Specific heat of $La_{1.2}Sr_{1.8}Mn_2O_7$

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The specific heat of a single crystal of the layered perovskite $La_{1.2}Sr_{1.8}Mn_2O_7$ has been measured for $83 < T < 290$ K. A high, narrow peak associated with the ferromagnetic ordering of the Mn^{3+}-Mn^{4+} ions is observed to have a maximum at $T_c = 115.57$ K, in agreement with magnetization, neutron scattering, and resistivity measurements. A second, hysteretic, peak at 260 K is also observed. An estimate is made of the substantial magnetic entropy removed by cooling the crystal from 290 K to T_c. [S0163-1829(99)11533-9]

Moritomo *et al.* showed that a single crystal of the layered compound $La_{1.2}Sr_{1.8}Mn_2O_7$ (2dLSMO) exhibits colossal magnetoresistance (CMR).[1] 2dLSMO, which is an $n=2$ member of the Ruddelesden-Popper series $(La,Sr)_{n+1}Mn_nO_{3n+1}$, is thought to have quasi-two-dimensional magnetic characteristics below the ferromagnetic (FM) ordering temperature, T_c, because the FM, metallic sheets are separated by nonmagnetic, SrO insulating barriers. The chemical formula can be represented in the familiar form: $SrO[La_{(1-x)}Sr_xMnO_3]_n$. Single crystals of this material have also been grown at Argonne and have been used in neutron-diffraction studies of structural response at the phase transition as well as for magnetic and resistivity measurements.[2–7] These neutron studies have provided evidence that the magnetic correlations are two dimensional above T_c, and are ferromagnetic although influenced by competition with antiferromagnetic interactions.[6–8] Specific-heat measurements can offer additional support for the view that the two-dimensional (2D) character of 2dLSMO is an important determinant of the compound's magnetic properties, since specific-heat data on other 2D FM materials confirm theoretical predictions that a larger fraction of the magnetic entropy is removed above T_c in the 2D than in the 3D case.[9] Specific-heat data on 2dLSMO can also be important in establishing whether the transition is truly second order, a question that arises because there is some evidence that the 2D correlation length does not diverge at T_c.[7] As discussed below, the specific-heat data show that a sizable specific-heat anomaly is present and is consistent with, but not unambiguous proof of, a 2D phase transition at $T_c \approx 115.6$ K. The data also reveal the existence of a hysteretic transition at ~260 K. In addition the specific-heat results make it possible to estimate the magnetic entropy removed by cooling the sample from room temperature to ~80 K.

SPECIFIC HEAT RESULTS

We have made specific-heat (C) measurements on the same 120-mg single crystal from Argonne that was used in a number of the other studies.[2–7] We employed a continuous heating (typically 5–10 mK/sec) technique that was tested by measuring the heat capacity of a 385-mg sample of high-purity copper as well as by making measurements at different heating rates. Changing the heating rate by a factor of 2 did not affect the data. These measurements gave results within 1% of the published results for Cu.[10] The heat capacity of our 2dLSMO crystal is $\sim\frac{1}{3}$ that of the copper sample. Thus, the data for the crystal should have an accuracy of ~3–4 %, even though the crystal-heat capacity was only 5–9 % of the total measured heat capacity (sample plus addenda) over the range of the measurements, $83 < T < 290$ K. The results for $T < 147$ K are shown in Fig. 1, both as C vs T [Fig. 1(a)] and as C/T vs T [Fig. 1(b)]. For clarity only, a small fraction of the actual data are included in these and the other figures. The temperature at which the maximum in the specific-heat anomaly occurs, ~115.6 K, is consistent with a Curie temperature, $T_c \approx 116$ K, obtained from the observed onset of the spontaneous magnetization.[5] The anomaly has a shape similar to that observed in specific-heat data on $La_{(1-x)}Ca_xMnO_3$ (3dLCMO) for $x=0.2$ (Ref. 11) and 0.33,[12] although those CMR's, unlike the 2dLSMO, are thought to be three dimensional in character.

Because of the narrow width of the 2dLSMO specific-heat anomaly, attempts to fit the data in the region below 147 K are not strongly dependent upon assumptions concerning the T dependence of the lattice specific heat $C_{\rm lat}$ in this region. It is adequate to represent $C_{\rm lat}$ as being linear in T, or in the reduced temperature ε, where $\varepsilon = T/T_c - 1$. Rather surprisingly, it was found that the data could be represented reasonably well [see the fit in Fig. 1(a)] by $C = C_{\rm lat} + C_{\rm mag} = (L_0 + L_1\varepsilon) + A_0/(\varepsilon^2 + \delta^2)$. That is, the magnetic anomaly is approximated by a Lorentzian function with amplitude A_0 and half-width δ. T_c and the constants L_0, L_1, A_0, and δ are obtained from a nonlinear least-squares (NLS) fit to the data. While a theoretical interpretation of this empirical Lorentzian representation of the magnetic anomaly is possible (see below), it is important to examine the data for evidence of critical behavior, especially since recent neutron-scattering data on the crystal[7] show that below T_c, M varies as $|\varepsilon|^\beta$ for $0 < |\varepsilon| < 0.1$, where $\beta = 0.13 \pm 0.01$ and $T_c = 111.7 \pm 0.2$ K. This is the predicted value for the critical exponent β for a 2D Ising ferromagnet, even though the magnetic fluctuations observed by neutron scattering[6,7] indicate that the system is

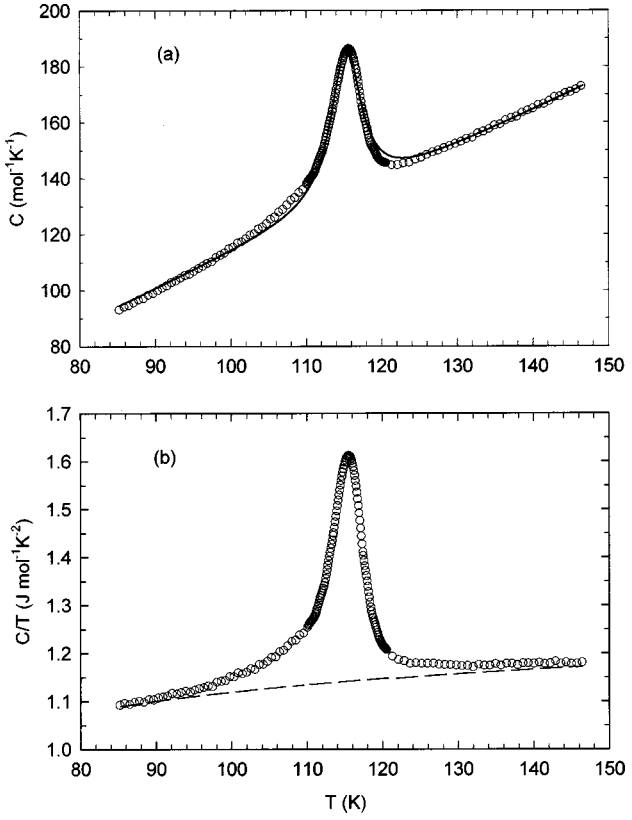

FIG. 1. (a) C vs T for $La_{1.2}Sr_{0.8}Mn_2O_7$. The solid line is obtained from an empirical fit to the data of the form $C=C_{\rm lat}+C_{\rm mag}$, where $C_{\rm mag}$ is a Lorentzian function of the reduced temperature $\varepsilon=(T/T_c-1)$. See text for details. (b) C/T vs T over the same temperature range, $85<T<147$ K. The dashed line is $C_{\rm lat}$ as obtained from the same fit.

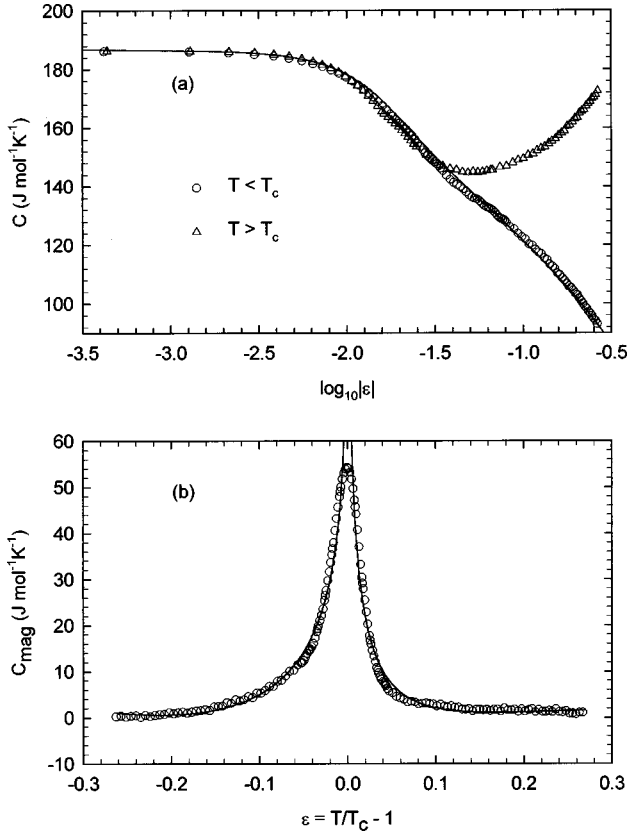

FIG. 2. (a) C vs $\log_{10}|\varepsilon|$. The solid line passing through the data for $T<T_c$ is obtained by fitting the data for $85<T<147$ K to $C=A\ln|\varepsilon|(1+B|\varepsilon|^x)+K_0+K_1\varepsilon$. See text for details. (b) $C_{\rm mag}$ vs ε where $T_c=115.57\pm0.08$ K and $C_{\rm mag}=C-C_{\rm lat}$. The solid line is obtained by subtracting the same estimate of $C_{\rm lat}$ from $C=A\ln|\varepsilon|(1+B|\varepsilon|^x)+K_0+K_1\varepsilon$.

in the 2D-XY class, a class for which β is undefined except by numerical finite-size scaling calculations.[13] Nevertheless, the experimental value of β is consistent with the two-dimensional nature of the transition. In the 2D-Ising model the critical exponent for the specific heat, α, should be ≈0. In this case $C_{\rm mag}$ can be written

$$C_{\rm mag}=C_{\rm crit}(1+B|\varepsilon|^x)+D, \tag{1}$$

where $C_{\rm crit}$ can be represented either by $A\ln|\varepsilon|$ or by $(A/\alpha)(|\varepsilon|^\alpha-1)$, two forms that are equivalent in the limit $\alpha\rightarrow0$. So long as $x>0$, the term $(1+B|\varepsilon|^x)$ on the right side of Eq. (1) represents a nonsingular correction to scaling. Clearly, for sufficiently small $|\varepsilon|$, $C_{\rm lat}$ is constant and $C_{\rm mag}\rightarrow C_{\rm crit}+D$. Therefore a graph of the measured specific heat C vs either $\ln|\varepsilon|$ or $\log_{10}|\varepsilon|$ should yield a straight line. For larger values of $|\varepsilon|$, departures from linearity will result from the correction term as well as from the temperature dependence of $C_{\rm lat}$. For sufficiently large $|\varepsilon|$, Eq. (1) will no longer apply.

It would be surprising in three dimensions, but not in two dimensions, to find a critical region that extends to as high a value of $|\varepsilon|$ as 0.1. In fact, since the neutron-scattering results below T_c show that $M\propto|\varepsilon|^\beta$ for $|\varepsilon|\leqslant0.1$, we might expect that $C_{\rm mag}$ can be described by Eq. (1) for $|\varepsilon|<0.1$. A plot of C vs $\log_{10}|\varepsilon|$ for $|\varepsilon|<0.27$ is shown in Fig. 2(a). Although the data for $\varepsilon<0$ and $\varepsilon>0$ very nearly coincide for $|\varepsilon|<\sim0.03$ (i.e., for $\log_{10}|\varepsilon|\lesssim-1.5$), they obviously depart from a linear dependence on $\log_{10}|\varepsilon|$ as $|\varepsilon|$ decreases below ~0.01. This departure can be understood in terms of a spread in T_c values over the sample. The line through the data in Fig. 2(a) was calculated assuming the sample is characterized by a Gaussian distribution in T_c with a ''half-width'' of 1.3 K. This assumption is consistent with the neutron-scattering data used to obtain the value for the critical exponent β,[7] providing the latter are also analyzed assuming a Gaussian distribution of T_c values.[14] Such an analysis hardly alters the value of β, but changes T_c from 111.7 ± 0.1 K to 113.1 ± 0.1 K and gives a half-width ~1.6 K. Similarly, as Fig. 2(a) shows, the specific-heat data are essentially linear in $\log_{10}|\varepsilon|$ over the interval $-0.15<\varepsilon<-0.01$, and are therefore consistent with the neutron-scattering results. However, as Fig. 2(a) also shows, the data for $T>T_c$ are linear in $\log_{10}|\varepsilon|$ only over a small interval. This result may indicate that corrections to scaling are more important above T_c than below.

For $T<147$ K it is possible to carry out an NLS fit to the data of the form

$$C=A\ln|\varepsilon|(1+B|\varepsilon|^x)+K_0+K_1\varepsilon. \tag{2}$$

The value of T_c, as well as values of the constants, are obtained from the fit and are listed in Table I. In the fit, the values of the constants A, B, K_0, and K_1 are allowed to take

TABLE I. Values for the constants in $C=A\ln|\varepsilon|(1+B|\varepsilon|^{x})+K_0+K_1\varepsilon$, where $\varepsilon\equiv T/T_c-1$. Fits to the data (see text) give $T_c=115.57\pm0.08$ K. A, B, K_0, and K_1 have units of J mol^{-1} K^{-1}.

	$\varepsilon<0$ $(T<T_c)$	$\varepsilon>0$ $(T>T_c)$
A	-20.32 ± 0.25	-25.65 ± 0.36
B	0.0 ± 0.3	-4.18 ± 0.19
K_0	80.71 ± 0.95	237.5 ± 9.1
K_1	52.90 ± 2.97	32.53 ± 14.03
x		0.22 ± 0.01

on different values above and below T_c, whereas x is assumed fixed over the entire region. It is of interest to note that the fit gives $B=0$ for $T<T_c$. The term $(K_0+K_1\varepsilon)$ contains possible contributions from $C_{\rm mag}$ as well as from $C_{\rm lat}$, hence the allowance for a change in the values of the constants at T_c. Allowing K_1, as well as K_0, to change at T_c is tantamount to assuming that the right-hand side of Eq. (1) contains an additional term, $E\varepsilon$. Such a term is an additional correction to scaling that becomes sizable as $|\varepsilon|$ increases. It is not possible to find a unique separation of $(K_0+K_1\varepsilon)$ into lattice and magnetic contributions. However, if we assume that $C_{\rm lat}=L_0+L_1\varepsilon$ over the temperature range $-0.27<\varepsilon<0.27$ $(85<T<147$ K), we can use the values for L_0 and L_1 obtained from the Lorentzian fit described above (132 and 149 J mol^{-1} K^{-1}, respectively) to compare an ''experimental'' determination of $C_{\rm mag}=C-C_{\rm lat}$ with the results obtained by subtracting $C_{\rm lat}$ from the NLS fit to C. The results are shown in Fig. 2(b). As is evident, the fit is reasonably good, except in the vicinity of $|\varepsilon|\approx0$, where the experimental peak is rounded. This rounding may arise from sample inhomogeneities that lead to variations in T_c over the sample volume, as discussed above. Although Figs. 2(a) and 2(b) are graphs of the measured C and the estimated $C_{\rm mag}$, respectively, they show essentially the same data but emphasize very different temperature regions.

It is also possible to fit the data using the form $C=(A/\alpha)(|\varepsilon|^{\alpha}-1)(1+B|\varepsilon|^{x})+(K_0+K_1\varepsilon)$. However, this form requires an additional fitting parameter, α, and does not noticeably improve the fit. Moreover, the value of α depends upon the temperature region used for the fit. It varies between $\alpha\approx0.002$ (consistent with $C_{\rm cr}\propto\ln|\varepsilon|$) for the region $|\varepsilon|<0.05$ and $\alpha\approx0.33$ for $|\varepsilon|<0.15$, thus giving an overall estimate of $\alpha\approx0.17\pm0.17$. On the other hand, it is easily shown that the data are inconsistent with an assumption that the specific-heat anomaly arises solely from 2D or 3D Gaussian fluctuation effects. It is somewhat surprising that the value of T_c obtained from fitting the specific-heat data, 115.57 ± 0.08 K (where 0.08 K is the statistical uncertainty in T_c obtained from the fit), differs from the value of 113.1 ± 0.2 K obtained from a fit to the neutron-scattering data,[14], although these data, like those in Ref. 5, indicate that the spontaneous magnetization begins to rise from zero at $T\approx116$ K.

We have noted above that the anomaly can also be represented with a Lorentzian dependence on ε. This representation can be understood if we assume that the range in $|\varepsilon|$ over which critical fluctuations exist is very small, say $0<|\varepsilon|<10^{-4}$. In this case the critical contribution in the experimentally accessible temperature region, $10^{-4}<|\varepsilon|$, is essentially a delta function centered on T_c as long as the sample is characterized by a single value of T_c. However, if there is a distribution in T_c, the critical region is broadened. The solid line in Fig. 1(a) is obtained by assuming that the distribution is a Lorentzian characterized by amplitude A_0 and ''half-width'' δ. The fit gives $\delta\approx0.02$ corresponding to a spread in values of T_c of $\sim\pm2$ K. It should also be noted that a model in which $C_{\rm mag}$ is essentially a Lorentzian-broadened spike is experimentally indistinguishable from a broadened first-order phase transition, except that effects of the latter transition might be expected to show a dependence upon the rate at which the sample is heated through the transition—a dependence that is *not* evident in the experiments.

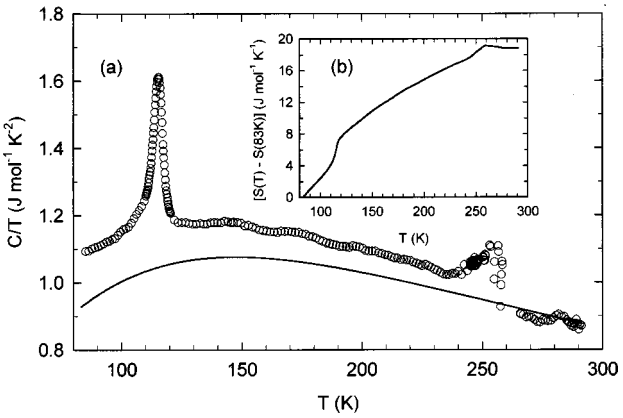

FIG. 3. (a) C/T vs T for $83<T<290$ K. The solid line is an estimate of $C_{\rm lat}$ obtained from Ref. 15. (b) Entropy $[S(T)-S(83\,{\rm K})]$ vs T.

MAGNETIC ENTROPY

If we assume that $C_{\rm lat}=132+149\varepsilon$ J mol^{-1} K^{-1}, we can estimate the entropy associated with ferromagnetic ordering of the Mn moments simply by calculating the area that lies between the anomaly and the dashed curve representing $C_{\rm lat}/T$ in Fig. 1(b). This area amounts to ~2 J mol^{-1} K^{-1}, less than 10% of the predicted value, $\Delta S_{\rm mag}=2R(0.6\ln5+0.4\ln4)=25.3$ J mol^{-1} K^{-1}. While this low value is consistent with that obtained from similar observations on other CMR's,[11,12,15] it is inconsistent with the expectation that short-range ordering above T_c should remove 25% or more of the entropy when a magnetic material is cooled from high temperatures to T_c.[16] In order to obtain a more realistic estimate of the magnetic entropy, it is necessary to have an alternate method for estimating $C_{\rm lat}$ for 2dLSMO. Lacking data for a nonmagnetic analog of 2dLSMO, we assume that $C_{\rm lat}$ can be approximated by scaling a recent estimate of the harmonic lattice contribution to $C_{\rm lat}$ for $Nd_{0.67}Sr_{0.33}MnO_3$ (Ref. 15) with a factor of 12/5, the ratio of the numbers of atoms/unit cell for the two compounds and by assuming that the anharmonic contributions are the same for the two CMR's. The results of this approximation for $C_{\rm lat}$ are shown in Fig. 3(a) where the data and $C_{\rm lat}$ are shown in a C/T vs T plot for $83<T<290$ K. The anomaly in the region $240<T<260$ K will be discussed below. Here we emphasize the fact that $C_{\rm lat}$ is essentially the same as $C_{\rm meas}$ for $T>260$ K, a result that provides the principal justification for this esti-

mate. The magnetic entropy removed from the sample by cooling it from ~290 to 83 K can then be obtained from the area between the data and $C_{\rm lat}/T$ in Fig. 3(a). This entropy is graphed in Fig. 3(b). The ΔS between ~290 K and T_c is ~12 $\rm J\,mol^{-1}\,K^{-1}$ or almost 50% of the predicted magnetic entropy.

This new estimate gives $C_{\rm lat} \approx 120 + 147\varepsilon\ \rm J\,mol^{-1}\,K^{-1}$ in the temperature region $|\varepsilon| < 0$, as compared to our earlier estimate $C_{\rm lat} = 132 + 149\varepsilon$. The similarity of these two approximations means that a calculation of $C_{\rm mag}$ from $(C - C_{\rm lat})$ with the new estimate will not alter the shape of the anomaly near T_c. Roughly speaking, the new estimate simply shifts the results shown in Fig. 2(b) upward by ~12 $\rm J\,mol^{-1}\,K^{-1}$, and therefore increases considerably the estimate of the magnetic entropy change in this region. Thus, both the shape of the anomaly and the crude estimate of the magnetic entropy removed by cooling from room temperature to T_c are consistent with, but by no means unambiguous evidence for, the 2D character of the ferromagnetic transition in 2dLSMO.

HIGH-TEMPERATURE RESULTS

At temperatures above ~140 K, the sample heat capacity becomes an increasingly small fraction of the measured heat capacity. Moreover, radiational heat leaks between the sample assembly and its surroundings make the continuous heating technique somewhat less reliable. It is likely the small ''ripples'' in the data in Fig. 3(a) in the region $140 < T < 235$ K are artifacts of the measuring technique, since a smoothly varying function representing the addenda heat capacity and comprising more than 95% of the measured C has been subtracted from the data. Therefore, all uncertainties and systematic errors associated with the continuous heating method appear in a graph of sample specific heat vs temperature. Similarly, the apparent rise in C for $240 < T < 260$ K must be regarded with some caution, especially since multiple sets of measurements made in this temperature region, unlike the data near 115 K, varied from run to run. They showed a good deal of scatter, even in a given run, and also a dependence on the rate at which the sample was cooled through this region before specific-heat measurements were made. Nonetheless, all measurements made on the 2dLSMO crystal showed a specific-heat anomaly in this region, whereas no such evidence was present in the measurements made on the copper sample or on the addenda alone. Thus, this 260 K anomaly appears to be characteristic of the sample and not of the measuring procedure. This behavior correlates well with recent neutron-scattering measurements on the same crystal[17] which show anomalous increases in the scattering intensity above 240 K that depend upon the rate of sample heating or cooling. The observation of hysteretic behavior close to 250 K in both the scattering and specific-heat data indicates that this is a bulk phenomenon. It is possible that the rate at which magnetic entropy is removed by the formation of magnetic polarons increases markedly in the interval 240–260 K. Such an effect could give rise to the specific-heat anomaly shown in Fig. 3(a). However, it might be expected that evidence for the formation of such polarons would also be present in the static magnetization data, an expectation that is not supported by magnetization measurements on this sample.[5] The low-temperature ''tail'' of this 260-K peak (a slow decrease of $C_{\rm mag}$ with decreasing T) would also tend to compensate for a high-temperature ''tail'' of the 115-K anomaly (a slow decrease of $C_{\rm mag}$ with increasing T), thereby yielding the almost temperature independent $C_{\rm mag}$ that can be inferred from Fig. 3(a) over the interval $150 < T < 240$ K.

SUMMARY

Specific-heat measurements on a single crystal of $La_{1.2}Sr_{1.8}Mn_2O_7$ provide clear evidence for a ferromagnetic phase transition with $T_c \approx 115.6$ K. Except for very small $|\varepsilon|$, where evidence of sample inhomogeneity is present, the observed shape of the anomaly is consistent with a critical fluctuation peak, planar XY or 2D Ising. A second, unexpected, anomaly, is also evident in the temperature region $240 < T < 260$ K. This anomaly is highly hysteretic, a behavior that is mirrored in diffuse neutron-scattering experiments on the same crystal. By subtracting a rough representation of $C_{\rm lat}$ from the data, it can be inferred that a sizable fraction of the magnetic entropy associated with the ordering of the Mn^{3+}-Mn^{4+} ions in $La_{1.2}Sr_{1.8}Mn_2O_7$ is removed in cooling the sample from room temperature to T_c.

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