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Specific heat of $Nd_{(1-x)}Sr_xMnO_3$

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Abstract

The specific heat (C) of the colossal magnetoresistance material $Nd_{0.67}Sr_{0.33}MnO_3$ was measured for $0.35 < T < 280$ K and $0 \leqslant H \leqslant 9$ T. Estimates were made of contributions to C from the hyperfine interactions, the lattice, Nd^{3+} magnetic ordering, ferromagnetic ordering of the Mn ions near $T_c \approx 205$ K, and a low-T γT term. The entropy associated with the last three terms is essentially equal to that expected for the ordering of the Nd and Mn moments.

Keywords: Specific heat; Entropy; Magneto-resistance; Phase transitions; Itinerant electrons

The specific heat, C, of the colossal magnetoresistance material (CMR) $Nd_{(1-x)}Sr_xMnO_3$ (NSMO, $x = 0.33$) was measured for $0.35 < T < 280$ K and $0 \leqslant H \leqslant 9$ T. Magnetization, M, measurements at 1 and 5 T were made for $6 < T < 300$ K. (C and M data on $x = 0.28$ and 0.21 samples will be reported elsewhere [1].) Fig. 1 is a plot of C/T versus T for $H = 0$ and $x = 0.33$. Some data near T_c for $x = 0.28$ and 0.21 are also shown. The peak in C/T near $T_c \sim 205$ K is associated with ferromagnetic (FM) ordering of Mn moments, while the peak at ~ 3 K arises from ordering of Nd moments in a ground-state doublet. The anomaly at ~ 43 K is not intrinsic to the $x = 0.33$ CMR material, but is associated with FM ordering of Mn moments in the spinel Mn_3O_4, an impurity phase [1].

Fig. 2 shows plots of the data below 30 K for $H = 0$ (including an inset for $T < 1.5$ K) and 9 T and of C_{fit}/T, where $C_{fit} = C_{hyp} + \gamma T + C_{Schot} + C_{Latt}$. C_{hyp} (negligible above ~ 1.5 K) is a hyperfine contribution, D/T^2, from the Mn and Nd nuclei. C_{Schot} is a sum of two Schottky functions, $n_i(\delta_i/T)^2 \exp(\delta_i/T)/[(1 + \exp(\delta_i/T)]^2$, where $i = 1, 2$ for Nd in non-CMR and CMR phases, respectively. C_{Latt}, the 'lattice' specific heat including a possible contribution from a crystal-field splitting of the Nd^{3+} energy levels, is the sum of four terms of the form B_nT^n, where $n = 3, 5, 7, 9$. The various constants are determined by least-squares fits to the data below 35 K and are listed in Table 1. Two significant results emerge from the analysis: The entropy change, ΔS_{Nd}, associated with both the $H = 0$ and 9 T Schottky functions is 15–20% lower than expected, and the γ value is 2–8 times higher than has been reported for the other perovskite CMRs [2–4]. These two results, possibly linked, may point to exchange coupling between the Nd and Mn ions. The fact that the Nd ordering peak is Schottky-like could support such an inference.

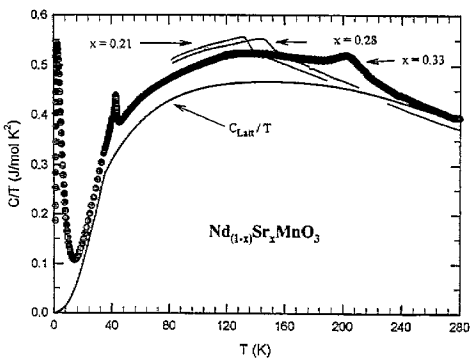

Fig. 1. C/T versus T for $Nd_{(1-x)}Sr_xMnO_3$ in $H = 0$.

The C data above 30 K appear to show an unexpectedly small value for the ΔS associated with Mn ordering. A first estimate for ΔS_{Mn}, obtained from the area between the C/T anomaly near 205 K and a smooth curve passing

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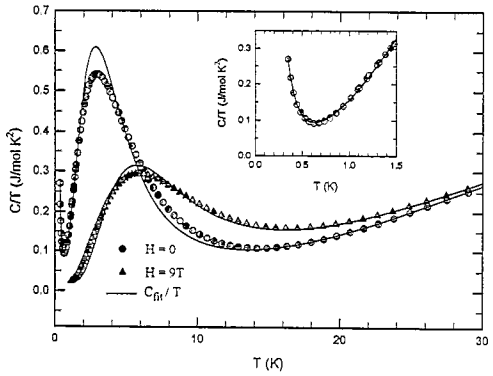

Fig. 2. C/T versus T for $Nd_{0.67}Sr_{0.33}MnO_3$ in $H = 0$ and 9 T.

through the data below ~175 K and above ~235 K, gives only about 10% of the expected value. Similar, although sometimes smaller, discrepancies have been reported for the other CMRs [3, 5–7]. A more reliable value of ΔS_{Mn} requires some means of estimating C_{Latt} above 35 K. We have made such an estimate by assuming $C_{Latt} = C - C_{mag} - \gamma(T)T$. Well below T_c, but above 30 K, we approximate C_{mag} using the mean-field expression $C_{mag} = -\alpha(dM^2/dT)$, where $\alpha = 3JRT_c/2(J+1)M_0^2$, J is the average Mn^{3+}–Mn^{4+} spin, R is the gas constant, M is the measured magnetization, and M_0 is the saturation spontaneous magnetization. In order to obtain consistency with the low-T C_{Latt} as well as to obtain a C_{Latt} that does not change abruptly at T_c, we assume that $\gamma(T)$, rather than being constant below T_c and zero above (as might be expected if NSMO becomes metallic at T_c), is given by $\gamma(T) = \gamma\{1-(T/T_0)^2\}$, where $\gamma = 0.025$ J/mol K^2, the low-T value, and T_0 is chosen to give a reasonable value for ΔS. A natural choice might be $T_0 = T_c$, but this yields too low a value for ΔS (see below) and also fails to take into account a possible Nd–Mn interaction above T_c. We assume $T_0 = 280$ K, which results in $\Delta S_\gamma = 4.7$ J/mol K. We subtract $\gamma(T)T$ and $-\alpha(dM^2/dT)$ from C and fit the results for $30 < T < 280$ K with a harmonic lattice approximation plus a dilatation term [8] with the regions $35 < T < 50$ K and $150 < T < 250$ K omitted. (Note: the region around T_c, where discrepancies between C_{mag} and its mean-field approximation are greatest, is excluded from the fit, as is the region near the impurity anomaly.) The results overlap smoothly with the lattice fit obtained from the data below 35 K. The resultant C_{Latt}/T over the entire temperature range is shown in Fig. 1. The area between the data and C_{Latt}/T is the sum of entropies associated with $\gamma(T)$, with the FM transition of the Mn, and with the Nd ordering. This sum is 15.7 J/mol K, in reasonable agreement with $\Delta S = 15.4$ J/mol K, calculated for the independent ordering of the two magnetic subsystems. This calculated value is the sum of $\Delta S_{Nd} = 3.9$ J/mol K and $\Delta S_{Mn} = 11.5$ J/mol K, where ΔS_{Mn} is calculated using the result obtained from the M data that only ~90% of the sample is in the CMR phase.

Table 1
Parameters characterizing $Nd_{0.67}Sr_{0.33}MnO_3$

Term	Symbol	$H = 0$ T	$H = 9$ T	Units
Hyperfine	D	10.0	~2.4	10^{-3} J K/mol
γ	γ	25.00	18.00	10^{-3} J/mol K^2
Lattice	B_3	2.071	2.071	10^{-4} J/mol K^4
	B_5	2.519	2.519	10^{-7} J/mol K^6
	B_7	−2.818	−2.818	10^{-10} J/mol K^8
	B_9	8.126	8.126	10^{-14} J/mol K^{10}
Schottky	n_1, n_2	0.05, 0.50	0.02, 0.53	–
	δ_1, δ_2	4.4, 9.6	12.5, 18.7	K

While there is arbitrariness in the technique used to determine C_{Latt} and ΔS, two useful conclusions can be drawn: (1) The large low-T value of γ for NSMO probably results from some kind of superexchange interaction between the Mn and Nd systems rather than from the conduction electrons. This conclusion is supported by the field-dependence of γ as well as by resistivity data on the $x = 0.21$ sample. These data indicate this CMR is an insulator below T_c even though its low-T C/T data also have a $\gamma \sim 0.025$ J/mol K^2 [1]. (2) The experimental and theoretical ΔS are essentially equal providing that the former includes the entropy associated with $\gamma(T)$. This inference provides support for the idea that γ is not due solely to the conduction electrons.

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