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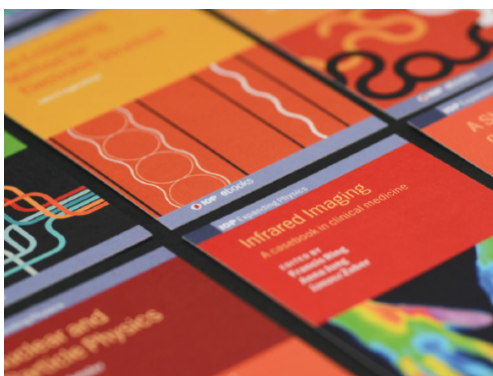
Heat capacity of a mixed-valence manganese oxide Pb$_3$Mn$_7$O$_{15}$

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Abstract
We present the results of a heat capacity study of Pb$_3$Mn$_7$O$_{15}$ single crystals with
approximately equal concentrations of Mn^{3+} and Mn^{4+} ions. In the temperature interval
between 210 and 260 K, an excess heat capacity of nonmagnetic origin, most likely associated
with the process of charge localization, has been observed. Also, three pronounced anomalies
corresponding to the changes in a magnetic subsystem of the crystal have been observed in the
temperature dependence of the heat capacity. A broad hump near 150 K is related to the
formation of a short-range magnetic order. This process of short-range ordering is rather
prominent, considering the appreciable value of the entropy loss accompanying the change in
the magnetic state. A clear lambda-shaped peak at 70 K marks the onset of a long-range
antiferromagnetic order. Another anomalous contribution to the heat capacity of magnetic
origin has been revealed at temperatures below 20 K. This contribution is associated with a
magnetic transition of an unknown nature, which is also clearly evident in magnetization versus
temperature curves. The total magnetic contribution to the entropy deduced from the actual
experimental data over the entire temperature range is much smaller than is expected for a
completely ordered Mn spin system in the crystal. We suggest several possible reasons that may
account for this 'missing' entropy.

1. Introduction

Perovskite-like manganites, layered manganites of the
Ruddlesden–Popper series, and some other manganese oxides
where Mn ions are in the 3+/4+ mixed-valence state, have
been a popular subject of contemporary research due to their
fascinating properties involving the colossal magnetoresistance
(CMR), competing magnetic order, magnetic phase separation,
and charge and orbital ordering [1]. Along with active
experimental and theoretical investigations of known mixed-valence
oxides, many research groups have searched for novel
oxides of the Mn^{3+}/Mn^{4+} family.

Recently, we reported the magnetic properties of the
undoped Pb$_3$Mn$_7$O$_{15}$ single crystal whose parent composition

suggests approximately equal Mn^{3+} and Mn^{4+} concentra-
tions [2]. The observed anomalies in magnetization behavior
imply that over the temperature region 2–900 K, several
different magnetic phases are distinguished. Down to ∼250 K,
the crystal is in the paramagnetic state. Below this tempera-
ture, short-range antiferromagnetic ordering apparently starts
forming in the crystal, although a transition to the long-
range magnetic order occurs at 70 K. The magnetization data
suggested that the magnetic state below this transition is canted
antiferromagnetic with the moments lying in the basal plane
of the crystal. In addition, below 20 K the crystal undergoes
one more magnetic transition that corresponds, presumably, to
spin reorientation. A clearer understanding of the origin of the

magnetic phase transitions and the magnetic structure of the crystal in different temperature ranges is still lacking.

In this paper, we report the results of the heat capacity measurements performed on a $Pb_3Mn_7O_{15}$ single crystal, together with some additional magnetization measurements. The heat capacity study in a wide temperature range is of crucial importance for understanding the origin of the changes in the magnetic state of the crystal as well as possibly providing various fundamental parameters, such as the Debye temperature, density of states at the Fermi level, local magnetic field at the Mn site, etc [3, 4].

2. Experimental details

The $Pb_3Mn_7O_{15}$ single crystals were grown using the flux method reported previously [2]. In the same study, using both powder and single-crystal x-ray diffraction data, the crystal structure was reported. All the reflections were indexed by the hexagonal space group $P6_3/mcm$. However, the results of our recent study by high-resolution powder diffraction studies at the Swiss Light Source Material Science beamline suggest that a description using the orthorhombic space group *Pnma* with lattice parameters $a = 13.5513$ Å, $b = 17.1490$ Å, and $c = 10.0909$ Å could improve the structural model [5]. Within the new model, manganese ions are contained in the crystal with two oxidation states, Mn^{3+} and Mn^{4+} (in the ratio 4:3) and occupy nine crystallographically nonequivalent sites, each being coordinated by six oxygen atoms in the octahedral configuration. A detailed description of the synchrotron measurements and a comparison study of the two structural models will be published soon. It is to be noted that both models have the similar structural 'motif': the crystal structure consists of edge-sharing MnO_6 octahedra and the neighboring layers are linked by 'bridges' formed by pairs of face-sharing octahedra, i.e. the structure of $Pb_3Mn_7O_{15}$ has a pronounced layered nature.

The heat capacity measurements were performed in the temperature range 2–390 K using two fundamentally different calorimetric techniques. One of them is a homemade automated adiabatic calorimeter [6], which allowed us to determine an absolute value of the zero-field heat capacity of the sample with a mass of about 1.61 g with high accuracy. These experiments were carried out via discrete ($\Delta T = 1.0$–2.5 K) and continuous (the temperature variation rate $dT/dt \approx (0.1$–0.3) K min^{-1}) heating. The measurement accuracy depended on the heating regime and varied within the limits 0.1–0.3%. The other measurement tool used is the heat capacity option of a Physical Property Measurement System (PPMS, Quantum Design, USA) based on the relaxation technique, which allowed us to obtain information on the heat capacity behavior in zero and 70 kOe magnetic fields. The specific heat was measured using the PPMS in the temperature range from 2 to 350 K at zero and 70 kOe magnetic fields. The absolute accuracy of the data was better than 1% over the entire temperature range. The dc magnetization of the crystal was also determined using the PPMS.
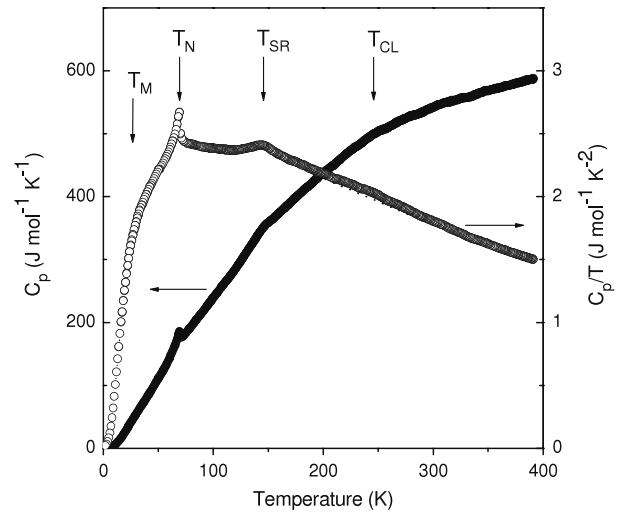

Figure 1. Heat capacity C_p (left axis) and C_p/T (right axis) as functions of temperature for the $Pb_3Mn_7O_{15}$ single crystal.

3. Results and discussion

The results of the heat capacity measurements obtained by the two aforementioned calorimetric methods were found to correlate well and are shown in figure 1 as C_p and C_p/T versus T plots. It must be noted that the $C_p(T)$ curves obtained both at zero field and in the presence of a magnetic field coincide with each other within the experimental error over the entire temperature range under consideration. In the temperature dependence of the heat capacity, near 70 K, one can clearly see a lambda-shaped anomaly associated with the onset of a long-range antiferromagnetic ordering. The temperature at which this peak occurs is in good agreement with the critical temperature T_N determined from the magnetization data [2]. The absence of hysteresis in the magnetization curves measured upon heating and cooling the samples suggests that the mentioned magnetic transition is of second-order type.

A broad hump in the temperature dependence of the heat capacity is also seen at around 150 K, just in the same temperature region where the pronounced maximum of the ac and dc magnetizations as a function of temperature is observed [2]. This suggests that the observed feature in the heat capacity is of magnetic origin and corresponds, apparently, to the onset of a cooperative effect in the magnetic subsystem of the crystal. At the same time, a detailed analysis of the results shows that the feature in the temperature dependence of magnetization is not related to the occurrence of a long-range magnetic order. This conclusion is consistent with the neutron diffraction data [7], which revealed the presence of magnetic peaks in diffraction patterns only below 70 K, whereas above this temperature no apparent magnetic contribution to the Bragg peaks was found. Presumably, at temperatures near 150 K, only a short-range antiferromagnetic order starts to develop.

At higher temperatures, the experimental $C_p(T)$ curve is not a smooth function, either, as one would expect in the case where only the lattice contributes to the total heat capacity. A broad diffuse hump near $T_{CL} \approx 250$ K in
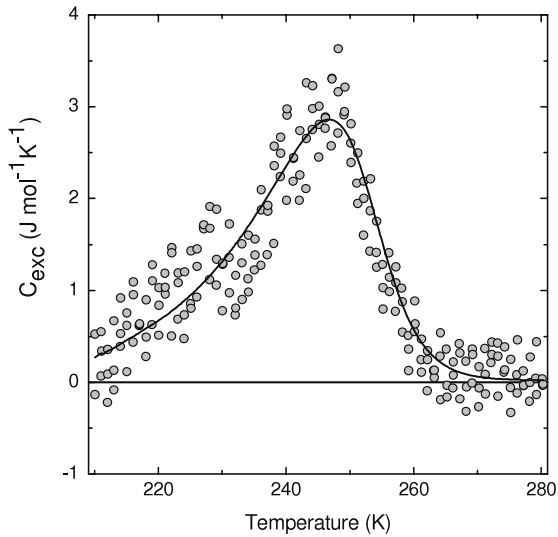
Figure 2. High-temperature heat capacity versus the T curve for the Pb$_3$Mn$_7$O$_{15}$ single crystal after subtracting a smooth background.

Figure 3. Temperature dependence of the lattice a-parameter for the Pb$_3$Mn$_7$O$_{15}$ single crystal.

the C_p/T versus T curve (figure 1) is seen. Subtracting a smooth background as the lattice contribution, we can more clearly see the excess contribution (C_{exc}) to the heat capacity (figure 2). We estimated the background by fitting a polynomial function to the C_p versus T curve in the temperature range, 180–300 K, sufficiently far from T_{CL}. The excess contribution to the heat capacity identified is not associated with any changes in the magnetic subsystem of the crystal. Indeed, no features are observed in these temperatures where the heat capacity anomaly occurs. However, we observed similar anomalies in both dc conductivity and the dielectric properties, at these temperatures [8]. The transport measurements indicate the presence of conductivity due to small polaron hopping occurring over the entire temperature range of 160–350 K. Moreover, near T_{CL} the character of the polaron conductivity changes: at $T > 250$ K the temperature dependence of the conductivity is described well by a nearest neighboring hopping model, whereas for $T < 250$ K, a variable range hopping model is found to be appropriate. Measurements of the dielectric properties show a step-like anomaly in the dielectric constant and a peak of dielectric loss at temperatures near T_{CL}. Such a behavior is typical for the charge relaxation process where the polarons are localized at the lattice sites [9]. Since the formation of small polarons inevitably induces a lattice distortion locally, one would expect that the polaron ordering may result in a cooperative lattice distortion. We examined the changes in the lattice parameters by a conventional x-ray diffraction technique. Figure 3 shows the temperature variation of the lattice parameter a determined from the analysis of the temperature dependence of the single-crystal reflection (6, 0, 0). One can see an irregular change in the lattice parameter a in the temperature interval where the transport and dielectric properties, as well as the heat capacity, reveal the anomalies. Apparently, the polarons in the crystal under study are formed due to the presence of the Mn^{3+} and Mn^{4+} ions occupying equivalent sites. Thus, the excess contribution to the heat capacity near T_{CL} may be attributed to
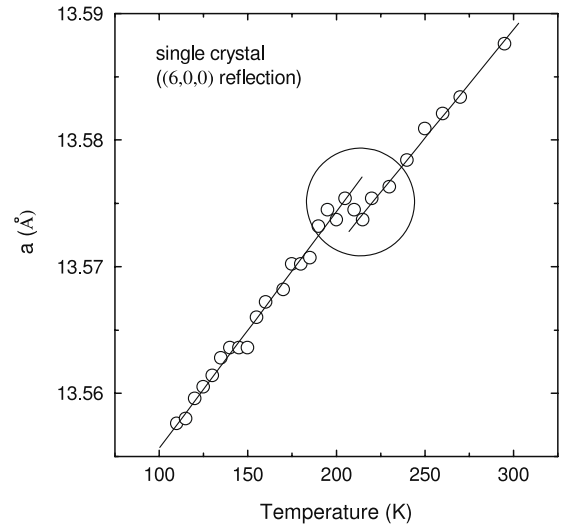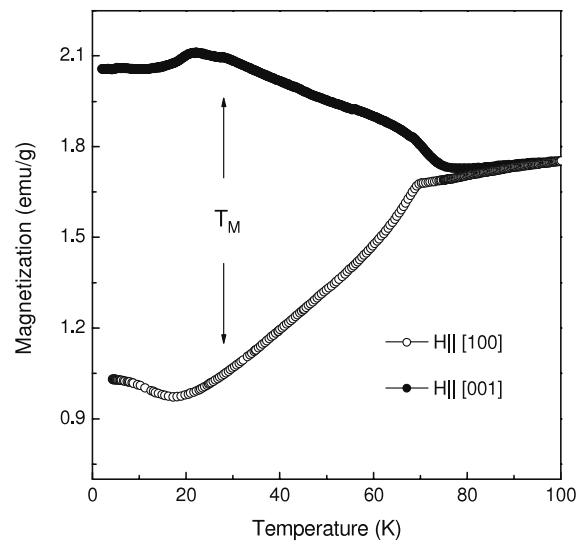

Figure 4. Magnetization versus temperature curves measured along [001] and [100] crystallographic axes at an applied field of 70 kOe for the Pb$_3$Mn$_7$O$_{15}$ single crystal.

the process of charge ordering in the system of the Mn^{3+}/Mn^{4+} ions in the crystal. The entropy associated with the change in the electronic subsystem, calculated as $S_{exc} = \int (C_{exc}/T)\,\mathrm{d}T$, amounts to nearly 0.32 J mol^{-1} K^{-1}. In order to draw a more definite conclusion about the nature of the observed anomalies near T_{CL} additional experiments are required.

Let us now examine the low-temperature region $T < T_N$ where the crystal is in a long-range magnetically ordered state. There are no features evident in the temperature dependence of the heat capacity. Note, however, that we observe fairly strong changes in the magnetization behavior at temperatures below $T_M \approx 30$ K (figure 4). A feature develops both at high and low magnetic fields applied along any principal crystallographic axis. This indicates that the crystal undergoes a magnetic transition. In our previous report [2], we assumed this feature

was due to a spin-reorientation transition. However, other variants, for instance, the coexistence of two weakly coupled magnetic subsystems in the crystal: one being ordered at T_N and the other starting to order magnetically only below T_M are also possible. More information on the origin of the observed changes in the magnetic state can be obtained by analysis of the neutron diffraction data [5]. In any case, considering the different contributions to the heat capacity at low temperatures, we should not exclude the possibility of the excess contribution to the heat capacity arising from the change in the magnetic subsystem of the crystal below T_M.

Generally, in order to use the heat capacity data in analyzing the magnetic properties and possible magnetic transitions in the crystal, we have to evaluate the magnetic contribution C_{mag} from the actually measured total heat capacity C_p. The heat capacity data are usually simulated under the assumption that C_p involves several distinct contributions:

$$C_p = C_{lat} + C_{elec} + C_{Sh} + C_{hyp} + C_{mag}.$$

The lattice contribution C_{lat} arises from phonons and since no structural phase transitions occur within the temperature range of interest, this contribution may be estimated, for example, in the framework of the Debye model. The electronic term C_{elec} corresponds to free charge carriers in the sample. This contribution can be neglected because of the very low electrical conductivity of the crystal in the temperature range where we observe the heat capacity anomalies associated with the magnetic contribution. The heat capacity may also include Schottky and hyperfine terms originating from the splitting of crystal-field ground state multiplets in some ions and the local magnetic field at the Mn nucleus due to electrons in unfilled shells, respectively. However, the electronic structure of the ions in the crystal excludes the Schottky-like contribution from consideration. The hyperfine contribution becomes noticeable only at very low temperatures (<3 K) and is adequately described by the expression $C_{hyp} = \alpha/T^2$.

In view of the aforesaid, the isolation of C_{mag}, in fact, is reduced to the suitable estimation of C_{lat}, in our case. The lattice contribution can be obtained by fitting the actual heat capacity in the temperature regions where the contributions associated with changes in the electronic and magnetic states vanish from the C_p data and then extrapolating the calculated C_{lat} to the entire temperature region of interest. In this approach, however, some difficulties arise. Indeed, it is obvious from our data that the anomalous contributions to C_p are expected to be associated with the magnetic and electronic subsystems within the entire temperature range under study. We attempted to extract the intervals in the $C_p(T)$ curve where the anomalous contributions may be neglected and then approximated them by a single Debye function. This procedure gave no satisfactory result. Application of a many Debye model [10], justified in the case when a compound contains atoms greatly differing in mass, also did not lead us to any physically feasible result. All the fits performed gave the values of entropy associated with the changes in magnetic state $S_{mag} = \int C_{mag}/T \, dT$, much larger than
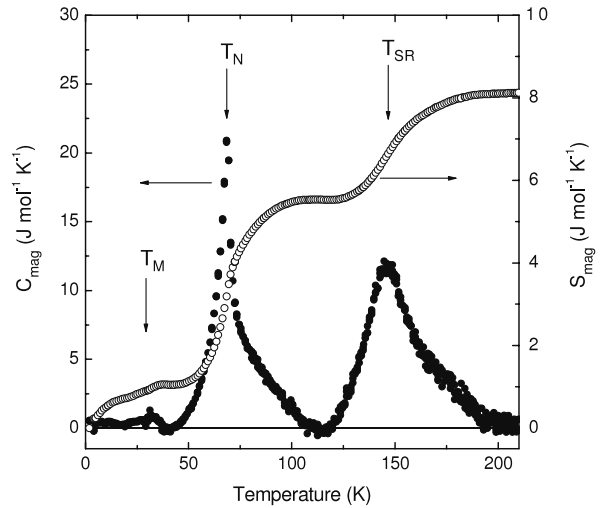

Figure 5. Temperature dependence of the magnetic contribution to the heat capacity C_{mag} (left axis) and the magnetic entropy S_{mag} (right axis).

$S_{Mn} = 4/7R \ln(2S_{Mn^{3+}} + 1) + 3/7R \ln(2S_{Mn^{4+}} + 1) = 12.47$ J mol^{-1} K^{-1} expected from the Mn spin system of the crystal, assuming a 4/3 ratio of the Mn^{3+} and Mn^{4+} ions.

Nevertheless, in order to obtain some information on the integral characteristic of the magnetic transitions, we made an attempt to estimate the nonmagnetic contribution by fitting a polynomial to the C_p versus T curve at temperatures far away from any anomalies in the data. We used a polynomial with powers empirically defined as $C_p(T) = a_{-2}T^{-2} + a_1T + a_2T^2 + a_3T^3 + a_4T^4 + a_4T^5$ [11]. Then, a smooth C_p background calculated in this way was subtracted from the actual experimental data, and the resulting dependence was used for further evaluation of the magnetic contribution to the heat capacity. The temperature dependence of C_{mag} and the corresponding magnetic entropy S_{mag} are depicted in figure 5. As seen in the figure, the slope of the $S_{mag}(T)$ curve changes strongly near the temperatures T_N and T_{SR}, corresponding to the transition to the antiferromagnetic long-range ordered state and to the occurrence of a short-range magnetic order, respectively. The entropy caused by the change in magnetic state near T_{SR} amounts roughly to 2.6 J mol^{-1} K^{-1}; comparable to the entropy value 4.5 J mol^{-1} K^{-1} corresponding to the long-range antiferromagnetic ordering at T_N. This fact may be an indication of the formation of a state with rather well-developed local magnetic ordering. A noticeable magnetic contribution to the heat capacity is also observed at temperatures near T_M. The amount of entropy that may be associated with the observed magnetic transition is equal to 1 J mol^{-1} K^{-1}. These results suggest that the transition occurring at temperature T_N does not result in a fully ordered spin state, rather the spin ordering process extends to temperatures much below T_M.

The total magnetic contribution to the entropy S_{mag} for the entire temperature range under study is 8.1 J mol^{-1} K^{-1}. This entropy value is smaller than S_{Mn} expected in the case of a complete ordering of the Mn spin system. There exist several ways of accounting for this 'missing' magnetic

entropy. One of the possible explanations is that a certain entropy amount is yielded above the temperature range under consideration (>210 K) due to the presence of the short-range magnetic correlations. However, the total amount of the missing entropy can hardly be accounted for in such a way. Indeed, the deviation of magnetic susceptibility from Curie–Weiss behavior becomes apparent only below 250 K and down to 200 K it has a negligible value. The observed excess contribution to the entropy in the temperature region 210–260 K reaches only 0.32 J mol^{-1} K^{-1}, which in accordance to our above conclusion, is of nonmagnetic origin. Another possible way to account for the missing entropy is to make an assumption that the transition to the fully ordered antiferromagnetic state is incomplete down to the lowest temperatures available in our experiments. Finally, the problem of the missing entropy most likely originates from the imperfection of the extraction of the nonmagnetic regular contribution from the actual heat capacity data. Indeed, the estimation of the background by fitting an empirical polynomial is only a rough approximation. A better solution to the problem would be to obtain the lattice contribution by measuring the heat capacity of an isomorphous nonmagnetic compound. Unfortunately, there are no nonmagnetic analogs to $Pb_3Mn_7O_{15}$.

4. Conclusion

We have investigated the heat capacity of the mixed-valence manganese oxide $Pb_3Mn_7O_{15}$ over the extended temperature range 2–350 K. We have paid special attention to the analysis of the heat capacity and other thermodynamic characteristics related to the changes in a magnetic subsystem of the crystal. Unfortunately, an exact quantitative determination of these characteristics faces difficulties arising from uncertainty in the estimation of the real lattice contribution to the heat capacity. However, even a rough polynomial approximation of the lattice contribution has allowed us to examine qualitatively the changes in the magnetic state occurring in the crystal. The magnetic contribution to the heat capacity and the related entropy change are consistent with the magnetization data reported previously and in this paper. The analysis of the magnetic contribution to the entropy over the entire

temperature range under study has revealed the prominent character of the short-range magnetic ordering at temperatures well above T_N, at the same time, we observed the absence of a fully ordered magnetic state in the crystal down to the very low temperatures we investigated. Also, we have noted that the excess contribution to the heat capacity at high temperatures, nonmagnetic in origin, is apparently related to the process of the ordering of Mn^{3+} and Mn^{4+} ions in the crystal.

Acknowledgments

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