Giant magnetothermal conductivity and magnetostriction effect in the charge ordered Nd$_{0.8}$Na$_{0.2}$MnO$_3$ compound

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Abstract – We present results on resistivity ($\rho$), magnetization ($M$), thermal conductivity ($\kappa$), magnetostriction ($\Delta L/L(0)$) and specific heat ($C_p$) of the charge-orbital ordered antiferromagnetic Nd$_{0.8}$Na$_{0.2}$MnO$_3$ compound. Magnetic-field–induced antiferromagnetic/charge-orbital ordered insulating to ferromagnetic metallic transition leads to giant magnetothermal conductivity and magnetostriction effect. The low-temperature irreversibility behavior in $\rho$, $M$, $\kappa$ and $\Delta L/L(0)$, due to field cycling together with a striking similarity among the field and temperature dependence of these parameters manifest the presence of a strong and complex spin-charge-lattice coupling in this compound. The giant magnetothermal conductivity is attributed mainly to the suppression of phonon scattering due to the destabilization of spin fluctuations and static/dynamic Jahn-Teller distortion by the application of magnetic field.

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Introduction. – Magnetic-field–induced transitions in prototype correlated electron systems, where spin, charge, lattice, and orbital degrees of freedom are coupled strongly, have drawn a considerable attention due to their huge impact on physical properties. Such fascinating phenomena are usually observed in rare-earth-based manganites close to half-doping. Several field-stimulated transitions, viz., the structural transition, the first-order to second-order ferromagnetic (FM) transition and the spin-flop metamagnetic transition from the antiferromagnetic (AFM)/charge ordered (CO) state to the FM state accompanied by the insulator to metal transition have been extensively studied in divalent doped manganites [1–5]. However, the study on monovalent hole-doped manganite systems is very much limited [6–10]. The monovalent doping has the advantage of creation of optimum concentration of Mn$^{4+}$ ions with a relatively small level of doping, as compared to its divalent counterpart. Though there are few reports on the electronic transport, the heat transport and its correlation with magnetic and magnetoelastic properties need to be explored. Magnetothermal transport may provide important insights into carrier localization due to spin-fluctuations and Jahn-Teller (JT) distortion as a result of strong lattice coupling through the orbital degree of freedom.

Recently, we have investigated the magnetic properties of a medium-sized $e_g$ electron bandwidth CO system Nd$_{1.2}$Na$_{0.8}$MnO$_3$ [6], where the quenching of the CO phase was achieved at a lower field relative to other narrowband manganites [1,4]. Repaka et al. [10] have observed a giant magneto-thermolectric power in a quite similar compound and suggested a close interplay between magnetization, electrical resistance and thermoelectric power. In order to understand the nature and strength of the spin-lattice coupling and JT distortion and their role on transport properties, we have carried out temperature and field dependence of resistivity ($\rho$), magnetization ($M$), thermal conductivity ($\kappa$), magnetostriction ($\Delta L/L(0)$) and specific-heat ($C_p$) measurements on Nd$_{0.8}$Na$_{0.2}$MnO$_3$. Magnetostriction is a sensitive tool to detect the strength of the coupling between the magnetic order parameter and the lattice structure, i.e., the spin-lattice interaction in the system. The observed giant magnetothermal conductivity, large magnetostriction effect, and their irreversibility characteristics associated with the metamagnetic transition are the manifestations of a complex and strong interplay...
Experimental. – The details of Nd$_{0.8}$Na$_{0.2}$MnO$_3$ polycrystalline sample preparation and its crystal and magnetic structures are described in earlier reports [6,7]. The magnetization measurements were carried out by using SQUID VSM (Quantum Design). The temperature and magnetic-field dependence of the electrical resistivity was measured in a cryostat (Cryogenic Ltd.) equipped with a 9 T superconducting magnet. Thermal conductivity and specific heat were measured by the conventional relaxation method using the Physical Property Measurement System (Quantum Design). The longitudinal magnetostriiction was measured by the capacitive method using a miniature tilted-plate dilatometer with applied field parallel to the sample’s length.

Results and discussion. – The temperature dependence of zero-field-cooled (ZFC) magnetization at 100 Oe as shown in fig. 1 exhibits a broad maximum at CO temperature $T_C = 180\text{K}$ [7]. With further decreasing temperature, a secondary rise below 100 K followed by a cusp-like transition at 42 K is observed in magnetization due to the formation of an inhomogeneous/cluster-glass-like magnetic phase [6]. The nature of different transitions has been further investigated by measuring the temperature dependence of the zero-field specific heat as shown in fig. 1. The lattice vibrations which contribute towards $C_p$ in terms of phononic excitations are dominant at high temperatures and decrease with a decrease in temperature. $C_p$ shows a broad peak around $T_{CO}$ and exhibits a weak $\lambda$-like anomaly at 42 K. A similar peak at $T_{CO}$ is observed in the specific-heat data of several half-doped CO manganites [11]. A further decrease in temperature below 10 K reveals a broad anomaly which could be attributed to the Schottky effect due to the splitting of the 4$f$ multiplet of the Nd$^{3+}$ ion.

To underscore the nature of interplay between spin, charge and lattice degrees of freedom in the present compound, we have studied magnetization, resistivity, and thermal conductivity as a function of temperature in both field-cooled-cooling (FCC) and field-cooled-warming (FCW) cycles for fields up to 8 T. Figure 2(a) shows $M(T)$ at different magnetic fields. With the increase of the magnetic field, the value of $M$ increases and the FM transition ($T_C$) shifts towards higher temperature. This behavior suggests that the FM phase fraction enhances with the magnetic field. The $\rho(T)$ curves in FCC and FCW conditions for different magnetic fields are shown in fig. 2(b). In zero field, $\rho$ shows semiconducting behavior and the value of $\rho$ is found to be $\sim 10^6\text{\Omega cm}$ at around 65 K. We could not measure $\rho$ below 65 K because of its steep increase. The application of a magnetic field of 2 T suppresses the resistivity by four orders of magnitude at around $T_{MI} = 80$ and 111 K in the FCC and FCW cycles, respectively, where the compound undergoes a sharp insulator to metal transition. As the field strength increases, $T_{MI}$ shifts towards higher temperature and the resistivity in the low-temperature region decreases substantially. The
thermal hysteresis width between FCC and FCW curves is found to be narrowing down progressively with increasing field strength.

The temperature dependence of thermal conductivity at different fields is shown in fig. 2(c). The zero-field $\kappa$ is quite small, decreases continuously with decreasing temperature ($d\kappa/dT > 0$) down to 2 K and exhibits a change in slope below $T_{CO}$. The nature of the $T$-dependence of $\kappa$ and its small value are comparable to that observed in other CO insulator and glassy systems [12–14]. The small value of $\kappa$ could be associated with phonon scattering by magnetic polarons and phononic vibration of Mn$^{3+}$ ions in static and dynamic JT modes. The phononic contribution to $\kappa$ is mainly determined by the phonon mean free path ($l_{ph}$) which gets restricted by static and dynamic JT modes [15,16]. Besides this, the scattering due to the Nd spin disordering further shortens the phonon mean free path. As a result, $\kappa$ does not show a broad phonon peak owing to the boundary scattering but falls sharply at low temperature [12,17,18]. For the application of magnetic field of 3 T, $\kappa$ in FCC cycle starts to increase from its zero-field value below $\sim 120$ K and shows a sharp transition around $T_{c} = 96$ K. Similar to $\rho(T)$ and $M(T)$ curves, a large thermal hysteresis is observed between FCC and FCW cycles of $\kappa(T)$. The total thermal conductivity can be written as sum of phononic ($\kappa_{ph}$), electronic ($\kappa_{e}$), and magnon ($\kappa_{m}$) contributions. $\kappa_{e}$ at a constant applied magnetic field is estimated by considering the validation of the Wiedemann-Franz Law, $\kappa_{e} = L_{0}T/\rho$, where $L_{0}$ is the Lorentz number. Below $T_{c}$, the deduced value of $\kappa_{e}$ at 5 T is found to be less than 1% of $\kappa$. So, $\kappa_{e}$ has negligible contribution towards total thermal conductivity. The magnon thermal conductivity can be estimated from kinetic theory which is also found to be very small [19]. Though the destabilization of JT distortion by applying magnetic field enhances the electronic contribution to thermal conductivity, the effect of phonon scattering suppression on $\kappa$ is much more significant. The inset of fig. 2(c) shows the temperature dependence of magnetothermal-conductivity ($\Delta\kappa/\kappa$), defined as $\Delta\kappa/\kappa = \kappa(H)/\kappa(0) - 1$. At 5 T, $\Delta\kappa/\kappa$ increases sharply below $T_{CO}$ and exhibits a broad peak. A giant value of $\Delta\kappa/\kappa$ (92%) is observed in the vicinity of the cluster-glass transition temperature and $\Delta\kappa/\kappa$ is more than 70% in the temperature range 27–117 K. The observed value of $\Delta\kappa/\kappa$ is significantly larger as compared to that reported for other doped manganites [15,16,20,21]. This giant magnetothermal conductivity suggests that the spin-phonon coupling in the studied sample is quite strong. The transition temperatures, $T_{C}$, $T_{MI}$ and $T_{c}$ in FCC and FCW cycles are obtained from the first derivative of $M(T)$, $\rho(T)$, and $\kappa(T)$ curves, respectively. The span of the thermal hysteresis at different magnetic fields is estimated from the difference between the transition temperatures in FCC and FCW modes. The inset of fig. 2(b) shows that the width of the thermal hysteresis, $\Delta T$, decreases with increasing field and creates a phase separation boundary between CO insulating and FM metallic regions. Finally, the large thermal hysteresis observed in $M(T)$, $\rho(T)$ and $\kappa(T)$ disappears above 7 T which suggests a change in the nature of transition from first order to second order.

We have also studied the field dependence of $M$, $\rho$, $\kappa$ and $\Delta L/L_{0}$ at different temperatures, where $L(0)$ is the length of the sample at zero field and $\Delta L$ is the increase in the sample length at field $H$. $M(H)$, $\rho(H)$, $\kappa(H)$ and $\Delta L/L_{0}$ measured at 5 and 100 K with $\pm 9$ T field cycling are shown in figs. 3 and 4, respectively. The $M(H)$ curve at 5 K (fig. 3(a)) displays a sharp transition from the CO/AFM to the FM state above a critical field of $\sim 5$ T. Unlike at 5 K, the $M(H)$ loop at 100 K, as shown in fig. 4(a), exhibits a field-induced metamagnetic transition from the

![Fig. 3: (Colour online) Field variation of (a) $M$, (b) $\rho$, (c) $\kappa$, and (d) $\Delta L/L_{0}$ at 5 K.](image-url)
CO/AFM state to the FM state with almost reversible behavior [4]. The critical fields for the transition in the ascending and descending branches of the field cycles are 3.5 and 2.5 T, respectively. The \( \rho(H) \) curves show a similar irreversible and reversible behavior at 5 K (fig. 3(b)) and 100 K (fig. 4(b)), respectively. At 5 K, a very sharp transition from a highly insulating state to a metallic state is observed at a critical field of \( \sim 5.5 \) T in the ascending branch. Such a sharp transition of \( \rho \) from an infinitely large value to few \( \text{m} \Omega \text{ cm} \) also signifies the first-order nature of the field-induced transition. With further field cycling from 9 T to \(-9 \) T and from \(-9 \) T to 9 T, the system no longer recovers its highly insulating state but continues to retain the metallic state. This irreversible behavior is observed up to about 50 K. The critical fields for the insulating to metallic transition obtained from the ascending branch of the magnetic field for different resistivity isotherms are 2.5, 3.5 and 4.5 T for \( T = 75, 100, \) and 125 K, respectively.

The isotherms of \( \kappa \) at 5 and 100 K exhibit very interesting features as can be seen from figs. 3(c) and 4(c) and show a clear evidence of strong and complex coupling between lattice and spin degrees of freedom. For the virgin curve at 5 K, \( \kappa \) decreases very slowly up to 4 T and then exhibits a dip-like feature at 5 T which is nearly the same field at which the metamagnetic transition occurs (fig. 3(c)). With further increasing field above 5 T, \( \kappa \) sharply increases as the system undergoes a transition from the insulating state to the FM metallic state and then exhibits a weak anomaly at 7 T where the secondary rise in the virgin \( M(H) \) curve has been observed. The slow decrease in \( \kappa \) up to 4 T is due to the increase of phonon scattering with spin disordering. In an AFM system, when external field is applied, the magnetic moment fluctuation enhances in one of the two AFM sublattices which is antiparallel to \( H \). With increasing \( H \), more and more spins in the antiparallel sublattice orient along the field direction, which, in turn, increases the spin disordering. However, the dip-like feature in \( \kappa(H) \) can be explained by considering the fact that at very low temperature, the Zeeman energy becomes gapless at some spin-flop field in the AFM ordered phase and the energy gap opens again at high fields [18,22]. The strongest scattering of phonons by magnons takes place in the vicinity of the spin-flop transition where \( \kappa \) attains its lowest value. \( \kappa \) shows a strong irreversibility behavior for the \( \pm 9 \) T field cycling. On the other hand, \( \kappa(H) \) at 100 K, as shown in fig. 4(c), depicts a strong field dependence with a sharp change in magnitude in the vicinity of the metamagnetic transition at around 3 T but \( \kappa(H) \) is found to be almost reversible in the field cycling process.

In fact, the longitudinal magnetostriction, \( \Delta L(H)/L(0) \), at different temperatures clearly reflects the strong spin-lattice coupling and the role of orbital degrees of freedom. Figure 3(d) shows \( \Delta L(H)/L(0) \) at 5 K and the same at 75 K and 100 K is shown in fig. 4(d). \( \Delta L(H)/L(0) \) at 5 K initially increases slowly and then decreases rapidly and changes sign in the vicinity of the CO/AFM to FM transition with increasing field strength. The magnetostriction remains large and negative during the field cycling process and shows similar irreversibility behavior as observed in \( M(H) \), \( \rho(H) \), and \( \kappa(H) \) at 5 K. The critical fields for the field-induced transitions obtained from the isothermal magnetostriction measurements are 5, 4.5, 3 and 2 T for 5, 10, 20 and 50 K, respectively. At 75 K, \( \Delta L(H)/L(0) \) remains almost constant up to a critical field of 1.5 T and then decreases sharply to a negative value. In the subsequent \( \pm 9 \) T field cycling process, \( \Delta L(H)/L(0) \) exhibits a partially reversible behavior. However, it becomes almost reversible but exhibits both
negative and positive magnetostriction effects during the field cycling process at 100 K. The above-mentioned sign change in magnetostriction along with field hysteresis are clearly visible up to 125 K and the span of the field hysteresis shrinks with increase in temperature. \( \frac{\Delta L(H)}{L(0)} \) is found to be very small, positive and an exhibits an almost linear behavior for temperatures above \( T_{CO} \).

The irreversibility in \( M(H) \), \( \rho(H) \), \( \kappa(H) \) and \( \frac{\Delta L(H)}{L(0)} \) is observed up to about 50 K and can be explained by kinetic arrest of the high-field FM metallic phase [23]. However, above 50 K, the traversed path of the virgin curve falls in the metastable region which is outside the kinetic arrest band and hence, the characteristic is reversible during the field cycling process due to the de-arrest of the FM metallic phase [23]. The striking similarity in the behavior of the \( T_\alpha \) and \( H \)-dependence of magnetization, charge transport, heat transport and magnetostriction firmly establishes that \( \text{Nd}_0.4\text{Sr}_{0.2}\text{MnO}_3 \) is a classic example of spin-charge-lattice coupled system. Also, the irreversibility in \( \kappa(H) \) and \( \frac{\Delta L(H)}{L(0)} \) strongly suggests the presence of an inhomogeneous long-range strain in the present system [14]. The observed features in \( \frac{\Delta L(H)}{L(0)} \) can be explained on the basis of the real space ordering of Mn\(^{3+}/\text{Mn}^{4+} \) ions accompanied by the \( d_{3z^2-r^2}/d_{3y^2-r^2} \) orbital ordering of Mn\(^{4+} \). The magnetic field stabilizes the \( d_{3z^2-r^2} \) orbital state, which results in a destruction of charge ordering and growth of the FM state with spin directed along the \( c \)-axis [24]. As a result, the MnO\(_6\) octahedron elongates along the \( c \)-axis and shrinks within the \( ab \)-plane which brings a net negative magnetostriction above the critical field. At 5 K, we have estimated about 0.07% volume contraction due to the field-induced transition from the CO/AFM to the FM state. This large volume contraction is comparable to that observed in the \( \text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) compound [25]. On the contrary, the nature of the magneto-volume change in divalent-doped \( \text{Nd}_0.4\text{Sr}_{0.2}\text{MnO}_3 \) is very different where a large volume expansion occurs during the field-induced transition from the CO-AFM insulator to the FM metallic state [3,4].

Conclusion. – The magnetic, transport and structural properties and their correlation have been investigated in the CO/AFM \( \text{Nd}_0.4\text{Na}_{0.2}\text{MnO}_3 \) compound. The large magnetothermal conductivity is attributed to the suppression of phonon scattering by spin fluctuations and by the dynamic Jahn-Teller distortion with the magnetic field. The giant magnetothermal conductivity and magnetostriction associated with a field-induced magnetic transition clearly demonstrate a strong spin-phonon coupling in the present compound.

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