Pressure-induced spin and charge transport in La$_{1.25}$Sr$_{1.75}$Mn$_2$O$_7$ single crystal

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Abstract

We investigated the effect of uniaxial and hydrostatic pressure on resistivity and ac-magnetic susceptibility of two-dimensional layered manganite, La$_{1.25}$Sr$_{1.75}$Mn$_2$O$_7$ (LSMO125) to investigate the lattice effect on magnetic and electronic properties. Asymmetric role of uniaxial pressure, || and \perp to c-axis on the spin flop and charge transport has been revealed while comparing hydrostatic pressure. Uniaxial pressure along c-axis increases metal–insulator transition temperature ($T_{MI}$) and ferromagnetic ordering temperature ($T_C$), whereas it decreases the resistivity along ab-plane ($\rho_{ab}$). In contrast to pressure along c-axis, $T_{MI}$ and $T_C$ decrease, whereas the resistivity along c-axis ($\rho_c$) increases with pressure || to ab-plane. $\rho_c/\rho_{ab}$ is quite large, increasing with pressure and shows a peak at around $T_{MI}$. Uniaxial pressure behaviour is strongly related to the Mn–O–Mn linkage between MnO$_2$ layers and the spin reorientation from the apical axis to the basal plane and vice versa with pressure. Both $\rho_{ab}$ and $\rho_c$ decrease whereas $T_{MI}$ and $T_C$ increases under hydrostatic pressure. Influence of spin and charge on magnetic and electrical properties under hydrostatic pressure are explained by pressure-induced cant between the MnO$_2$ bilayers and variation in bond lengths. The different pressure driving rates of $T_{MI}$ while measuring $\rho_{ab}$ and $\rho_c$ confirms that there is a strong competition between the in and out plane components under hydrostatic pressure.

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1. Introduction

The discovery of colossal magnetoresistance (CMR) effect in low-dimensional manganites with perovskite structure has attracted the considerable interest for the understanding of their unrevealed physical properties [1]. CMR in the doped manganites is related to a temperature-dependent phase transition that occurs from a paramagnetic insulator to a ferromagnetic metal. Just above this transition, an applied magnetic field not only restores the magnetic phase but also stabilizes the metallic state. Though the insulator-to-metal transition and its associated CMR properties are well explained on the basis of the double-exchange (DE) model, it is to be considered that the dynamic Jahn–Teller (JT) effect due to the strong electron–phonon interaction, plays a key role in the appearance of CMR as well as the DE interaction [2,3]. In bilayer manganites La$_2$-$_x$Sr$_{1+2x}$Mn$_2$O$_7$. MnO$_2$ conducting bilayer is alternatively stacked with a (La,Sr)$_2$O$_2$ insulating rock-salt blocking layer along the c-axis. As a consequence, bilayer manganites show highly anisotropic transport properties with the magnitude of resistivity along the c-axis about two or more orders higher than that along the ab-plane, extremely large interplane tunneling magnetoresistance, and a reduced Curie temperature [4]. Another important feature of this system is that the interlayer tunneling conduction is extremely sensitive to external pressure and hole doping ($x$) [5]. For $x = 0.30$, both $\rho_c$ and $\rho_{ab}$ increase dramatically with hydrostatic pressure up to 1.4 GPa [6], but for $x = 0.32$ resistivity along both directions decreases with the hydrostatic pressure up to 1.8 GPa [7]. For both $x = 0.3$ and 0.32 one can find the ferromagnetic order within the bilayer and 3D ferromagnetic alignment...
between the bilayers for 0.4 > x > 0.32. In the case of x = 0.30, the weak interbilayer coupling is antiferromagnetic (AF), producing an A-type AF ground state with moments aligned along the c-axis [8]. Investigations over the structural studies on bilayer manganites have revealed that the compressibility along the c-axis is different from that along the ab-plane [9]. Particularly, c-axis Mn–O(1) and Mn–O(2) bond lengths show the reciprocal response to temperature and pressure which reflects the asymmetric c-axis bonding at a Mn atom and Mn–O(2) bonds are free to adjust their length for retaining the equilibrium bond length sum for the Mn valences. It has also been proved that there is a-axis compressibility by the reduction of the Mn–O(3) bond length and no change in Mn–O(3)–Mn bond angle which indicates no additional buckling of MnO6 octahedra occurring with applied pressure. This is in contrast to other perovskite materials [10,11]. We believe that the effect of uniaxial pressure on transport properties would be very different from that of hydrostatic pressure hence the bilayer manganites show the strong anisotropic structural, electronic, and magnetic coupling. Our previous report about the uniaxial pressure effect on electrical resistivity reveals the importance of the lattice parameter over the transport properties [12]. To the best of our knowledge, there are no such reports on ac-magnetic susceptibility under uniaxial pressure in bilayer manganites up to now. By keeping these positive remarks in mind, we have studied the followings: (1) ab-plane and c-axis resistivities with pressure always perpendicular to the direction of the flow of current. (2) ab-plane and c-axis ac-susceptibilities with pressure and weak ac-field parallel to each other. We also studied ab-plane and c-axis resistivities and susceptibilities with hydrostatic pressure up to 2 GPa for comparison.

2. Experimental details

High quality single crystal samples are indispensable for experimental investigations of the mechanisms related to the CMR effect. Single crystals with nominal composition La1.25Sr1.75Mn2O7 (LSMO125) were grown from polycrystalline rods using an optical floating-zone furnace in a controlled atmosphere because of its high melting temperature [13]. Different experimental techniques were adopted to confirm the phase purity, structure, and crystalline quality. The nature of the crystal surface was checked by optical and scanning electron microscopy. X-ray powder diffraction reveals high purity of the phase, and the sharp diffraction spots in Laue diffraction indicate good crystalline quality. The elemental analysis was done using electron probe microanalysis and found to be very close to the nominal composition. The magnetic properties were studied by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) with a small field applied parallel and perpendicular to the ab-plane. Both field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements show a sharp ferromagnetic transition close to the metal–insulator transition (TMI) at ~128 K. All these measurements clearly show that our single crystals are of high quality. Well characterized crystals were aligned with a goniometer using Lane back diffraction pattern and cut along the ab-plane and c-axis with typical dimensions 1 mm × 1 mm × 1 mm using diamond wire cutter and all the faces were polished finely using Al2O3 (50 nm) powder with water.

2.1. Uniaxial pressure technique

The temperature dependence of DC resistivity under uniaxial pressure in zero field (ρ(T,P)) was measured by van der Pauw geometry [14] with the current between 10 and 100 μA using a simple uniaxial pressure device specially designed for electrical resistivity measurements suitable for closed cycle refrigeration system [15]. Electrical resistivity measurements under uniaxial pressure were performed on highly polished samples prepared by epoxy crystal bare surface (ECBS) technique [16]. ECBS samples were placed in between the anvils made of Be (2%)–Cu alloy. The surfaces of the anvils were electrically insulated by introducing the fine layer of GE varnish (GE 7031). The pads for electrical contacts on the samples were made by Au paint and then annealed at an appropriate temperature. The details about the sample mounting techniques has been published elsewhere [15]. Temperature dependence of ac-susceptibility measurements under uniaxial pressure were also performed on the samples from the same batch using a home-built ac-susceptometer with uniaxial pressure device specially designed for ac-magnetic susceptibility measurements [16] under an ac-probe field of ≈2 Oe and an excitation frequency of 133 Hz. The in-phase component of ac-susceptibility (χ′) alone considered for further discussion as (χ′) is negligibly small. In case of ac-magnetic susceptibility measurements under uniaxial pressure, the similar procedures were followed like resistivity measurements under uniaxial pressure. The same ECBS sample preparation technique were adopted to prepare the sample for magnetic studies and the prepared sample were mounted in between the suitable Be (2%)–Cu anvils, which was inserted into the suitable former-coil assembly for magnetic studies, details about the sample mounting techniques have been published elsewhere [16]. Cernox (CX-1030) magnetic free sensors were used for measuring the temperature with the accuracy of 0.2 K. In this device pressure was applied through a force generator by rotating a micrometer and the pressure was calculated directly from the surface area of the crystal, the rotations of the micrometer, and the force-constant value of the spring.

2.2. Hydrostatic pressure technique

A self-clamp type hybrid double cylinder (nonmagnetic Ni–Cr–Al inner cylinder; Be–Cu outer cylinder) pressure cell was used to generate various hydrostatic pressures up to 2 GPa, which was monitored using a manganin resistance technique. The mixture of fluorinate FC70:FC77 was used as a pressure-transmitting medium. The temperature variation was monitored using a chromel–constantan thermocouple calibrated for the pressure-induced changes placed near the sample (inside the Teflon capsule). Pressure decreased continuously with the lowering of temperature at the average rate of 0.0013 GPa/K from 300 to 77 K. The values of various pressures appearing in this manuscript refer to the values measured at room temperature and the data to be considered here are during warming process only.

3. Results and discussion

The temperature dependence of ρab with pressure || to c-axis and ρc with pressure ⊥ to c-axis at different uniaxial pressures (P) are shown in Fig. 1(a) and (b), respectively. At ambient pressure and temperature the electrical resistivity is highly anisotropic with ρc/ρab ~ 60 (not shown), which is comparable with earlier reports [6,7]. Both ρab and ρc increase with the decrease of temperature and exhibit an insulator-to-metal transition at TMI 128 ± 0.5 K. The temperature dependence of FC and ZFC magnetization (M) shows that M increases sharply just below TMI [12] and TMI coincides with TC. With increasing P, ρab decreases and TMI shifts monotonically towards higher temperature. The effect of P on reducing ρab is stronger close to the vicinity of TMI. In contrast to ρab, ρc increases sharply with increasing pressure, TMI shifts towards lower temperature, and the effect of pressure is stronger and extended over a much wider range of temperature both above and below TMI. Neglecting the weak nonlinear dependence of TMI on P, we find that for P || to c-axis, TMI increases at a rate of d(TMI/dP) of 46.33 K/GPa while TMI decreases at a rate of 16.58 K/GPa, for P ⊥ to c-axis. The rate of increase of TMI in LSMO125 under uniaxial pressure is comparable to 38 K/GPa in La1.36Sr1.64Mn2O7 under hydro-
Fig. 1. Temperature dependence of (a) $\rho_{ab}$ with pressure $||$ to $c$-axis and (b) $\rho_c$ with pressure $\perp$ to $c$-axis of La$_{1.25}$Sr$_{1.75}$Mn$_2$O$_7$. The arrows indicate the direction of metal–insulator transition temperature shift.

static pressure but much higher than that observed in perovskite manganites La$_{3/4}$Ca$_{1/4}$MnO$_3$ (10 K/GPa). The results obtained for the $T$ dependence of the ac-susceptibility, at different uniaxial pressures $||$ and $\perp$ to $c$-axis are presented in Fig. 2(a) and (b), respectively. The sample exhibits a very sharp paramagnetic (PM)–ferromagnetic (FM) transition at the Curie temperature ($T_C$). We have defined the inflection point of the $\chi$–$T$ curve as $T_C$ $128 \pm 0.5$ K, at ambient pressure, which is comparable with the previous results [12]. With increasing pressure $||$ to $c$-axis the $T_C$ increases at the rate of $18.2 \pm 0.2$ K/GPa, in contrast to pressure $||$ to $c$-axis, $T_C$ decreases at the rate of $10.03 \pm 0.2$ K/GPa with the application of pressure $\perp$ to $c$-axis. Temperature dependence of ac-susceptibility is weak at $T > T_C$ for both direction of uniaxial pressure $||$ and $\perp$ to $c$-axis. Fig. 3(a) and (b) shows the temperature dependence of $\rho_{ab}$ and $\rho_c$ of the LCMO125 under different hydrostatic pressures. It is found that, with decreasing temperature both $\rho_c$ and $\rho_{ab}$ are increased and showed a sharp maximum at temperature, $T_{MI}$ $128 \pm 0.5$ K. When the temperature is further decreased below $T_{MI}$, both $\rho_{ab}$ and $\rho_c$ are decreased. Hydrostatic pressure suppress $\rho_{ab}$ and $\rho_c$ monotonically throughout the whole range of measurement. Considering the near linear response of $T_{MI}$ while measuring $\rho_{ab}$ and $\rho_c$ under hydrostatic pressure, it is observed that pressure shifts $T_{MI}$ to higher temperatures with pressure coefficients $14.6 \pm 0.2$ K/GPa and $8.2 \pm 0.2$ K/GPa, respectively, which are comparable with the previous results [17]. Fig. 4(a) and (b) shows the temperature dependence of $\chi_{ab}$ and $\chi_c$ for LCMO125 under hydrostatic pres-

Fig. 2. Temperature dependence of ac-susceptibility at different uniaxial pressures: (a) $||$ to $c$-axis and (b) $\perp$ to $c$-axis La$_{1.25}$Sr$_{1.75}$Mn$_2$O$_7$. The arrows indicate the direction of ferromagnetic ordering temperature shift.

Fig. 3. Temperature dependence of (a) $\rho_{ab}$ and (b) $\rho_c$ of La$_{1.25}$Sr$_{1.75}$Mn$_2$O$_7$ under different hydrostatic pressures. The arrows indicate the direction of metal–insulator transition temperature shift.
The change in Mn–O bond lengths rather than by the tilting of the structure appears to accommodate the pressure effects through the double-exchange mechanism\[20\]. The two-layer distortion in the metallic regime where the charge is delocalized within the bilayer and 3D ferromagnetic alignment between them. As a result of this electron transfer manganese ions and these ionic states fluctuate due to electron transfer (5) effect of hydrostatic pressure on the spin and charge transfer is stronger than the applied weak magnetic field; (4) effect of hydrostatic pressure on the spin and charge transfer is the result of the competition between the in and out plane components. While measuring $\rho_{ab}$ and ac-susceptibility with pressure along the c-axis, the apical Mn–O bond length gets compressed and as a result the system anisotropy is reduced monotonically. Also, the shorter apical Mn–O bond favors the flop of the spins and charge transfer from the apical axis to the conduction plane, further pressure applying along the apical axis increases the strength of coupling between and within the conducting MnO$_2$ layers. All these effects enhance the in-plane conductivity of the system and $T_C$. In contrast, the increase of $\rho_c$ and the decrease of $T_{MI}$ as well as $T_C$ with pressure along the ab-plane can be explained by considering the effect of small expansion along the c-axis due to the Poisson ratio. In this case the pressure enhances the in-plane coupling along the direction of the applied pressure but reduces the interlayer linkage due to the expansion along the c-axis. As the coupling between the planes is very weak and the conductivity along the c-axis is due to the tunneling of charge carriers, a small increase in the apical Mn–O bond length may suppress the conductivity due to the in-plane compression. The small increase of the c-axis Mn–O–Mn bond length may also change the spin orientation from the basal plane to c-axis. This effect will further reduce the conductivity in the vicinity of $T_C$ and $T_{MI}$, and increase the anisotropy of the system. On the other hand, both magnetic and electronic couplings between the layers are responsible for the sharp increase of the anisotropy at $T_C$ and $T_{MI}$ [12]. The different pressure driving rate of $T_{MI}$ and $T_C$ confirms that the electronic and magnetic anomaly induced by uniaxial pressure is different.

To interpret the unusual uniaxial pressure dependence of resistivity and ac-susceptibility while comparing hydrostatic pressure response we must be accountable for the followings: (1) the magnitude of the interlayer charge and spin couplings are highly sensitive to pressure; (2) the electronic and spin coupling along c-axis is very weak due to the presence of the insulating rock salt-type (La,Sr)$_2$O$_2$ layers in the conducting MnO$_2$ layers; (3) in-plane compressibility is smaller than the interplane compressibility; (4) effect of uniaxial pressure on the spin and charge transfer is stronger than the applied weak magnetic field; (5) effect of hydrostatic pressure on the spin and charge transfer is the result of the competition between the in and out plane components.

At ambient pressure, the electrical and magnetic properties of LSMO125 can be basically understood on the basis of double exchange (DE) interaction theory [18,19]. According to this theory, these manganese oxide compounds have Mn$^{3+}$ and Mn$^{4+}$ ions and these ionic states fluctuate due to electron transfer between them. As a result of this electron transfer manganese spins cant, and both magnetization and metallic conductivity appear simultaneously. The magnetization increases as the canting angle decreases. LSMO125 shows the ferromagnetic order within the bilayer and 3D ferromagnetic alignment between the bilayers in ground state [8]. Neutron diffraction experiments on La$_{1.25}$Sr$_{1.75}$Mn$_2$O$_7$ (LSMO12) single crystals reveal that the MnO$_6$ octahedra in the layered manganite undergoes enhanced distortion in the metallic regime where the charge is delocalized through the double-exchange mechanism [20]. The two-layer structure appears to accommodate the pressure through the change in Mn–O bond lengths rather than by the tilting of the MnO$_6$ octahedra under pressure, which happens in the perovskite oxide. A general feature of all those layered compounds is the fact that the interbilayer coupling is orders of magnitudes smaller than the intrabilayer coupling. The electrical anomaly bound to the metal–insulator transition shifted by pressure is different with the magnetic anomaly. The structural response due to external pressure leads to modifying the electronic transfer integral between Mn–Mn. It has been recently proved that the electronic and magnetic transitions of many manganites may be significantly decoupled, especially under hydrostatic pressure [21]. Therefore, the applied pressure affects the different conduction channels and in turn results in the variation of $T_{MI}$ and $T_C$.

Fig. 4. Temperature dependence of (a) $\chi_{ab}$ (ab-plane || to ac-field) and (b) $\chi_c$ (ab-plane ⊥ to ac-field) of La$_{1.25}$Sr$_{1.75}$Mn$_2$O$_7$ under different hydrostatic pressures. The arrows indicate the direction of ferromagnetic ordering temperature shift.
hydrostatic pressure [22]. This makes the FM state more and more anisotropic with pressure and leads to increase the $T_C$ and drop the resistance effectively. Increasing hydrostatic pressure reducing the cant angle between the MnO$_2$ sheets and leads to the positive $dT_C/dP$. Under hydrostatic pressure temperature dependence of $\rho_c$ is so strong in the vicinity of $T_{MI}$ in comparison with $\rho_{ab}$, which suggests that the transport properties are very sensitive to small change in apical Mn–O bond length.

Increasing pressure broadens $\rho_{ab}$ and $\rho_c$ in the vicinity of $T_{MI}$, which provides the evidence of the stabilization of 2D like conduction. The different pressure driving rates of $T_{MI}$ for $\rho_{ab}$ and $\rho_c$ confirms that there is a strong competition between in and out plane components.

4. Conclusions

In summary, we have studied the temperature dependence of uniaxial and hydrostatic pressure effects on resistivity and ac-susceptibility in single crystals of the bilayer manganite La$_{1.25}$Sr$_{1.75}$Mn$_2$O$_7$. With increasing uniaxial pressure along the c-axis, $\rho_{ab}$ decreases whereas $T_{MI}$ and $T_C$ shifts towards higher temperature due to the enhancement of the interlayer coupling and spin flop from c-axis to conduction plane. On the other hand, the application of uniaxial pressure along the ab-plane reduces the interlayer coupling, and as a result $\rho_c$ increases whereas $T_{MI}$ and $T_C$ decreases. Application of hydrostatic pressure, decreases $\rho_{ab}$ and $\rho_c$ whereas $T_{MI}$ and $T_C$ shifts to the higher temperature. Increasing hydrostatic pressure leads to stabilize the 2D like conduction in LCMO125. The electronic and magnetic anomaly tuned by the uniaxial and hydrostatic pressure is highly sensitive to pressure.

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