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Magnetism and the charge order transition in lightly doped $La_{1-x}Sr_xMnO_3$

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Measuring the magnetization and the specific heat of $La_{1-x}Sr_xMnO_3$ single crystals with $0.11 \leqslant x \leqslant 0.15$ we have investigated the charge order (CO) transition in lightly doped manganites. Though the properties of the ferromagnetic insulating state at low temperatures hardly depend on x, there is a very strong concentration dependence of the specific heat and the magnetization. While the specific-heat anomaly due to ferromagnetic order strongly increases with x, the jumps of both, entropy and magnetization at the CO transition decreases drastically. The analysis of our data shows that the entropy changes at the CO transition are mainly due to spin degrees of freedom, which strongly suggests that the melting of charge order is driven by magnetic energy.

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The tendency to charge segregation and charge order (CO) seems to be a general feature of doped transition-metal oxides whose properties are determined by electronic correlations and magnetic interactions. In particular, the real space ordering of charge carriers, which has been observed in high T_C cuprates[1] and isostructural nickelates,[2] has attracted a lot of interest. Characteristic for all these systems is a periodic superstructure of the charge density which is linked to a spatially modulated magnetic order, such as the stripe order in the cuprates.[3] While the crucial role of the CO for the magnetic order is apparent from the experimental data, it is difficult to prove that a gain of magnetic interaction energy is important in order to establish the CO. Usually, the CO temperatures are larger than the magnetic transition temperatures giving evidence that charge degrees of freedom are the driving force for both ordering processes.[4,5]

In this paper we will show an example where it is possible to prove experimentally that a CO transition is driven by magnetic degrees of freedom. The evidence is extracted from the analysis of the thermodynamic properties of lightly hole doped $La_{1-x}Sr_xMnO_3$ at $x \simeq 1/8$. We find that in these compounds the specific-heat anomalies and the entropy changes at the CO transition drastically depend on the doping. Comparing the data with model calculations shows unambiguously that the changes of the free energy at the CO transitions are predominantly due to spin degrees of freedom.

Undoped $LaMnO_3$ is an antiferromagnetic insulator with a cooperative Jahn-Teller (JT) distortion. Replacing a small amount of La^{3+} by Sr^{2+}, i.e. doping the compound with a small number of holelike charge carriers, induces drastic changes of these properties. The cooperative JT effect is suppressed, ferromagnetism develops and metallic behavior is observed.[6–10] The main features of the phase diagram agree with the bare double exchange model.[11] In addition, orbital degrees of freedom have to be taken into account in perovskite manganites.[12–15] Moreover, CO phenomena, which strongly influence magnetic and electronic properties have been detected in the vicinity of several commensurate doping concentrations (see, e.g., Ref. 16).

Here, we focus on the lightly doped regime of $La_{1-x}Sr_xMnO_3$ in the vicinity of $x = 1/8$, where a complex interplay of different ordering phenomena has been found.[18–22] Single crystalline samples for Sr contents 0.11, 0.125, 0.14, and 0.15 have been prepared by the floating zone method.[23] The magnetization and the specific heat of these crystals was studied in magnetic fields up to 14 T. For the magnetization measurements we have used a vibrating sample magnetometer. The specific heat was measured with a high-resolution calorimeter using two quasiadiabatic methods utilizing a continuous heating and heating pulses, respectively.[24] Close to the different phase transitions we have applied different constant heating powers and heat pulses, respectively, in order to obtain reliable measurements of the specific heat and entropy jumps.[25]

In order to introduce some of the basic properties of the lightly Sr doped lanthanum manganites we present the phase diagram for $0.09 \leqslant x \leqslant 0.18$ in Fig. 1. A cooperative JT effect is present below T_{JT}. For $T \leqslant T_C$ ferromagnetic order is present for compounds with a Sr content higher than $x \sim 0.1$, while for lower doping canted antiferromagnetism is

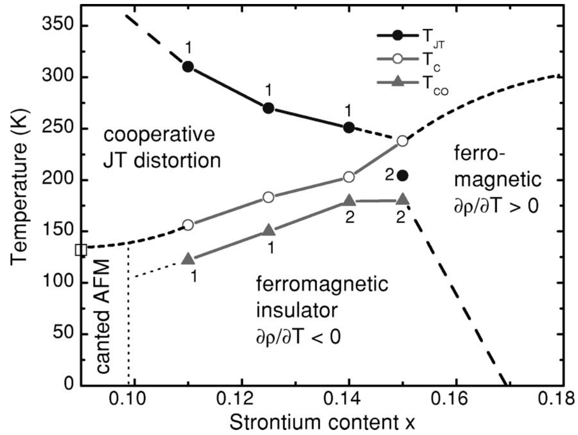

FIG. 1. Phase diagram of lightly doped $La_{1-x}Sr_xMnO_3$ with $x \simeq 1/8$ as extracted from specific-heat, magnetization, and x-ray diffraction data (Ref. 17). The open circles (square) mark the development of (anti)ferromagnetic ordering, the full circles the onset of cooperative JT distortions, the triangles the CO transition. The numbers refer to the order of the phase transitions, respectively.

observed below T_N.[26,27] At temperatures below but close to T_C there is a metallic characteristic of the resistivity, which qualitatively agrees with the double exchange model. In the same temperature range the macroscopic JT strain decreases upon cooling and at T_{CO} a further phase transition is found. The low-temperature state is ferromagnetic and insulating, which clearly contradicts any description within a bare double exchange model.[18] Moreover, this phase is characterized by a superstructure observed in neutron and x-ray diffraction.[13,17,28] For all four crystals studied in this work x-ray diffraction reveals the characteristic superstructure.[17] Usually this superstructure is interpreted in terms of a long-range charge order. However, based on resonant x-ray experiments this interpretation was questioned and it was stressed that the main characteristic of the low-temperature phase is orbital ordering.[29] Meanwhile, a variety of models for the pattern of the orbital order has been suggested based on these experiments.[30,14,13,22,10] More recent resonant x-ray studies, which have been performed on our crystals with $x=0.11$ and $x=0.125$, do not support the conclusions in Ref. 29. There are striking differences in the data for both, the low-temperature phase and the JT distorted phase.[31] Further diffraction studies are necessary to clarify the origin for the striking differences of these experimental results. These additional experiments are also necessary to determine the spatial arrangement of holes and orbitals in lightly doped manganites. Theoretical considerations yield that charge and orbital order are closely related in lightly doped manganites.[13,14] In particular, it is apparent that a static spatial order of the doped holes implies a (local) orbital order. In the context of our paper the details of the structure are not important and in the following we will name the low-temperature phase as CO phase.

As a function of the hole concentration there is an increase of T_{CO} and T_C, while T_{JT} decreases with increasing doping. The phase transition at T_{JT} is of first order for $x \leqslant 0.14$. We emphasize that the compound with $x=0.15$ differs qualitatively from the compounds with smaller doping. As displayed in Fig. 1 this sample shows an additional phase transition at T_{JT} below T_C (and above T_{CO}), indicating the development of a small JT distortion. In contrast, T_{JT} is much larger than T_C for the samples with $x=0.11$, $x=0.125$, and $x=0.14$, which are strongly JT distorted at T_C. In our analysis of the ferromagnetic phase presented below we will mainly focus on the three isostructural samples with $x<0.15$, which have only a single phase transition below T_C.

All transitions shown in the phase diagram (Fig. 1) influence the magnetic interactions and cause anomalies in the magnetization. In Fig. 2(a) we display the low-field magnetization of $La_{1-x}Sr_xMnO_3$ for $x=0.11$, $x=0.125$, and $x=0.14$. For all compounds the data indicate the onset of a spontaneous magnetization at T_C. In addition, the discontinuous CO transition causes a sharp jump of M for $x=0.11$ and $x=0.125$, which is most pronounced for $x=0.11$. At the slightly higher doping $x=0.14$ there is a continuous CO transition[17] and, therefore, T_{CO} leads only to a small kink in the $M(T)$ curve. The jump ΔM_{CO} of $x=0.11$ and $x=0.125$ is not only visible in the low-field magnetization, which is affected by magnetic anisotropy and domains. Even in large magnetic fields of several tesla there are clear jumps of M as shown in Fig. 2(b), where the magnetization in an external field of 5 T is plotted. Note that the low-field as well as the high-field magnetization in the CO phase depends only weakly on temperature and is nearly independent of doping. The latter indicates a very similar magnetic state for the three compounds. The weak temperature dependence as well as the absolute values of M suggest a nearly perfect ferromagnetic alignment of the Mn spins below T_{CO}. These conclusions are supported by measurements of the field dependent magnetization at low temperatures (see Fig. 4 of Ref. 26), which are almost identical for the three compounds. Moreover, the saturation magnetization is already obtained for small applied fields.

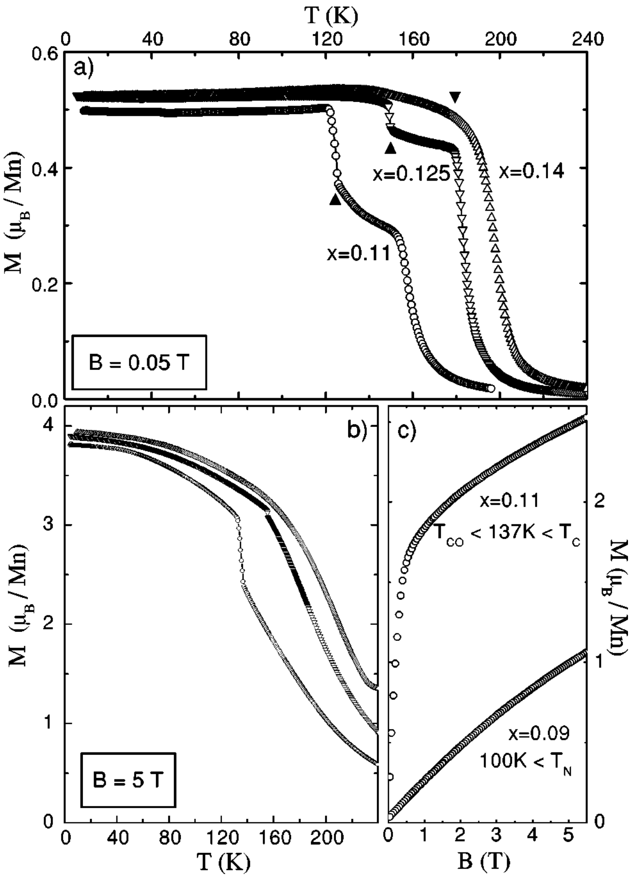

FIG. 2. Magnetization of $La_{1-x}Sr_xMnO_3$ versus temperature for $x=0.11$, $x=0.125$, and $x=0.14$ at an applied field of 0.05 T (a) and 5 T (b). In (a) the triangles mark the onset of the superstructure in zero magnetic field. (c) Magnetization versus field for $x=0.11$ at $T_{CO}<T=137\ \mathrm{K}<T_C$ and for the canted antiferromagnet $x=0.09$ at $T=100\ \mathrm{K}<T_N$ (see Ref. 26).

Thus, in the CO phase we find a nearly perfect ferromagnetic state, which hardly depends on the strontium content. In contrast, there is a strong Sr concentration dependence of the magnetization at intermediate temperatures $T_{CO} \leqslant T \leqslant T_C$. In this temperature range, M is reduced (with respect to the low-temperature value) on the one hand, and the magnetization increases with increasing Sr content on the other

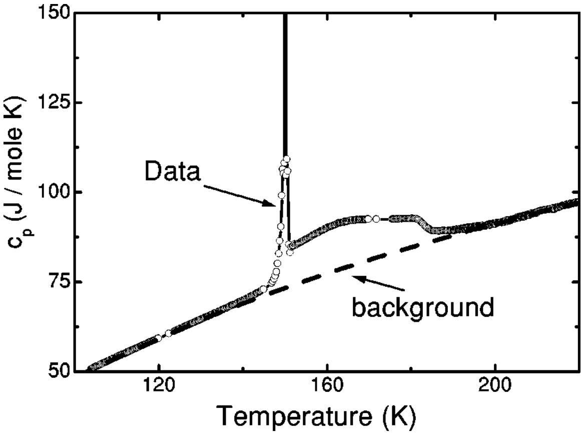

FIG. 3. Specific heat of $La_{0.875}Sr_{0.125}MnO_3$ in the regime where anomalous entropy changes are evident. In addition the estimated background is sketched (see text).

hand. Note that the ratio T_{CO}/T_C is very similar in all three samples. This implies that an increase of M with x is present not only at constant T, but also at constant reduced temperature T/T_C. This qualitative consideration reveals that at $T_{CO} \leqslant T \leqslant T_C$ the data deviate from the magnetization of an ideal ferromagnet. This deviation increases strongly with decreasing x and seems to disappear at T_{CO}. In other words, at T_{CO} the magnetization reflects a reduction of the ''disorder of the spin system,'' i.e., a decrease of the spin entropy. This enhancement of spin order due to the CO transition strongly increases with decreasing x.

We mention that there is a qualitative difference between the canted antiferromagnetism for $x<0.1$ below T_N and the reduced magnetization for $x>0.1$ in the ferromagnetic but *not* CO phase at $T_{CO} \leqslant T \leqslant T_C$ (see the vertical line in the phase diagram Fig. 1). In order to sketch this difference Fig. 2(c) displays the field dependence of the magnetization for $x=0.09$ at $T=100$ K$<T_N$ (Ref. 26) and for $x=0.11$ at $T=137$ K, i.e., for $T_{CO} \leqslant T \leqslant T_C$. The data show a spontaneous magnetization for $x=0.11$, which is clearly absent for the lower doped compound.

In order to clarify the crucial role of the spin entropy at the CO transition we consider the specific heat. As displayed in Fig. 3 for $x=0.125$ the magnetic and the CO transition both cause large anomalies of the specific heat. In order to analyze these anomalies we have subtracted a smooth background from the data. This background was determined by fitting the specific heat well below T_{CO} and well above T_C by a polynomal function as shown in Fig. 3. The background specific heat mainly reflects the phonon contribution, though an unambiguous separation of the different contributions to c_p is impossible. However, due to the enormous size of the anomalies our procedure yields a reliable estimate for the contributions due to the phase transitions. Using different temperature ranges for the determination of the background and/or choosing different fit functions does not change the results significantly.

The obtained anomalous contributions to the specific heat are shown in Fig. 4. For $x=0.11$ there is a large anomaly of c_p at $T_{CO} \simeq 123$ K due to a first-order phase transition. This anomaly is connected with an entropy jump $\Delta S_{CO} \approx 2$ J/mole K.[32] The ferromagnetic ordering causes a jump of $\Delta c_p \approx 3$ J/mole K in the specific heat at $T_C \simeq 156$ K. Additionally, at $T_{CO} \leqslant T \leqslant T_C$ we observe anomalous contributions to the specific heat. For the compound with the slightly higher doping $x=0.125$ the data show the same features: Again there is a first-order phase transition at $T_{CO} \simeq 150$ K, a jump of c_p at $T_C \simeq 183$ K, and a regime of anomalous contributions at $T_{CO} \leqslant T \leqslant T_C$. However, the magnitude of the respective anomalies changes drastically as a function of x. ΔS_{CO} is much smaller and amounts to only about 0.7 J/mole K, whereas $\Delta c_p \approx 7$ J/mole K at T_C is much larger. In addition, the amount of the anomalous contributions to the specific heat in the intermediate temperature regime is strongly enhanced.

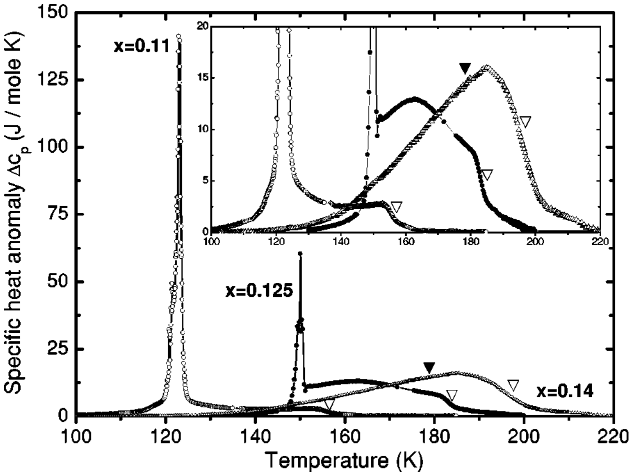

FIG. 4. Specific-heat anomalies of $La_{1-x}Sr_xMnO_3$ for $x=0.11$, $x=0.125$, and $x=0.14$. Open triangles mark T_C, the full triangle refers to T_{CO} of $x=0.14$. The inset shows an enlargement of the same temperature range.

These trends are confirmed when a further increase in the doping is taken into account. In the sample with $x=0.14$ there is no entropy jump at T_{CO}, i.e., $\Delta S_{CO}=0$. The specific heat shows only one broad anomaly without any indication of a second anomaly at the CO transition. Note that the absence of a jump of the entropy is consistent with the continuous development of the superstructure found for $x=0.14$ and $x=0.15$.[17] While the anomaly at T_{CO} is much smaller than for the compounds with smaller x, the jump $\Delta c_p \approx 16$ J/mole K at $T_C \simeq 198$ K is much larger. Moreover, there is a larger temperature range with pronounced entropy changes. We mention that the findings for $x=0.15$ are very similar to those for $x=0.14$ (except for the additional anomaly at $T_{JT} \simeq 200$ K): the specific-heat jump at T_C is of a similar size as for $x=0.14$ and there is no anomaly at $T_{CO} \simeq 180$ K (see Fig. 5).

To summarize the experimental results of our specific-heat measurements we find that the transitions from the paramagnetic phase to the ferromagnetic CO phase are connected with two anomalies of c_p. These anomalies change drastically as a function of doping: First, by increasing x both the jump Δc_p at T_C and the continuous entropy changes in the intermediate-temperature regime increase strongly. Second,

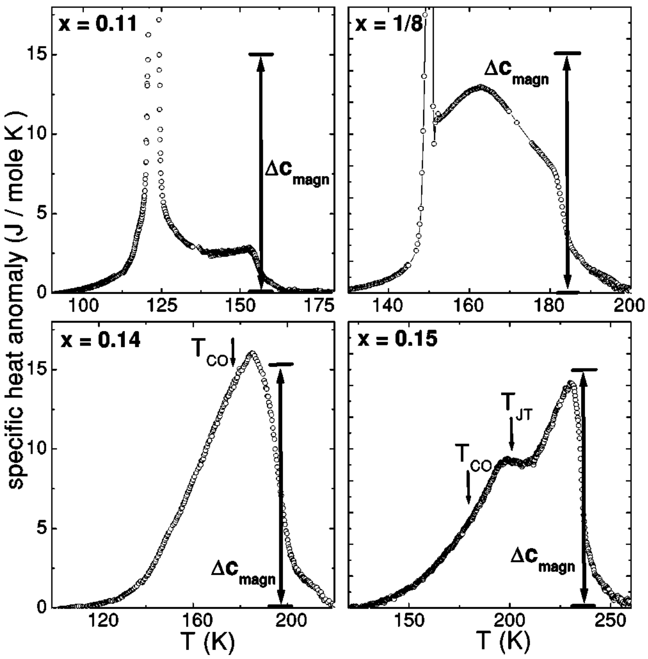

FIG. 5. Specific-heat anomalies of $La_{1-x}Sr_xMnO_3$ for $x=0.11$, $x=0.125$, $x=0.14$, and $x=0.15$ and the jumps Δc_{magn} at T_{C}, which are calculated from the magnetization data for each compound (see text).

the entropy jump at T_{CO} decreases with increasing the doping from $x=0.11$ to $x=0.125$, and vanishes completely for $x=0.14$. The data suggest that the decrease in the first-order entropy changes at T_{CO} is compensated by an increase in continuous entropy changes at $T_{\mathrm{CO}}<T\leqslant T_{\mathrm{C}}$. In fact the experiment shows that the sum of all anomalous entropy contributions in the temperature range $T_{\mathrm{CO}}\leqslant T\leqslant T_{\mathrm{C}}$, i.e., $\Delta S_{\mathrm{tot}}=\int[\Delta c_p(T)/T]dT$, hardly changes as a function of the doping. For the three compounds we find $\Delta S_{\mathrm{tot}}\approx 3$ J/mole K.

This similarity of ΔS_{tot} is not surprising if we consider the phase diagram. For both, the paramagnetic JT distorted state at $T\geqslant T_{\mathrm{C}}$ and the ferromagnetic CO state at $T\leqslant T_{\mathrm{CO}}$, the properties and thus the entropy are similar in the small range of Sr content $0.11\leqslant x\leqslant 0.14$. This implies that ΔS_{tot} hardly changes as a function of x as we observe in the experiment. The surprising result of our study is the enormous doping dependence of the entropy for $T_{\mathrm{CO}}<T<T_{\mathrm{C}}$. Consequently, but even more surprising, we observe strong differences of the specific-heat anomalies at T_{C} and T_{CO} when varying x, i.e., the same ordering phenomena cause completely different changes of the "disorder."

In order to analyze the nature of the entropy changes, we first consider the contribution due to the ferromagnetic spin ordering. It is possible to estimate this contribution by employing the theory of a spin pair in a molecular field (Oguchi method).[33] In this approximation the Hamiltonian for a pair of spins S_1 and S_2 reads

$$\mathcal{H}=-2J\vec{S}_1\cdot\vec{S}_2-g\mu_B(\vec{S}_1+\vec{S}_2)\cdot\vec{H}_{\mathrm{eff}}, \tag{1}$$

where H_{eff} denotes an effective field which we treat within the usual mean-field approach, i.e., taking $H_{\mathrm{eff}}=H_{\mathrm{ext}}+\lambda M$ with the mean-field parameter $\lambda\sim J$. We assume $S=2$ for all Mn ions. Then the inverse of the susceptibility at $T>T_{\mathrm{C}}$ gives the exchange constant J that has been extracted separately for all compounds. The results of this procedure read

J(meV)	x
1.250	0.11
1.399	0.125
1.469	0.14
1.747	0.15

Moreover, from the magnetization data the effective field can be extracted. Determining these two parameters from the measured magnetization it is possible to calculate the total energy of the spin system, which is written in a flame of the Oguchi approximation as

$$U=-0.25NzJ\tau \tag{2}$$

with the total number of spins N, the number of next neighbors z, and a correlation parameter τ, which reads

$$\tau=12\frac{-2-5e^{2\beta J}-5e^{6\beta J}+12e^{20\beta J}}{1+3e^{2\beta J}+5e^{6\beta J}+7e^{12\beta J}+9e^{20\beta J}}. \tag{3}$$

Employing these formulas we calculated the specific-heat jump, which is expected at the ferromagnetic transition. This quantity can directly be compared with the experimental data. Note that in contrast to the total magnetic entropy $\Delta S_{\mathrm{magn}}=R\ln(2S+1)$ the anomalies Δc_p and ΔS_{CO} can be extracted with high precision from the measurements, since they hardly depend on the choice of the background.

In Fig. 5 the calculated jumps Δc_{magn} are compared to the measured specific heat anomalies for $0.11\leqslant x\leqslant 0.15$. It is apparent that calculated and measured anomalies are in a fair agreement for $x=0.14$ and $x=0.15$, whereas there are pronounced differences for smaller doping. We conclude that the large anomaly at T_{C}, which we observe for $x=0.14$, is expected only due to the ferromagnetic ordering. Since for $x=0.14$ there is no additional anomaly at T_{CO}, it is possible to attribute the entire entropy changes ΔS_{tot} to the ordering of the spin degrees of freedom. This conclusion is supported by the analysis of the entropy for smaller x. For these compounds, i.e., for $x=0.11$ and $x=0.125$, the theoretical Δc_{magn} is obviously much larger than the experimentally observed jump. In other words, the observed anomalies at T_{C} are too small to account for the decrease in spin entropy connected to the change from paramagnetism to full ferromagnetic order. This means that the ferromagnetic phase at intermediate temperatures contains much spin disorder that increases with decreasing x. Note that a similar conclusion is possible from the magnetization data discussed above.

Analyzing the doping dependence of the specific heat and, in particular, taking into account the result for $x=0.14$, we have to conclude that the overall entropy changes ΔS_{tot} are dominated by the increase in spin ordering for $x=0.11$, $x=0.125$, and $x=0.14$. This means that the large entropy jumps at the CO transition for $x=0.11$ and $x=0.125$ are

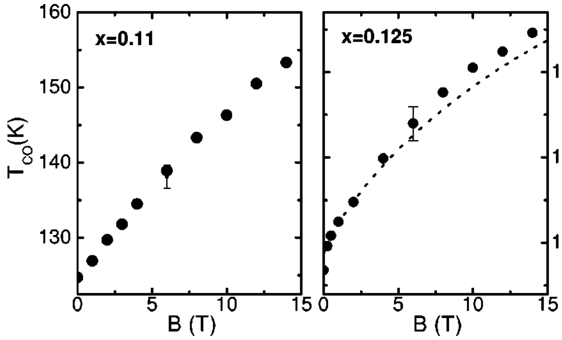

FIG. 6. Magnetic-field dependence of the CO transition temperature $T_{\rm CO}$ as seen by experiment (black circles) and as computed for $x=0.125$ from $\Delta M_{\rm CO}$ and $\Delta S_{\rm CO}$ (dotted line).

mainly due to the spin entropy, which decreases discontinuously when entering the CO phase.

Even more evidence for attributing $\Delta S_{\rm CO}$ mainly to the spin degrees of freedom is given by a separate numerical analysis of the data from the CO anomaly itself. For this analysis we again use the Oguchi approach [Eq. (1)]. The only additional input parameter is the measured increase in the magnetization M at $T_{\rm CO}$ for $x=0.125$. In order to rule out the effects of the demagnetization field that amounts to about 0.5 T, we consider magnetization jumps and entropy changes $\Delta S_{\rm CO}$ measured in an external field of 1 T. Using Eq. (1) and calculating the partition function $\mathcal{Z}=\mathrm{Tr}[\exp(-\mathcal{H}/k_BT)]$ allows to compute the free-energy function and the magnetic entropy $S_{\rm magn}(T,H_{\rm ext},J,M)$. The entropy changes at the CO transition $\Delta S_{\rm magn}=[S(J_{T>T_{\rm CO}},M_{T>T_{\rm CO}})-S(J_{\rm CO},M_{\rm CO})]_{T_{\rm CO},H_{\rm ext}}$ are estimated assuming that J changes at $T_{\rm CO}$ as signaled by the jump of the magnetization. Taking the magnetization data as input, this approach leads to $\Delta S_{\rm magn}\simeq 0.5$ J/mole K in an applied magnetic field of 1 T. The experimental value for the *total* entropy jump in a field of 1 T is $\Delta S_{\rm CO}=0.6\pm 0.03$ J/mole K, which nicely corresponds to the calculated jump of the *magnetic* entropy. Therefore, this analysis strongly confirms that $\Delta S_{\rm CO}$ is predominantly due to an enhancement of spin ordering.

Thus, the crucial role of the spin degrees of freedom for the charge ordering is apparent from our data and their analysis. There is no evidence that charge or structural degrees of freedom cause significant anomalies of the entropy at the CO transition, neither for small *x*, where the large values of $\Delta S_{\rm CO}$ are dominated by spin entropy, nor for larger strontium content $x=0.14$ and $x=0.15$, where the development of the CO superstructure reflections does not correspond to any anomaly of the specific heat. From the thermodynamic point of view the CO transition behaves like an usual magnetic transition: the CO melts at $T_{\rm CO}$ in order to allow a gain of the free energy with respect to the CO energy via increasing the spin entropy. Our data show that the CO with large spin disorder does not occur. This strongly suggests that ferromagnetic order is crucial to stabilize the CO state in lightly hole doped manganites.

This conclusion is strongly supported by the magnetic-field dependence of the CO transition. In Fig. 6 we show the magnetic-field dependence of $T_{\rm CO}$ as determined from magnetization, specific-heat, and resistivity measurements. For $x=0.11$ $T_{\rm CO}$ increases by about 30 K, i.e., by 25%, in an external field of 14 T and a strong increase of about 20 K is also observed for $x=0.125$. As has been mentioned in Ref. 18 the field dependence of the transition temperature is related to the jumps of the magnetization and the entropy due to general thermodynamic relations, i.e., $dT_{\rm CO}/dB_{\rm ext}=-\Delta M_{\rm CO}/\Delta S_{\rm CO}$. In the right part of Fig. 6 we show that in the entire field range the transition temperatures observed in experiment are in a fair agreement with the predictions due to this relation. The increase in $T_{\rm CO}$ with increasing field clearly shows that the charge ordered state is stabilized by a ferromagnetic alignment of the spins, in agreement with the conclusions from our analysis of the specific heat discussed above.

The important role of the magnetic degrees of freedom for the CO in $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_3$ at $x\simeq 1/8$ explains a further surprising result of our study: the absence of a particular role of the commensurate doping 1/8. Often, CO transitions are most pronounced for particular doping concentrations, such as $x=1/2$ or $x=1/3$, which allow a commensurate superstructure.[1,2,15] For our samples the periodicity of the superstructure in the CO phase does not depend on *x* and corresponds to the doping $x=1/8$.[18,28] However, the transition temperature, as well as the magnitude of the anomalies of M, c_p, etc., shows a monotonous doping dependence, i.e., no particular role of $x=1/8$. This supports our argument that the thermodynamics of the CO transition is not determined by the charge degrees of freedom but by spin disorder.

Our results show not only similarities, but also striking differences to the findings at the CO transition in other transition-metal oxides. For example, in the stripe ordered nickelates and cuprates a static CO seems to be a precondition for magnetism, in contrast to our findings in lightly doped manganites.[1,4,5] However, due to the low-dimensional magnetic interactions the spin entropy is already strongly reduced well above the magnetic transition temperature in the nickelates and cuprates and an important role of magnetic interactions for the CO cannot be excluded. A recent analysis of thermodynamic properties of cuprates with static stripes could not resolve anomalies of the entropy due to CO.[34] Similarly as in the case considered here, the CO itself seems to cause only minor changes of the entropy, possibly due to short-range dynamic charge order above $T_{\rm CO}$.

In conclusion, we have measured the specific heat and the magnetization of $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_3$ single crystals with $0.11\leqslant x\leqslant 0.15$. The total entropy and magnetization changes at the transition from the paramagnetic high-temperature phase to the ferromagnetic charge ordered phase hardly depend on the doping. However, the anomalies of both the specific heat as well as the magnetization at $T_{\rm C}$ and $T_{\rm CO}$ change drastically for different *x*. From our data and their analysis we argue that the entropy changes at both transitions are mainly due to spin degrees of freedom. This suggests that the melting of charge order with increasing temperature is due to a gain of the magnetic free energy.

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