Specific heat of $Nd_{0.67}Sr_{0.33}MnO_3$

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The specific heat of the colossal magnetoresistance material $Nd_{0.67}Sr_{0.33}MnO_3$ is reported for $0.35 \leq T \leq 280$ K, $H=0$ and $1 \leq T \leq 120$ K, $H=9$ T. The results include a Schottky-like specific-heat anomaly for the Nd ordering, an ''attenuation'' of the Mn ordering anomaly, and a T-dependent ''linear term,'' $\gamma(T)T$. This unusual combination of features is interpreted as arising from an interaction between the Nd and Mn spin systems. The expected magnetic entropy is recovered only if a contribution from the $\gamma(T)T$ term is included. [S0163-1829(99)03501-8]

It is almost a half century since Jonker and Van Santen[1] studied the magnetic properties of the mixed-valent perovskite manganites and discovered that in some of these materials ferromagnetic (FM) ordering was accompanied by a metal-insulator (MI) transition with the magnetically ordered phase showing metallic properties. However, the current intense interest in these manganites dates from the recent discovery of their ''colossal magnetoresistance'' (CMR).[2] Since that discovery there have been many measurements of other properties, but relatively few of the specific heat (C). There have been only a few measurements that characterize the specific-heat anomaly at the FM ordering temperature of the Mn spins (T_c) and no detailed analysis of those data to obtain the entropy associated with the ordering. The anomaly gives the impression that the entropy change near T_c may be substantially less than expected. However, measurements on CMR materials have pointed to the existence of magnetic polarons[3,4] and spin complexes[5] well above T_c, which would contribute to this entropy. At low T there have been even fewer measurements of C, and there have been no measurements in magnetic fields (H). In this paper we report measurements of C for $Nd_{1-x}Sr_xMnO_3$ (NSMO), $x=0.33$, from below 1 K to well above T_c for $H=0$, and at low T for $H=9$ T. Our analysis of the data accounts for $\sim$95% of the expected spin entropy for Nd and Mn, and suggests that any contribution above 280 K from polarons or complexes may be small.

The results also show evidence of a previously unrecognized interaction between the Nd and Mn spin systems that is relevant to understanding the properties of CMR materials with two spin systems, and possibly those of other materials with several spin systems. Specifically, three features in C point to a coupling of the two spin systems that mixes their contributions to the entropy: (1) The Nd spins order at an unusually high T for Nd-Nd exchange interactions, producing a Schottky-like anomaly, which is suggestive of an effective molecular-field mechanism. Furthermore, the anomaly accounts for only $\sim$85% of the expected entropy. (2) At low T there is a $\gamma(0)T$ term that is strongly enhanced relative to that in $La_{0.7}Sr_{0.3}MnO_3$,[6] and which makes a significant contribution to the entropy. (3) The anomaly at T_c is broadened and attenuated relative to those in CMR materials with La in place of Nd, e.g., $La_{0.67}Ca_{0.33}MnO_3$.[7] As shown by a comparison with $LaCu_2O_4$, $NdCu_2O_4$, which differs both magnetically and structurally from NSMO, exhibits the same three features,[8] suggesting that they may be even more general. A preliminary report of the results has been given elsewhere.[9]

The specific-heat data, obtained using a semi-adiabatic, heat-pulse technique below 30 K and continuous heating above, had a precision of $\sim$0.1% and an accuracy of $\sim$0.5%. A sharp, double-peaked anomaly near 43 K, precisely similar to that in Mn_3O_4 (Ref. 10) showed the presence of 1.5 mol % Mn_3O_4, and the data were correspondingly corrected.[11] The data were analyzed as the sum of six contributions to C: C_{cf}, a contribution from the crystal-field levels of the Nd ions, calculated from the level splitting for Nd in $NdBa_2Cu_3O_7$;[12] C_{lat}, the lattice contribution; $C_{hyp}=DT^{-2}$, the hyperfine contribution; C_{Sch}, a broadened Schottky-like anomaly that includes the major part of the entropy of the Nd spin system; C_{mag}, a term that includes the major part of the entropy of the Mn spin system; and $\gamma(T)T=\gamma(0)[1-(T/T_0)^2]T$ ($T_0=280$ K, see below), a term that arises primarily from interactions between the two spin systems, and includes additional magnetic entropy. The major results of the analysis are not sensitive to the choice of Nd crystal-field (cf) parameters. This has been shown by carrying out similar analyses using cf parameters for seven other Nd compounds[13] as well as for

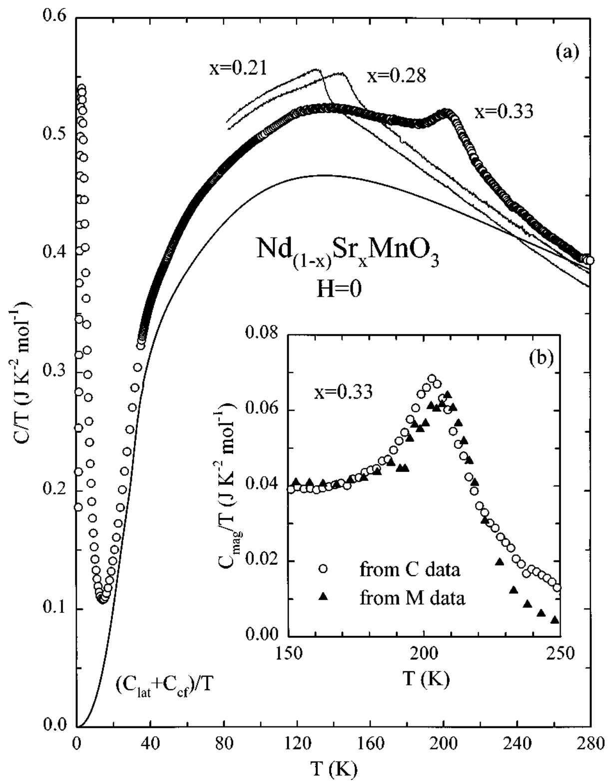

FIG. 1. (a) C/T vs T for $Nd_{1-x}Sr_xMnO_3$ for $H=0$. The solid curve is an estimate of $(C_{lat}+C_{cf})/T$. (b) C_{mag}/T vs T near T_c. The triangles are estimates obtained from the magnetization data; the circles are obtained by an analysis of the specific-heat data (see text).

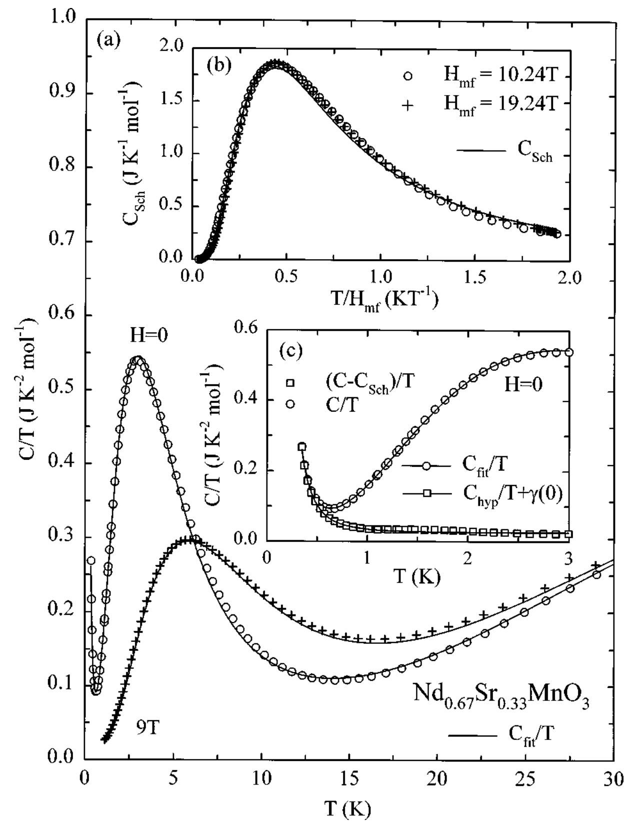

FIG. 2. (a) C/T vs T for $x=0.33$ at low T for $H=0$ and 9 T. (b) C_{Sch} vs T/H_{mf}, where $H_{mf}=10.24$ and 19.24 T for $H=0$ and 9 T, respectively. The points represent experimental data from which the other contributions have been subtracted; the curves represent the Schottky-like fits described in the text. (c) C/T vs T for $T\leqslant 3$ K and $H=0$. The squares represent experimental data from which C_{Sch} has been subtracted; the associated curve represents a fit for $T\leqslant 1.5$ K extrapolated to 3 K.

$C_{cf}=0$. Each of these analyses gave essentially the same result for C_{mag}. This insensitivity of the derived C_{mag} and associated entropy comes about because changes in the assumed C_{cf} produce compensating changes in the higher-order terms in C_{lat} that are obtained by fitting the data (see below). Consequently, the sum $(C_{cf}+C_{lat})$, which is all that is relevant to the determination of C_{mag} and $\gamma(T)$, is essentially unaffected. Similarly, neither the T^3 term in the low-temperature C_{lat} nor $\gamma(0)$ depends upon the choice of C_{cf}. Features in C that correspond to some of these contributions are evident in the plots of C/T vs T for $H=0$ in Figs. 1(a) and 2(a). The peak at ~3 K in both figures is associated with C_{Sch}; the peak at ~205 K in Fig. 1(a), where data for $x=0.21$ and 0.28 are included for comparison, is associated with C_{mag}; the upturn in C/T below ~0.6 K in Fig. 2(a) [omitted in Fig. 1(a)] is associated with C_{hyp}. The data were fitted in several different intervals of T with procedures that gave continuity of the fits. The fitting procedures and results are outlined in the following paragraphs. Additional detail and more complete results for $x=0.21$ and 0.28 will be given elsewhere.[11]

Analysis of low-T data. The data for $H=0$ and $T\leqslant 1.5$ K were fitted with an expression that included C_{hyp}, $\gamma(0)T$, and the low-temperature ''tail'' of a Schottky anomaly, giving $D=10.0\pm 0.5$ mJ K mol^{-1} and $\gamma(0)=25\pm 1$ mJ K^{-2} mol^{-1}. (The contributions of C_{cf} and C_{lat} are negligible in this temperature interval.) A similar analysis of the 9-T data gave $\gamma(0)=22\pm 1$ mJ K^{-2} mol^{-1}, but no reliable value of D was obtained because the data did not extend to sufficiently low T. Data for $H=0$ and 9 T, and $11\leqslant T\leqslant 37$ K, corrected for C_{cf}, were fitted simultaneously with an expression that included $\gamma(0)T$ [with the $\gamma(0)$'s fixed at their low-temperature values], the two leading terms in this high-temperature ''tail'' of two-level Schottky anomalies, and four H-independent terms of the form B_nT^n, $n=3$, 5, 7, 9 to represent C_{lat}. The well-determined, low-temperature $\gamma(0)$ values were used since the contribution of the $\gamma(0)T$ terms in this higher temperature interval is $\leqslant$15%. However, allowing the $\gamma(0)$'s to be variables in the fit did not significantly affect the values of the other parameters.[11] For $1.5\leqslant T\leqslant 20$ K and each value of H, $C-C_{hyp}-\gamma(0)T-(C_{cf}+C_{lat})$ was fitted with the sum of two Gaussian-broadened Schottky terms. Two terms were used because the fits below 1.5 and above 11 K gave high- and low-temperature Schottky ''tails'' corresponding to different level separations.

The hyperfine term. The hyperfine constant, D, is the sum of contributions from Mn and Nd nuclei. For $La_{0.7}Sr_{0.3}MnO_3$ specific-heat data[6] give $D_{Mn}=8.7$ mJ K mol^{-1} and NMR results[14] give 8.2 mJ K mol^{-1}. For $H=0$, D_{Nd} for NSMO can be estimated as $D_{Nd}=(D-D_{Mn})/0.67\sim 3$ mJ K (mol Nd)$^{-1}$, which is comparable to values reported for Nd in other environments. For $H=7$ T, $D=6.8$ mJ K mol^{-1},[11] implying that for Mn the hyperfine and applied fields are oppositely directed, in agreement with the NMR measurements.[14]

The neodymium Schottky-like ordering anomalies. The shape of the anomalies [see Figs. 2(a) and 2(b)], and the relatively high temperature at which they occur, suggest that the Nd moments are primarily ordered by a molecular-field-like interaction rather than the usual Nd-Nd exchange interaction. From the temperatures of the maxima in C_{Sch}, 4.44 and 8.34 K for $H=0$ and 9 T, respectively, the effective molecular field (H_{mf}) at the Nd sites can be estimated if it is assumed to be unchanged by the applied field. A field will split each of the five crystal-field doublets, but only the ground-state doublet need be considered at low-T. If the effective moment of the Nd^{3+} ions in the ground state is μ, and the splitting of the doublet is $\Delta_0=2\mu H_{\mathrm{mf}}(0)$ for $H=0$ and $\Delta_{9\,\mathrm{T}}=2\mu[H_{\mathrm{mf}}(0)+9]$ for 9 T, then the mean values (an average over all directions) are $H_{\mathrm{mf}}(0)\sim 10\,\mathrm{T}$ and $\mu\sim 0.8\mu_B$. This value of μ is smaller than the free-ion value of $3.3\mu_B$, but similar to $0.85\mu_B$, obtained for the Nd^{3+} moments in Nd_2CuO_4.[15] In Fig. 2(b) the 0- and 9-T anomalies are plotted versus T/H_{mf}, where $H_{\mathrm{mf}}=10.24$ and 19.24 T for $H=0$ and 9 T, respectively. The fact that the two sets of data are virtually identical, unlike that for Nd_2CuO_4,[15] indicates that the Nd-Nd interaction is small compared to the Nd-Mn interaction. It also lends support to the method for calculating H_{mf}, as well as to the values for $\gamma(0)$ in the two applied fields, and to our low-T representation of C_{lat}. The anomalies for both $H=0$ and 9 T give ~85% of the expected entropy of ordering of the Nd moments, $\Delta S_{\mathrm{Nd}}=0.67R\ \ln 2$. However, the missing entropy appears to be recovered as part of that associated with the $\gamma(T)T$ term (see below).

$\gamma(T)T$ term. Because NSMO, $x=0.33$, is metallic for $T<T_c$, a conduction-electron contribution of the form $\gamma(0)T$ is to be expected. However, the $H=0$ value of $\gamma(0)$, 25 $\mathrm{mJ\,K^{-2}\,mol^{-1}}$, is eight times larger than that for $La_{0.7}Sr_{0.3}MnO_3$.[6] The effect of H on $\gamma(0)$ [$\gamma(0)$ decreases with H] argues that it is not a simple conduction-electron effect. As noted above, there is also a $\gamma(0)T$ term in the specific heat of $NdCu_2O_4$,[8] which is nonmetallic, and which shows features in the specific heat associated with Nd and Cu ordering similar to those for Nd and Mn in NSMO. For these reasons it is reasonable to assume that in NSMO, as in Nd_2CuO_4, $\gamma(T)$ is largely magnetic in origin, and that it should decrease as $T\rightarrow T_c$.

Analysis of higher-T data. The data in the vicinity of T_c appear to show an unexpectedly small value for the entropy change arising from Mn ordering. An estimate, obtained as the area between the anomaly in C/T near T_c and a smooth curve passing through the data below ~175 and above ~235 K, gives only ~10% of the expected entropy. Similar discrepancies can be inferred from data on other CMR materials.[7,16–18] The shape of the anomaly in C/T notwithstanding, it is reasonable to expect that the magnetic entropy, including that of short-range order that typically exists well above T_c, is recovered over a substantially wider interval in T.[19] To obtain a more realistic value of ΔS_{Mn}, it is necessary to extend the separation of the various contributions to C to the data above 37 K, the upper limit of the low-T analysis. To that end, C_{mag} was calculated from magnetization data using a mean-field-like approximation[20] and, somewhat arbitrarily, the T dependence of $\gamma(T)$ was represented by $\gamma(T)=\gamma(0)[1-(T/T_0)^2]$, with T_0 taken as 280 K, $\sim 1.4T_c$, and the upper limit of the data. [Another obvious choice for T_0 would be T_c, but it would not take into account a possible residual Nd-Mn interaction above T_c (Ref. 14).] With the calculated C_{mag} and $\gamma(T)$, C_{lat} was obtained from $C_{\mathrm{lat}}=C-C_{\mathrm{cf}}-C_{\mathrm{mag}}-\gamma(T)T$ for the intervals $30\leqslant T\leqslant 150$ K and $250\leqslant T\leqslant 280$ K, omitting a region near T_c in which the approximation for C_{mag} might be less accurate. C_{lat} obtained in this way was interpolated through the omitted region by fitting with a harmonic-lattice approximation plus a dilatation term,[21] with six adjustable parameters, to obtain an expression for C_{lat} for $30\leqslant T\leqslant 280$ K. The derived C_{lat} was in good agreement with that obtained in the low-T fit and, together with the other terms in C, it gave an accurate representation of the experimental data in the two temperature intervals in which the data were fitted. Its validity, as well as that of the calculation of C_{mag}, is also supported by the agreement of the calculated C_{mag} with $C_{\mathrm{mag}}=C-(C_{\mathrm{lat}}+C_{\mathrm{cf}})-\gamma(T)T$ in the region omitted from the fit [see Fig. 1(b)].

Since the sum $(C_{\mathrm{lat}}+C_{\mathrm{cf}})$ is insensitive to the choice of cf parameters, the derived contributions to the magnetic entropy are also only weakly affected. The assumption about the form of $\gamma(T)$ is a source of uncertainly, but $\gamma(0)$ is well-defined and any plausible change in the T dependence that left $\gamma(T)\sim 0$ for $T\sim T_c$ (or somewhat higher) would not have a large effect on the entropy.

Contributions to the entropy of spin ordering. Theoretically, the entropy for independent ordering of the spins is $\Delta S_{\mathrm{th}}=\Delta S_{\mathrm{Nd}}+\Delta S_{\mathrm{Mn}}=16.6\ \mathrm{J\,K^{-1}\,mol^{-1}}$, where $\Delta S_{\mathrm{Nd}}=0.67R\ \ln 2=3.8$ and $\Delta S_{\mathrm{Mn}}=0.67R\ \ln 5+0.33R\ \ln 4=12.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$ (for $x=0.33$, 2/3 of the Mn ions are Mn^{3+} with spin $S=2$ and 1/3 are Mn^{4+} with $S=3/2$). The area between the data and $(C_{\mathrm{lat}}+C_{\mathrm{cf}})/T$ in Fig. 1(a), the experimental value of the spin entropy at 280 K, is $\Delta S_{\mathrm{exp}}=15.7\ \mathrm{J\,K^{-1}\,mol^{-1}}$, 95% of ΔS_{th}. It is the sum of $\Delta S_{\mathrm{Sch}}=3.3$, $\Delta S_{\mathrm{mag}}=7.7$, and $\Delta S_{\gamma}=4.7\ \mathrm{J\,K^{-1}\,mol^{-1}}$, derived from C_{Sch}, C_{mag}, and $\gamma(T)T$, respectively. It is difficult to estimate the uncertainty in ΔS_{exp} quantitatively, but a reasonable guess is $\pm 10\%$, of which only ~1% can be attributed to the choice of C_{cf}. The magnitude of the contribution to ΔS_{exp} of the $\gamma(T)T$ term in C, ΔS_{γ}, is noteworthy. Evidently, a significant part of the expected ΔS_{th} appears in ΔS_{γ}.

Related features in the specific heats of other materials. The combination of the three features associated with the ordering of the spin systems reported here for NSMO, and also observed in $NdCu_2O_4$,[8] [the broadened Schottky-like anomaly for the Nd ordering, the $\gamma(0)T$ term, and the broadened anomalies for the Mn and Cu ordering] has not been recognized in other materials. However, several other systems show similarities to the first or to the first two of these features. Two cases in which $\gamma(T)T$ terms make significant contributions to the magnetic entropy have been suggested recently, although the $\gamma(T)T$ terms differ in detail in physical origin from that reported here. For $La_{0.67}Ca_{0.33}MnO_3$, a CMR material with a MI transition at T_c, it has been suggested that the conduction-electron contribution to C, which would disappear at T_c, should be taken into account in calculating the magnetic entropy.[7] For $SrRuO_3$, a metallic ferromagnet, it has been suggested that the very high value of

$\gamma(0)$ reflects a spin-fluctuation enhancement, and the associated entropy should be included in the magnetic entropy at T_c.[22]

Both a broadened Schottky-like anomaly for the Nd ordering and, for $x \neq 0$, a large $\gamma(0)T$ term have been observed for $(Nd_{2-x}Ce_x)CuO_4$,[23] but the Cu ordering has not been studied calorimetrically. In that case, however, $\gamma(0)$ is as much as two orders of magnitude higher than for NSMO. A recent theoretical calculation[24] accounts qualitatively for both of these features as observed in $(Nd_{2-x}Ce_x)CuO_4$. Another model[25] directed to an interpretation of the $\gamma(0)$ values accounts for the very large value observed for $x=0.15$ on the basis of a spin-wave contribution. [That picture would be consistent with the decrease in $\gamma(0)$ with increasing H reported here for NSMO]. In both of these models the Nd moments order in an effective magnetic field produced by ordered Cu moments, giving the $\gamma(T)T$ term. An interaction of this general type must be involved in NSMO, but any attempt to apply either model in detail would have to take into account the structural and magnetic differences between the two materials.

Summary. The specific heat of $Nd_{0.67}Sr_{0.33}MnO_3$ shows unusual features that are interpreted in terms of a Nd-Mn exchange interaction that couples the orderings of the two spin systems, modifies the form of the specific-heat anomaly associated with each, and produces a term $\gamma(T)T$ that also contributes to the magnetic entropy. Within the experimental uncertainty, the total expected spin entropy is accounted for.

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