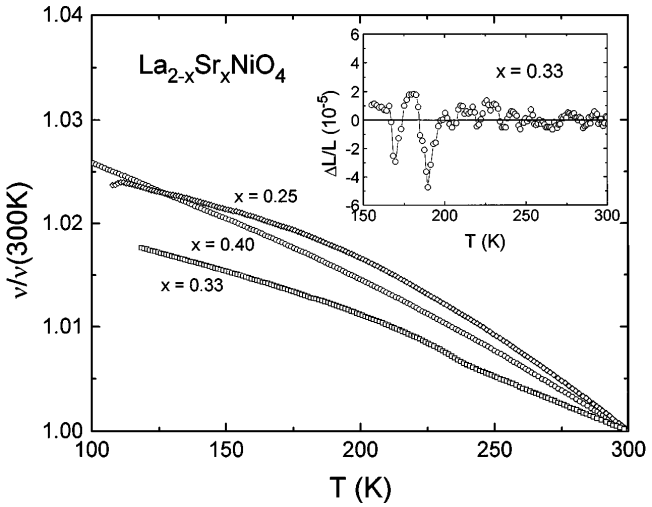

FIG. 1. Frequency shift, normalized to the value at 300 K in $La_{2-x}Sr_xNiO_4$ samples with $x = 0.25$, 0.33, and 0.40. The inset shows the temperature dependent length change for the $x = 0.33$ sample.

$x = 0.33$ case displays a distinct kink at $T_c = 240$ K, the same temperature where $\rho(T)$ and $\chi(T)$ show anomalies. It is really the deviation from linear hardening upon cooling that interests us; in order to display this behavior, we subtract a term linear in temperature from the data of Fig. 1 for the interval $260 < T < 300$ K, and the resulting plots are shown in Fig. 2. The $x = 0.33$ curve displays the most dramatic behavior in Fig. 2; we note that there is significant hardening below the transition ($\approx$0.1%) but *negligible* softening ($\approx$0.01%) above it. Furthermore, whereas in a typical antiferromagnet such as $RbMnF_3$ the hardening observed below T_N is significantly enhanced [17] by an applied magnetic field ($H \approx 1$ T), the behavior displayed in Fig. 2 is *insensitive* to fields up to 9 T. These data suggest that the transition in

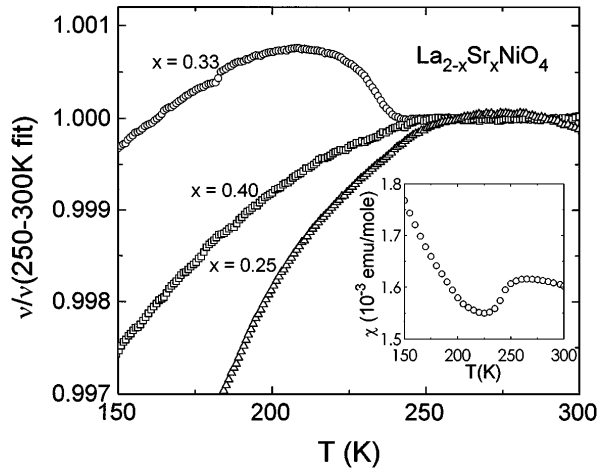

FIG. 2. The sound velocity of LSNO(x) for three different values of x. The data have been normalized with a linear temperature dependence in the temperature region $250 < T < 300$ K. Inset: the susceptibility for $x = 0.33$.

LSNO($\frac{1}{3}$) at $T_c = 240$ K does not involve the long-range ordering of the Ni spins. As an aside, we note that single-crystal samples of LSNO($\frac{1}{3}$) are not yet available; hence we must infer the magnetic structure of this material from thermodynamic measurements. The observed hardening in the sound velocity at $T = T_c$ with negligible softening bears some resemblance to that observed in spin-density wave systems like chromium [18]. This possibility is consistent with the *decrease* in the observed susceptibility (Fig. 2, inset) for LSNO($\frac{1}{3}$) at $T = T_c$ which is reminiscent of that seen at a charge-density wave transition as in, for example, blue bronze ($K_{0.3}MoO_3$) [19,20].

In order to provide further characterization of the transition in LSNO($\frac{1}{3}$), we measured its specific heat [$C(T)$] as displayed in Fig. 3; its most pronounced anomaly occurs at the same temperature as those previously observed in ν, χ, and ρ. We also note a small precursor peak in $C(T)$ at $T^* = 264$ K that suggests another transition that has not been previously discussed. We can estimate the entropy involved in both transitions by subtracting a smooth background from the specific heat data, as shown in Fig. 3. The resulting excess entropy is $\Delta\tilde{S} \sim 0.25 \ln 2 = 0.17$ where $\Delta\tilde{S} \equiv \Delta S/R$; this estimate of $\Delta\tilde{S}$ is subject to the usual concerns about homogeneity in a solid-solution compound [21]. Naturally, the interpretation of this excess entropy depends somewhat on the microscopic details of the system. Here we shall assume that the holes reside on the Ni^{2+} sites to form spin-$\frac{1}{2}$ objects, Zhang-Rice "doublets"; this conjecture is supported by neutron scattering studies

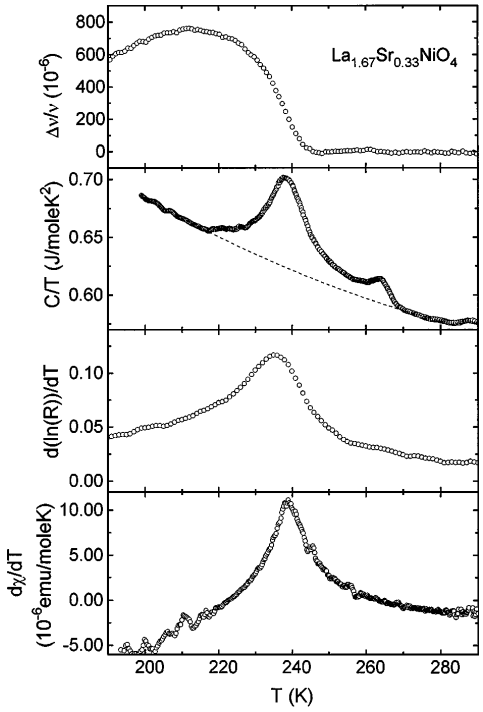

FIG. 3. The sound velocity, ν, normalized as in Fig. 2; c_p/T, $d \ln \rho/dT$, and $d\chi/dT$ for LSNO($\frac{1}{3}$).

[9–11]. We note that $\Delta\tilde{S}$ is significantly less than the configurational entropy associated with real-space hole ordering, $\Delta\tilde{S}_c \sim 0.64$. This result, $\Delta\tilde{S} \ll \Delta\tilde{S}_c$, is consistent with the fact that charged domain-wall formation has been observed for several hole concentrations in the doped nickelates; however, the anomalies [14] in the magnetic, transport, and elastic measurements are observed *only* for $x = 0.33$.

The observed excess entropy could be due to the development of magnetic structure. In LSNO(x) there exist two distinct spin species associated with the doped ($S = \frac{1}{2}$) and the "bare" ($S = 1$) nickel atoms. Both spin types order simultaneously in the domain-wall models studied [6,7], though all such calculations are performed in a low-temperature regime where the $S = 1$ spin correlation length is significantly longer than the interwall spacing so that the hole spins are coupled to their "bare" ($S = 1$) nickel counterparts. Diagonal domain walls have been observed in the doped nickelates [9–11], consistent with theoretical treatments for large on-site repulsion [4–7]. In this case, one might expect the "bare" nickel spins to order prior to the $S = \frac{1}{2}$ hole spins, simply due to the nearest and next-nearest neighbor couplings involved. The entropy associated with such $S = 1$ spin ordering, $\Delta\tilde{S}_N \sim \frac{2}{3}\ln 3 \sim 0.73$, is significantly greater than that observed ($\Delta\tilde{S} \sim 0.17$). There is, of course, the possibility that the singular component of $C(T)$ (which we estimate has $\Delta\tilde{S} \sim 0.17$) is small compared with its analytic part and that we are therefore underestimating the entropy at T_c. The size of the observed $\Delta\tilde{S}$ suggests the development of a gap in a preexisting band; we note that this possibility is consistent with χ (Fig. 2, inset) which is reminiscent of that observed in the vicinity of charge and spin density wave (CDW and SDW) formation [22]. However, the expected entropy change at a weak-coupling CDW-SDW transition, $\Delta\tilde{S}_{DW} \sim T_c/T_F \approx 10^{-2}$, is an order of magnitude *smaller* than that observed for LSNO($\frac{1}{3}$); e.g., in chromium $\Delta\tilde{S} \sim 0.034$ at the paramagnetic-antiferromagnetic transition [18]. Even at a strong-coupling CDW transition, e.g., in blue bronze, the observed entropy change is an order of magnitude less than that measured here [23].

Assuming that we have accurately estimated $\Delta\tilde{S}$ at the transition, it seems unlikely that it can be solely due to configurational hole entropy ($\Delta\tilde{S}_c \sim 0.64$); furthermore, its observed magnitude ($\Delta\tilde{S} \sim 0.17$) is significantly smaller than that expected for $S = 1$ spin ordering ($\Delta\tilde{S}_N \sim 0.73$) of the "bare" nickel atoms. *Independent* hole-spin ordering might provide an explanation for $\Delta\tilde{S}$; in this scenario the spin regions on the two sides of a domain wall would be uncorrelated so that the hole spins would be effectively decoupled from their $S = 1$ counterparts [24]. Such $S = 1$ magnetic structure has been observed in LSNO($\frac{1}{5}$) [9,10,25], and it seems reasonable to expect that the associated spin correlation length *decreases* with increasing hole concentration (x) [5]. In this picture antiferromagnetic coupling of the independent hole spins would lead to their dimerization into spin singlets [26] with $\Delta\tilde{S}_S^H \approx \frac{1}{3}\ln 2 \approx 0.23$ that is consistent with that observed ($\Delta\tilde{S} \sim 0.17$); furthermore the resulting electronic gap would account for the anomalies in $d\rho/dT$ and $d\chi/dT$ at $T_c = 240$ K displayed in Fig. 3. Alternatively the localization of the holes into domain walls could produce an increase in the short-range order of *all* the moments; the magnetic ordering might occur at a significantly lower temperature. We emphasize that only neutron scattering experiments on single crystals can unambiguously determine the magnetic structure of LSNO($\frac{1}{3}$) and thus the presence or absence of simultaneous ordering of its two spin species.

Finally, we treat the ultrasonic and the specific heat measurements of LSNO($\frac{1}{3}$) within the same framework using a simple thermodynamic analysis [27,28]. Using a phenomenological effective medium approach, we may write the free energy difference at the transition as $F = F\{T - T_c(V)\}$ where we consider the strain as an incremental volume change ($\epsilon = \Delta V/V$); the functional dependence of $T_c(V)$ results from the coupling between the hole modulation and the lattice. Since the coefficient of thermal expansion in a solid is small, we may effectively equate the measured ν_s with ν_T which is related to F above. Here we assume that the order parameter responds quickly to the local strain so that the lattice can adjust between each sound wave. Expanding T_c as a function of incremental, volume change (strain) and taking the appropriate derivatives of the free energy, we find that

$$\frac{\Delta C_p}{T_c} = \frac{\rho}{V}\left\{\mathcal{A}\left(\frac{\Delta\nu}{\nu}\right) + \mathcal{B}\,\frac{d}{dT}\left(\frac{\Delta\nu}{\nu}\right)\right\}\Bigg|_{T\sim T_c}, \quad (1)$$

where $\mathcal{A} = 1/\alpha^2$, $\mathcal{B} = \{\beta - \alpha^2/T_c\}^{-1}$, $\alpha = (\partial T_c/\partial V)_P$, and $\beta = -(\partial^2 T_c/\partial V^2)_P$. In Fig. 4 we display $C(T)/T$ and $d(\Delta\nu/\nu)/dT$ and note their striking similarity; Fig. 4 graphically indicates that $\mathcal{B} \gg \mathcal{A}$ in (1). As an aside we remark that the precursor structure observed directly in c_v/T is also present in $d(\Delta\nu/\nu)/dT$. We also comment that in a strictly isotropic material the data presented in Fig. 4 would suggest a strong coupling between the underlying order parameter and shear distortions at the transition; however, such a deduction here relies heavily on an isotropic effective medium approach to polycrystalline samples which may not be justified for such an anisotropic material with domain walls. For this same reason, we have not attempted a detailed quantitative analysis of the coefficients $\mathcal{A}$ and $\mathcal{B}$ since any such meaningful treatment would lead to results that would be strongly dependent on the underlying assumptions (e.g., constant strain or stress at the polycrystallite boundaries) of the underlying effective medium analysis. Figure 4 suggests that physically the longitudinal sound couples more effectively to the energy than to fluctuations in the energy; a more detailed analysis of this effect awaits further ultrasound measurements on single-crystal samples.

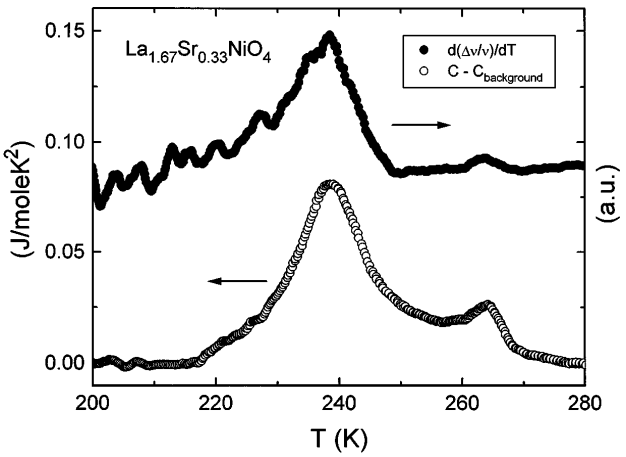

FIG. 4. The temperature derivative of the sound velocity (normalized as in Fig. 2), and the specific heat (with a smooth background removed).

In conclusion, we have performed the first bulk thermodynamic study of microscopic hole segregation in a doped Mott insulator. Our ultrasound and specific heat measurements indicate a transition in LSNO($\frac{1}{3}$) consistent with prior observation. We find an entropy change at the transition that is significantly less than that expected from either configurational or long-range $S = 1$ ordering. This entropy change is, however, close to that expected from *independent* hole-spin ordering; the associated dimerization into hole-spin singlets results in the development of an electronic gap that would also account for the anomalies observed in transport, susceptibility, and ultrasound measurements. A more detailed and unambiguous characterization of the transition in LSNO($\frac{1}{3}$) requires single-crystal samples; more generally further study of this nickelate will add to our growing understanding of the interplay between spin and charge fluctuations in a two-dimensional doped Mott insulator.

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