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Disorder effects at low temperatures in $La_{0.7-x}Y_xCa_{0.3}MnO_3$ manganites

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Abstract

With the aim of probing the effect of magnetic disorder in the low-temperature excitations of manganites, specific heat measurements were performed in zero field, and in magnetic fields up to 9 T in polycrystalline samples of $La_{0.7-x}Y_xCa_{0.3}MnO_3$, with Y concentrations $x = 0$, 0.10, and 0.15. Yttrium doping yielded the appearance of a cluster-glass state, giving rise to unusual low-temperature behavior of the specific heat. The main feature observed in the results is a strong enhancement of the specific heat linear term, which is interpreted as a direct consequence of magnetic disorder. The analysis was further corroborated by resistivity measurements in the same compounds.

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The specific heat of manganites has attracted considerable interest in recent years, yet several fundamental questions remain unanswered or only loosely addressed. Starting with Ba- and Ca-doped $LaMnO_3$, initial measurements at higher temperatures identified specific heat anomalies associated with phase transitions [1,2], while low-temperature data [2–4] showed a linear term associated with an electronic contribution, and a cubic phonon term. Subsequent studies were performed on a variety of samples, including cation-deficient $LaMnO_{3+\delta}$ [5], Nd- [6] and Pr- [7–10] based compounds, or layered manganites [11]. Recent studies [12,13] addressed the issue of isotope effect in the specific heat of manganites.

The existence of a spin-wave magnetic term in the specific heat of several ferromagnetic (FM) manganite compounds is still a controversial issue. Spin waves were not resolved in the specific heat of Ca-doped $LaMnO_3$ [4,2] and Pr-based manganites [7,13]. They were detected in neutron experiments on various compounds of the family, but either coexisting with spin diffusion [14] or presenting excitation gaps that can be large enough [15] to yield their suppression at low temperatures. A magnetic term was used to fit specific heat data for $La_{1-x}Ca_xMnO_3$ [16] and $La_{1-x}Sr_xMnO_3$ [3,16]. In Ref. [3], it is clear that various sets of fitting parameters are possible, with very different values of the spin-wave coefficient. Such ambiguities are not uncommon, and high-resolution data combined with sophisticated fitting techniques are often needed [12] in order to extract a FM spin-wave contribution from specific heat measurements. Apart from difficulties of the fitting procedure, disorder might play a major role in suppressing these excitations, as we will discuss below.

The most puzzling issue which emerged from previous

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investigations of the specific heat is the observation of a large linear term in insulating manganites [5–7,9]. The nature of the excitations giving rise to this contribution remains unknown. Explanations based on charge localization and/or spin disorder [5,9] have been put forward. An additional anomalous contribution, arising from excitations following a dispersion relation $\Delta + \xi k^2$, has also been proposed [9,13], and it has been suggested that these excitations are related to charge ordering, although this interpretation still lacks confirmation.

This paper presents low-temperature specific heat and dc transport measurements in $La_{0.7-x}Y_xCa_{0.3}MnO_3$ manganites. Our main goal is to address the origin of the large linear term of the specific heat in samples where the carrier concentration is held constant but the carrier mobility and magnetic properties are systematically modified by increasing x. As Y is added in $La_{0.7}Ca_{0.3}MnO_3$, magnetic disorder starts to play a major role in the system's properties. The compound evolves from a nearly collinear ferromagnet at $x = 0$ to a magnetic cluster-glass phase at $x = 0.15$ [17], while a minimum that is observed in the dc resistivity at low temperatures becomes more pronounced. Specific heat and resistivity data in this system, with and without an applied magnetic field, provide invaluable insight into the effect of disorder in the low-temperature excitations of manganite compounds.

The investigated compounds are polycrystalline samples of $La_{0.7-x}Y_xCa_{0.3}MnO_3$, with $x = 0$, 0.10, and 0.15, prepared by solid-state reaction. X-ray analysis confirmed a single-phase orthorhombic perovskite structure. Scanning electron microscopy revealed an average grain size of 3–6 μm, without significant variations from sample to sample. The specific heat measurements were performed by relaxation calorimetry, using a Quantum Design PPMS. The data were obtained for temperatures between 2 and 20 K, and under applied magnetic fields up to 9 T. The absolute accuracy of the system, checked against a copper sample, is of the order of ±2–3%. All samples had masses between 15 and 20 mg. The background signal, including the amount of Apiezon N grease used to glue the sample on the platform, was recorded separately at all applied fields, and subtracted from the measured heat capacity. The resistivity was measured by a standard four-point technique. Magnetization and resistivity results, measured in a wider temperature range (up to 300 K), can be found in Ref. [17].

The specific heat data at low temperatures (2–12 K) for all the studied samples and various applied magnetic fields are plotted as $c/T \times T^2$ in Fig. 1. We also show linear fittings to the data in the upper temperature range.

The main features observed in those plots are: a large overall increase of the specific heat with yttrium content, a reduction of the specific heat with magnetic-field intensity, and a pronounced downturn of the data with decreasing temperature in the low-T region for the yttrium-doped samples. The low-temperature downturn is much weaker in the yttrium-free sample, which also shows a slightly upward curvature of the data with increasing temperature.

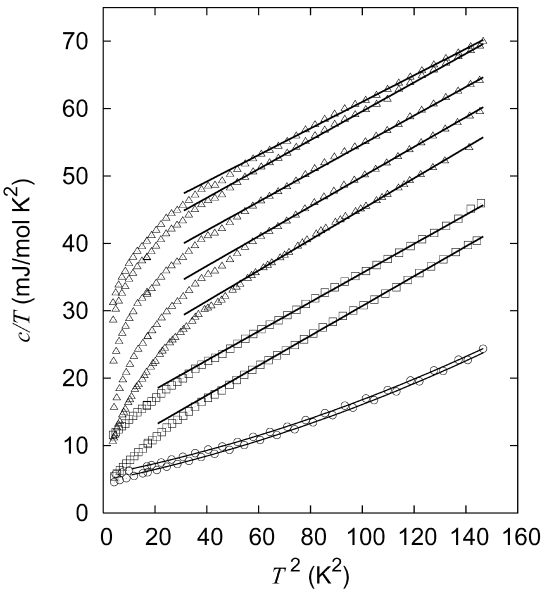

Fig. 1. Specific heat measurements for $x = 0.15$ (upper set—triangles), 0.10 (middle set—squares), and 0 (bottom set—circles). The highest and lowest curves of each set correspond to zero applied field and to $\mu_0 H = 9$ T, respectively. The intermediate curves for $x = 0.15$ correspond to $\mu_0 H = 1$, 3, and 6 T, respectively from top to bottom. The solid lines are fittings to Eq. (1) or (2).

Let us first concentrate on the 'high' temperature range, where the straight lines of Fig. 1 indicate a good fitting with the standard expression

$$c(T) = \gamma T + \beta T^3, \tag{1}$$

where the T^3-term describes the phonon contribution, and the linear term would be normally attributed to conduction electrons. However, this latter interpretation has to be reviewed in the present case, as we will discuss below. For the yttrium-free sample, we used

$$c(T) = \gamma T + \beta T^3 + \eta T^5, \tag{2}$$

including a T^5 correction to the phonon term, which accounts for the observed upward curvature of the results. The best-fitting values of the specific heat coefficients γ, β, and η are listed in Table 1. The quality of the fitting is within 1% in all cases, and arbitrary variations of the fitting temperature range above 7 K yield changes in the obtained coefficients by less than 1%. It is worth mentioning that we have attempted to fit the specific heat data down to low temperatures including a ferromagnetic $T^{3/2}$ term, as done in other investigations [16]. However, in our case the quality of the fittings are very poor below ~4 K, with an error above 20% in some cases. Furthermore, the magnitude of this contribution turns out to be essentially insensitive to the applied magnetic field, in contrast to what should be expected of magnetic excitations.

Table 1
Specific heat coefficients of Eqs. (1) and (2) for the fittings shown in Fig. 1

Y (%)	$\mu_0 H$ (T)	γ (mJ/mol K^2)	β (mJ/mol K^4)	η (mJ/mol K^6)
0	0	5.65	0.0766	3.49×10^{-4}
	9	4.73	0.0790	3.46×10^{-4}
10	0	14.0	0.216	–
	9	8.61	0.221	–
15	0	41.3	0.197	–
	1	38.2	0.214	–
	3	33.4	0.213	–
	6	27.8	0.221	–
	9	22.3	0.228	–

We now turn to a critical analysis of the results described above. In relation to the phonon terms, inspection of Table 1 shows that the absence of a T^5 correction in the yttrium-doped samples is accompanied by an increase in the T^3 coefficient β, which indicates a reduction of the Debye temperature. This is consistent with the generally expected qualitative change of the phonon spectrum due to substitutional impurities, i.e. localization of band-edge states, with the consequent reduction of the effective band width. Suppression of the T^5 term may be understood by the same argument, since the states that are detached from the phonon band belong to the region where deviations from a linear dispersion relation are more noticeable.

The absence of FM spin-wave contributions can be viewed as a consequence of magnetic disorder in the samples. A cluster-glass structure has already been observed in several manganites [18,5,17] and related compounds [19,20]. Such a structure corresponds to microscopic magnetic moments, which align ferromagnetically within finite-size clusters, with a random orientation of the cluster moments with respect to each other. In this picture, long-wavelength spin waves would be suppressed, and their effect not detected in low-temperature specific heat measurements. One could consider a spin-wave contribution with a long-wavelength cutoff, or in other words, a gapped spin-wave spectrum with a dispersion relation of the form $\omega(k) = \Delta + \xi k^2$. Contributions from this kind of dispersion relation have been included by other authors [9], although attributed to excitations of a different nature. Despite the fact that part of the low-temperature downturn of the specific heat observed in Fig. 1 can be accounted for by such a term, its inclusion did not yield a reliable fitting of the data. The same happens if one considers the existence of a gap in the charge spectrum. As a general observation, these kind of terms tend to compete with the linear one, so that weight can be shifted from one to the other without affecting the quality of the fitting. Unfortunately, the analysis of low-temperature specific heat data is prone to ambiguities of this sort, which have been noticed in other situations [8]. For instance, a recent work by Hardy et al. [21] reports a similar downturn of the low-temperature specific heat for a system doped at the manganese site. They try to fit the data including a phenomenological term corresponding to some kind of gapped excitation, but various sets of fitting parameters give equivalent results. In order to avoid these ambiguities, we decided to concentrate in the most prominent features, which can be unambiguously represented by the fittings to Eqs. (1) and (2) shown in Fig. 1.

The large values of the linear coefficient γ (see Table 1), and the strong reduction of the specific heat in the lower temperature range can also be interpreted as manifestations of magnetic disorder. It is clear that the observed values of γ are too large to be attributed to conduction electrons. Furthermore, these values are higher for lower-conductivity samples, which contradict a naive interpretation in terms of an enhanced density of states at the Fermi level. The significant reduction of the γ values under high applied magnetic fields leads naturally to an interpretation in terms of excitations of magnetic origin. Indeed, a linear behavior of the specific heat with temperature is also observed in spin glasses [22], which constitute a classical example of magnetically disordered systems. The temperatures and coefficients are much higher in the present case, undoubtedly related to the fact that here we are dealing with a system of large (cluster) magnetic moments rather than a dilute spin system. It is worth noticing that a large linear term in the specific heat was previously observed in another cluster-glass manganite compound [5].

The low-temperature behavior of the electrical resistivity, shown in Fig. 2, provides further clues. All samples show a shallow minimum in the resistivity as a function of temperature, and the resistivity values are significantly reduced by an applied magnetic field. This is not the usual (negative) colossal magnetoresistance shown by manganites, which mainly occurs in a region around the Curie temperature. It is important to notice that, although the resistivity grows as $T \to 0$, we do not have carrier localization, since the conduction is not exponentially activated. This can be seen in the log–log plots of Fig. 2, where the nearly straight lines at low temperature indicate a power-law behavior that probably crosses over to a finite resistivity at $T = 0$. The large low-temperature magnetoresistance effect implies magnetic disorder that is suppressed in a dc field. The increase of the absolute value of resistivity with increasing x supports this idea.

A similar low-temperature minimum of the resistivity was also observed in manganite thin films [23], and its origin has been discussed in detail by Rozenberg et al. [24]. They argue against an interpretation in terms of weak-localization effects, in which case the field dependence would be much weaker, and interpret the resistivity behavior as due to spin-polarized inter-grain tunneling conduction. We adapt this model for our samples, and interpret the transport behavior in terms of spin-polarized inter-cluster tunneling. With such a model, the following expression for

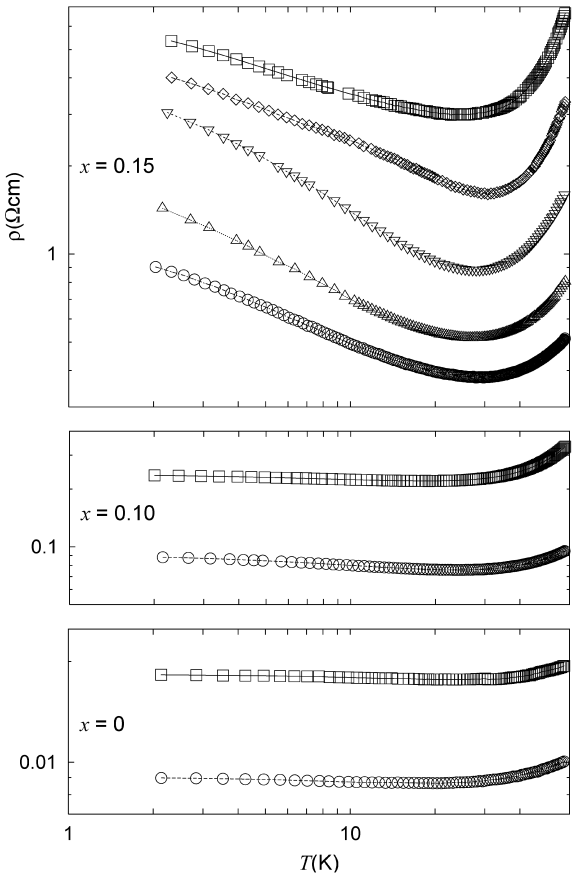

Fig. 2. Log–log plot of the low-temperature resistivity for all samples. The highest curve of each set (squares) is the zero-field result. The lowest curve of each set (circles) corresponds to $\mu_0 H = 9$ T. The intermediate curves for $x = 0.15$ correspond to $\mu_0 H = 1$, 3, and 6 T, respectively from top to bottom. The lines joining the points are just guides for the eye.

the low-temperature resistivity is proposed in Ref. [24]:

$$\rho(T,H) = \frac{\rho_U}{1 + \varepsilon\langle\cos\theta_{ij}\rangle}, \tag{3}$$

where θ_{ij} is the angle between the magnetizations of clusters i and j, the brackets denote both thermal and configurational average, ρ_U is an intrinsic tunneling resistivity, independent of the magnetization orientations, and ε measures the degree of spin polarization of the charge carriers in each cluster. The above expression shows that the resistivity tends to be reduced if the inter-cluster correlations are ferromagnetic, and greatly enhanced if they are dominantly antiferromagnetic. The very definition of FM clusters implies that the AF superexchange interactions will dominate over the double-exchange FM coupling at the cluster boundaries, which is consistent with the resistivity increase at low temperatures. Nevertheless, the system does not develop long-range AF order, as the random distribution of clusters will tend to frustrate the AF interactions.

The above discussion has shown that the same magnetically disordered cluster structure accounts for both observed behaviors: enhanced linear term in the specific heat, and low-temperature increase of the resistivity. This consistency strengthens the reliability of this interpretation. One could argue that the resistivity behavior could be due to inter-grain tunneling, as the samples are polycrystalline. However, as we mentioned before, the grain-size differences among the samples are very small, and cannot account for the observed differences in the low-temperature resistivities.

In summary, we have studied the specific heat of $La_{0.7-x}Y_xCa_{0.3}MnO_3$ with $x = 0$, 0.10, and 0.15, under applied magnetic fields up to $\mu_0 H = 9$ T, in the temperature region below 12 K. The system is viewed as a collection of ferromagnetic clusters that tend to align their moments antiferromagnetically, but their random distribution prevents stabilization of long-range AF order, resulting in a cluster-glass state. Low-energy excitations of this system yield a contribution to the specific heat that is linear in T, with a coefficient γ that increases with x and is strongly reduced by the presence of an applied magnetic field, which suppresses magnetic disorder. At very low temperatures, these magnetic excitations tend to be frozen out, reducing the total specific heat, which shows a pronounced downturn in this temperature region. Resistivity measurements, and the interpretation of those measurements in terms of spin-polarized carrier tunneling between antiferromagnetically correlated clusters, support the specific heat observations.

To our knowledge, there are no theoretical predictions for the behavior of the specific heat, or even further development of Eq. (3) for the resistivity, in this kind of model. Such predictions are needed for a quantitative fit of the specific heat results in the whole low-temperature region, and to provide a better understanding about the nature of the excitations occurring in this magnetically disordered system.

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