Low-field-induced magnetic entropy change in single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$

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LETTER TO THE EDITOR

Low-field-induced magnetic entropy change in single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$

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Abstract

In this work, the discovery of a large low-field-induced magnetic entropy change in single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$ with A-type layered antiferromagnetic structure is reported. The magnetic entropy changes reach values of 11.0 and 11.5 J kg^{-1} K^{-1} for field changes of 20 kOe along the *ab*-plane and *c*-axis, respectively. The large magnetic entropy change occurring near T_N was attributed to a low-field-induced antiferromagnetic $\leftrightarrow$ ferromagnetic phase transition. Our results provide a possibility for development of magnetic refrigerant substances that are operable with a permanent magnet rather than a superconducting one as the magnetic field source.

The magnetocaloric effect (MCE) is currently attracting considerable interest from both fundamental and practical points of view. A large MCE is required in order to improve the energy efficiency of magnetic refrigeration technology. To date, the highest magnetocaloric effect for a second-order transition is produced by the rare-earth element Gd and its ferromagnetic alloys with diverse structure of composition [1–3]. Since the discovery of the giant magnetic entropy change in $Gd_5Si_2Ge_2$ [4], MCEs have been extensively investigated in other series of compounds, such as Gd-based intermetallics [4–6], $LaFe_{13-x}(Al, Si)_x$ with $NaZn_{13}$-type structure [7, 8], $MnFeP_{1-x}As_x$ [9], $MnAs_{1-x}Sb_x$ [10], as well as perovskite-type ferromagnetic oxides [11–13], which demonstrate giant or very large magnetic entropy changes in an applied magnetic field of 70 kOe near the Curie temperature T_C. The giant or very large magnetic entropy changes in these magnetic materials suggest that they are expected to be potential candidates for use as magnetic refrigerants. However, before magnetic refrigeration becomes a viable cooling technology, one must reduce the applied magnetic field so as to allow the use of a permanent magnet instead of a superconducting magnet as the magnetic field source. Therefore, a very important task is to search for novel magnetic materials possessing giant low-field-induced MCEs.

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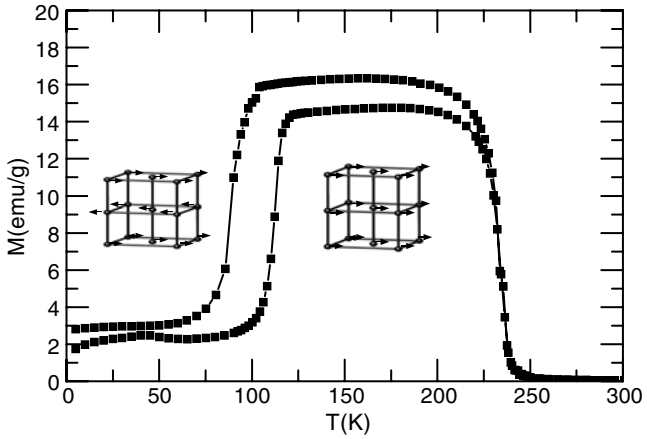

Figure 1. The temperature dependence of the magnetization in an applied field of 100 Oe along the easy magnetization *ab*-plane of single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$. The inset illustrates the layered magnetic structure (only Mn ions).

In the case of order–disorder magnetic phase transition, the existence of spin fluctuation above T_C generally requires a relatively large magnetic field to align the random magnetic moment and a large magnetic entropy change occurs often under high magnetic fields. Alternatively, for materials with layered antiferromagnetic (AFM) structure, if the interlayer AFM coupling is weak, a small magnetic field can trigger a transition from AFM order to ferromagnetic (FM) one and a large magnetic entropy change can be expected around Néel temperature T_N with a small field change. Previous neutron diffraction results confirmed that single crystals of $Nd_{1-x}Sr_xMnO_3$ with $x \simeq 0.5$ exhibit layered AFM structure [14, 15]. Below T_N the layered AFM $Nd_{0.47}Sr_{0.53}MnO_3$ crystal is metallic within the FM layers (*ab*-plane), while it is insulating along the AFM coupling direction (*c*-axis). A small magnetic field can induce both magnetic and structural phase transitions at T_N [16]. These considerations motivated us to investigate the magnetocaloric effect in perovskite manganites with layered AFM structure. Here, we report the discovery of a large low-field-induced magnetic entropy change in single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$ with A-type layered AFM structure.

$Nd_{0.47}Sr_{0.53}MnO_3$ single crystal was prepared using the Czochralski method at a pulling rate of 2 mm h^{-1}. First, polycrystalline $Nd_{0.47}Sr_{0.53}MnO_3$ was prepared by solid-state reaction from Nd_2O_3, $SrCO_3$ and $MnCO_3$. The oxides with purities higher than 99.9% were weighed in stoichiometric amounts, then mixed and prefired at 1073 K for 12 h. The ball-milled powder was pressed to 10 MPa and sintered at 1523 K for 24 h with 30% O_2 + Ar flowing. This procedure was repeated three times to ensure chemical homogeneity and full reaction. The polycrystalline $Nd_{0.47}Sr_{0.53}MnO_3$ powder obtained was finely ground and loaded into an Ir crucible. The loaded crucible was heated in an Ar atmosphere from room temperature to about 1800 K until the sample powder melted. All magnetization measurements were carried out with a Quantum Design SQUID magnetometer.

Figure 1 illustrates the temperature dependence of the magnetization in an applied field of 100 Oe along the easy magnetization *ab*-plane of single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$. In the low-temperature region, magnetizations in low fields are very small, corresponding to A-type layered AFM structure (illustrated in the inset of figure 1). With temperature increasing up to 102 K, a small magnetic field can trigger a transition from AFM order to FM order. With further increasing temperature, long-range-order FM correlations suddenly disappear at 230 K.

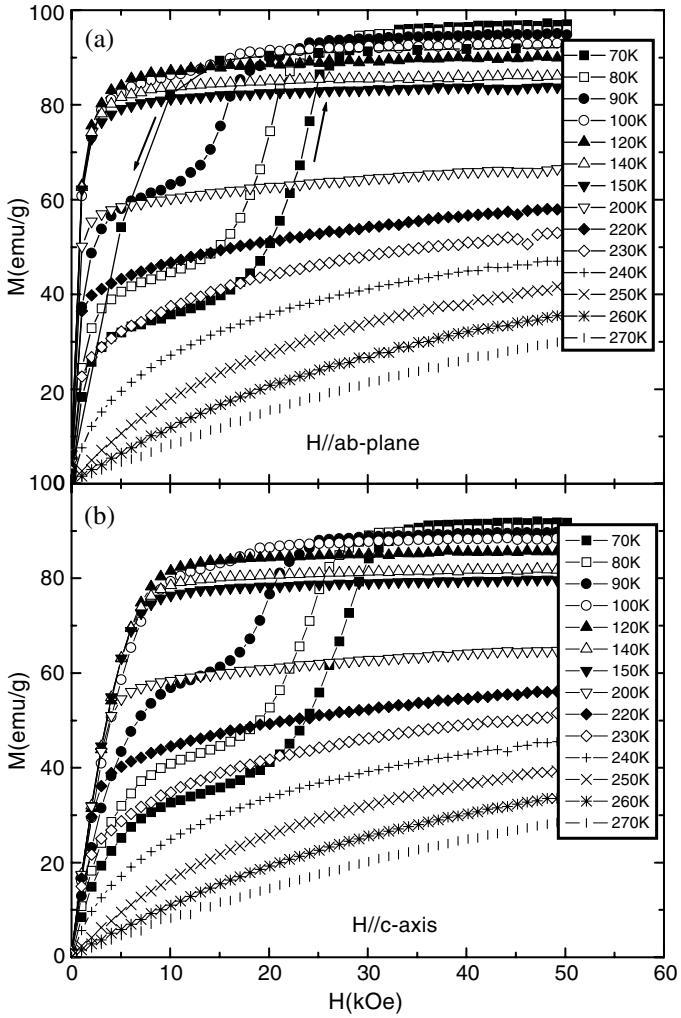

Figure 2. Isothermal magnetization curves at various temperatures measured in increasing and decreasing fields along the *ab*-plane (a) and the *c*-axis (b) of single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$.

With decreasing temperature, reversible thermomagnetization curves were observed near T_C. However, owing to the first-order nature of this FM $\longleftrightarrow$ AFM transition, the FM $\longleftrightarrow$ AFM transition occurs at lower temperature than that for increasing temperature, resulting in a thermal hysteresis near T_N. The sharp change in magnetization either at T_N or at T_C suggests that a large magnetic entropy change can be achieved around these transition points.

Figures 2(a) and (b) show the isothermal magnetization curves at various temperatures measured in increasing and decreasing fields along the *ab*-plane and *c*-axis of single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$, respectively. A slight magnetocrystalline anisotropy was detected between the *ab*-plane and *c*-axis. The low-temperature data show that the sample undergoes an AFM to FM transition at a certain critical field. The critical field for these transitions depend on the temperature as well as the direction of the field change (increasing and decreasing fields). At low field the small increase in magnetization may reflect the presence of a ferromagnetic region. With the applied field increasing up to the critical field, the spins in one layer flip

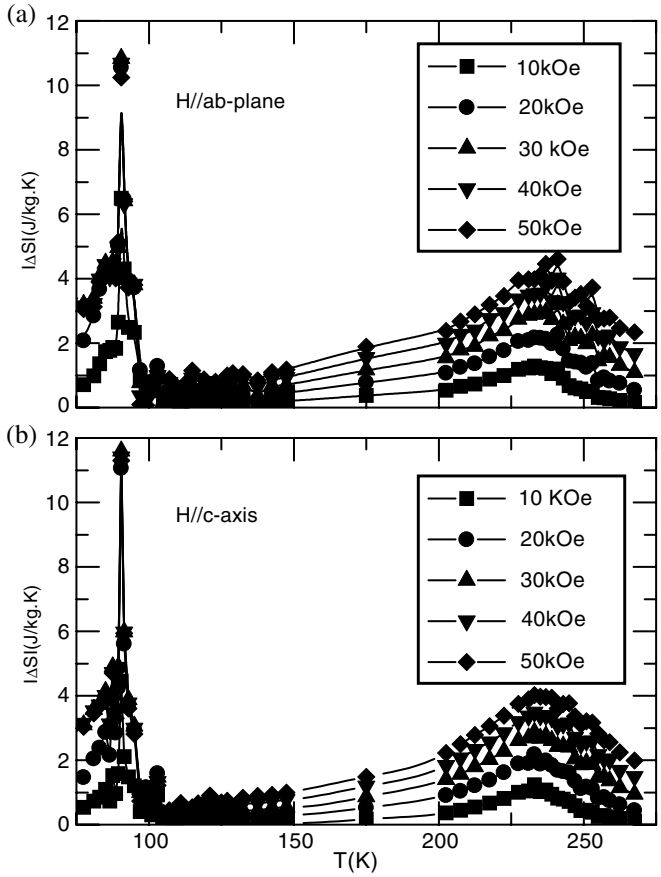

Figure 3. The temperature dependence of $|\Delta S_{\mathrm{M}}|$ in various applied fields for single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$ along the *ab*-plane (a) and *c*-axis (b).

in unison toward the direction of the applied field, resulting in a ferromagnetic order. In decreasing fields, the ferromagnetic orders collapse in lower fields to induce the transition. It is noteworthy that a relatively weak magnetic field induces a transition from the AFM state (low magnetic field) to the FM state (high magnetic field), suggesting that a large entropy can be induced by a weak field. Furthermore, we found that the hysteresis of the AFM $\leftrightarrow$ FM transition is limited to a small field range and, most importantly, it does not extend to zero field where the structure for high magnetic field (ferromagnetic coupling) changes back to that for low magnetic field when the field is reduced to zero.

From the thermodynamical theory, the magnetic entropy change $\Delta S_{\mathrm{M}}(T, H)$ is given by

$$\Delta S_{\mathrm{M}}(T, H) = S_{\mathrm{M}}(T, H) - S_{\mathrm{M}}(T, 0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H.$$

By using the integrated Maxwell relation, the values of $\Delta S_{\mathrm{M}}(T, H)$ are obtained from isothermal magnetization curves. Figures 3(a) and (b) show the temperature dependence of the absolute values of ΔS_{M} in various applied fields for single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$ along the *ab*-plane and *c*-axis, respectively. One sharp peak and a broader one appear around T_{N} and T_{C}, respectively. At the Curie temperature $T_{\mathrm{C}} = 230$ K, $|\Delta S_{\mathrm{M}}|$ attains about 5 J kg^{-1} K^{-1}, which is comparable with that of $La_{1-x}Ca_xMnO_3$, and smaller than that of Gd. At the Néel

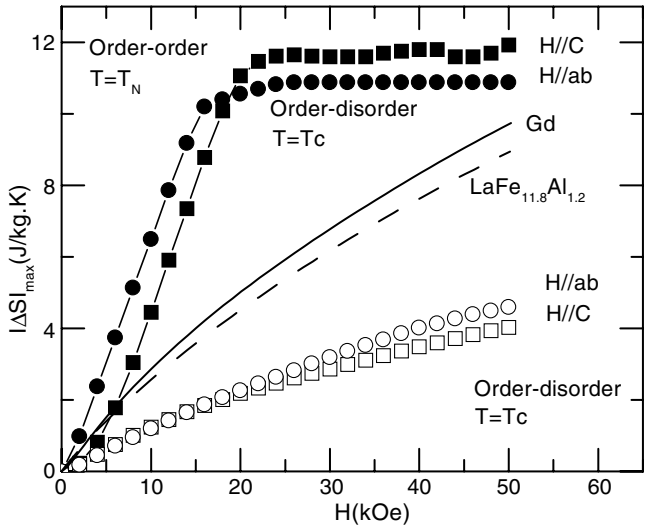

Figure 4. The field dependence of the magnetic entropy change $|\Delta S_M|$ of single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$ at temperatures around T_N and T_C. The field dependence of the magnetic entropy changes for Gd and $LaFe_{11.8}Al_{1.2}$ was also plotted for comparison.

temperature, values of the magnetic entropy change of $|\Delta S_M| \approx 11.0$ and 11.5 J kg^{-1} K^{-1} were achieved along the *ab*-plane and *c*-axis, respectively. A slight difference between the *ab*-plane and *c*-axis results is attributed to the magnetocrystalline anisotropy. The values of $|\Delta S_M|$ at T_N are not only much larger than that at T_C, but also the width of the peak is much narrower (about 3 K), thus concentrating the entropy change to over a smaller temperature interval. More interestingly, it seems that a larger magnetic entropy change can be induced by a small magnetic field at T_N, while it requires a very strong magnetic field to attain a relatively large magnetic entropy change at T_C.

Figure 4 illustrates the field dependence of the magnetic entropy change of single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$ at temperatures around T_N and T_C. The field dependence of the magnetic entropy changes for Gd and $LaFe_{11.8}Al_{1.2}$ was also plotted for comparison [8]. Although the absolute values of the magnetic entropy change at high magnetic field are comparable with those of Gd and $LaFe_{11.8}Al_{1.2}$, the magnetic entropy changes of $Nd_{0.47}Sr_{0.53}MnO_3$ can be easily saturated, to be 11.0 and 11.5 J kg^{-1} K^{-1} in a relatively weak magnetic field of 20 kOe. A significant difference was observed in the field dependence of the magnetic entropy change between the order–order transition and order–disorder transition. This difference originates from the change of the magnetic order parameters. It was well known that the MCE is induced via the coupling of the magnetic sublattices with the magnetic field, which alters the magnetic part of the total entropy of the magnetic sublattice. It is related to the magnetic field dependent, gradual change of the magnetic order itself. At temperatures above T_C, thermal fluctuation results in random alignment of magnetic moments. In order to overcome the thermal energy, it requires a relatively large magnetic field to align the random magnetic moment. Therefore, for single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$, a large magnetic entropy change at the order–disorder magnetic phase transition occurs in high magnetic fields. The same situation was observed in other systems, such as Gd and $LaFe_{11.8}Al_{1.2}$, which exhibit an order–disorder transition. On the other hand, at T_N, since a small magnetic field can trigger a transition from AFM $\longleftrightarrow$ FM due to the weak antiferromagnetic coupling between layers, a larger magnetic entropy change induced by a lower magnetic field was observed around T_N.

Although the large thermal hysteresis and low T_N limit its application as a magnetic refrigerant, the discovery of the excellent magnetocaloric features of single-crystal $Nd_{0.47}Sr_{0.53}MnO_3$ in a small field can provide some ideas for exploring novel magnetic refrigerants operating with a permanent magnet rather than a superconducting one as the magnetic field source.

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