Tunneling Evidence of Half-Metallic Ferromagnetism in La$_{0.7}$Ca$_{0.3}$MnO$_3$

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ABSTRACT

Direct experimental evidence of half-metallic density of states (DOS) is observed by scanning tunneling spectroscopy on ferromagnetic La$_0$Ca$_{0.3}$MnO$_3$ which exhibits colossal magnetoresistance (CMR). Tunneling conductance data taken at 77K, well below the Curie temperature $T_c \approx 260$K, show close resemblance to the spin-split DOS spectrum calculated for the itinerant bands in the ferromagnetic state. The half-metallic spectral characteristics are absent in the paramagnetic state at room temperature, as well as in the undoped antiferromagnetic compound LaMnO$_3$ which shows no CMR. These results directly implicate the half-metallic ferromagnetism in the phenomenon of CMR.

The recent discovery of colossal magnetoresistance (CMR) in the perovskite manganites $Ln_{1-x}A_xMnO_{3-\delta}$ (Ln=trivalent rare earth ions, A=divalent alkaline earth ions) has rekindled interest in these compounds [1-6], with particular focus on the magnetic behavior of the conduction electrons. While the parent compound $LnMnO_{3-\delta}$ is known to be an antiferromagnetic (AFM) insulator with Neel temperature T_N - 150K, the doped compounds in the nominal regime $0.2 < x < 0.5$ behave as paramagnetic (PM) insulators at high temperatures and ferromagnetic (FM) metals below the Curie temperature T_c, near which the magnetoresistance peaks. The FM ordering has been attributed to the double-exchange interaction between the valence electronic states of Mn^{3+}-O^{2-}-Mn^{4+} [7-10], The double-exchange mechanism is also believed to be responsible for the occurrence of CMR [3,11,12], in conjunction with the effects of lattice distortion in the manganites [13]. A direct consequence of the double-exchange and the lattice distortion is a large spin-splitting of the conduction band into majority and minority sub-bands in the FM state [14]. These sub-bands are separated by the on-site Hund's rule energy, which is about several eV's, depending on the A-site doping. The large spin-splitting renders the conduction band half-metallic, i.e. with the ground-state electrons nearly perfectly spin-polarized [15].

Theoretically, half-metallic FM in the CMR manganites has been justified by *ab initio* band structure calculations. Hamada, Sawada and Terakura used linear augmented plane wave methods to study $LaMnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$, showing their respective ground states to be AFM insulating and FM half-metallic [16]. Satpathy, Popovic and Vukajlovic reached similar conclusions about the $La_{1-x}Ca_xMnO_3$ system using density-functional techniques [17]. Pickett and Singh also performed calculations of the La_1.

$_x$Ca$_x$MnO$_3$ system, using the local spin-density approximation [14]. This latter work demonstrated the importance of lattice distortion induced by both cation size-mismatch and the Jahn-Teller effect, in enhancing the FM exchange splitting of the itinerant bands.

Experimentally, both optical and transport studies have provided evidence in support of half-metallic FM in the CMR manganites. Okimoto *et al.* reported temperature dependent optical conductivity spectra on La$_{1-x}$Sr$_x$MnO$_3$ (x=O. 175) single crystals, consistent with a fully spin-polarized conduction band associated with exchange splitting [18]. Hwang et *al.* reported temperature dependent magnetoresistance in polycrystalline La$_{1-x}$Sr$_x$MnO$_3$ (x=1/3), attributable to spin-pol.arized tunneling between field-alligned half-metallic grains [19]. Sun et *al.* demonstrated large field-induced resistance modulation in trilayer devices based on La$_{1-x}$Sr$_x$MnO$_3$ and La$_{1-x}$Ca$_x$MnO$_3$ (x=1/3), in accordance with the model of spin-polarized tunneling through a half-metal/insulator/half-metal junction [20].

Despite these evidence supporting half-metallic FM in the CMR manganites, detailed understanding of the electronic structure involved requires direct measurement of the electronic density of states (DOS). Tunneling spectroscopy has been known to provide a sensitive probe of the DOS [21], particularly if the tunneling is into a many-body system characterized by a renormalized quasiparticle dispersion [22]. This letter reports direct evidence of half-metallic DOS by scanning tunneling spectroscopy on an epitaxial film sample of FM La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO). At 77K, well below T_c, the tunneling conductance data exhibit pronounced peak structures, bearing close resemblance to the half-metallic DOS spectrum calculated for the itinerant bands in FM La$_{1-x}$Ca$_x$MnO$_3$. The half-metallic spectral characteristics are absent at room temperature

in the PM state, as well as in the undoped compound LaMn03 (LMO) which shows no CMR. These observations directly implicate the half-metallic FM, as a combined effect of double-exchange and lattice distortion, in the phenomenon of CMR.

Epitaxial film samples of LCMO and LMO were grown by pulsed laser deposition on (100) $LaAlO_3$ substrates using stoichiometric targets. The films were 100nm thick and grown at 700°C in 100 mTorr of oxygen, and subsequently annealed at 900°C of 1 atm oxygen for several hours. X-ray diffraction and photoemission spectroscopy confirmed the samples to be stoichiometric, single-phase and epitaxial [24]. Optical measurements on the LCMO film indicated phonon modes consistent with those obtained on bulk LCMO of the same chemical composition [25]. The Curie temperature for the LCMO film was determined to be $T_c \approx 260$ K by measuring the spontaneous magnetization versus temperature with a SQUID magnetometer, Details of the sample synthesis and characterization are given in Refs. *[26-28].*

Tunneling spectroscopy was performed on the same LCMO and LMO films which had been fully characterized with the measurements described above. A home-built low-temperature scanning tunneling microscope (STM) was used, with a platinum tip as counter-electrode. The film surfaces were imaged by constant-current topography [26]. An example of the STM image (150x $150nm^2$, 50nm greyscale) for the LCMO film at room temperature is given in Fig. 1, showing atomically smooth "rice-paddy" terraces with unit-cell step heights. Images taken at 77K showed no significant difference. The spectroscopy measurements were made at constant tip-sample separation, i.e. with the STM feedback momentarily interrupted during a scan and the tunneling current measured as a function of the sample bias voltage. Typical junction impedence was -1 $G\Omega$. The

measured spectra were **highly** reproducible, showing little variation with tip position on the sample, The current vs. voltage *I-V* data were converted numerically into the normalized tunneling conductance $(dI/W)/(\overline{I/V})$ according to the procedure developed by **Feenstra** *et al.* [29]. The normalization is necessary to divide out inherent bias dependence in the **STM** barrier transmission, and $(\overline{I/V})$ represents integration over a weighting function of adjustable width ΔV to smooth out any numerical divergences, thus yielding a dimensionless quantity which is proportional to the local DOS [21].

Fig.2(a) shows the $(dI/dV)/(\overline{I/V})$ data plotted **vs.** *V* for LCMO in the FM state at 77K. Pronounced peaks are present at $\sim\pm1$.75 V, with half-height widths of -1 V. These peaks can be compared with the exchange-split, spin-polarized peaks in the DOS spectrum calculated by **Pickett** and **Singh** for the itinerant Mn *3d* and O 2p bands in FM $La_{1-x}Ca_xMnO_3$ (x=0.25) [14]. These half-metallic peaks are clearly absent at room temperature for LCMO in the PM state **(Fig.3(a))**, where there is no exchange interaction among the conduction electrons. The peaks also do not appear in the undoped LMO **(Fig.2(b)** and **Fig.3(b))** which is an AFM insulator with 7'~150K and shows no CMR. These observations directly correlate the half-metallic FM with the occurrence of CMR in the doped **manganites.** The energy separation between the half-metallic peaks provides a measurement of the **intra-atomic** Mn d-electron exchange splitting ΔE, which is simply related the on-site Hund's **rule** energy in the double-exchange model [7-11]. Our data indicate $\Delta E \approx 3.5$eV, in close agreement with the value calculated for FM $La_{1-x}Ca_xMnO_3$ (x=0.25) [14].

Also noticeable in the tunneling data for LCMO at 77K (**Fig.2(a)**) is a **gap-**structure with sharp edges at ~±0.5V. Such a gap is present as well in the data for LMO at 77K (**Fig.2(b)**), although slightly smaller at ~±0.35V. For LMO, this could be evidence for an insulator gap resulting from structural distortion induced by both the cation **size-**mismatch and the **Jahn-Teller** effect [14]. For **LCMO**, such evidence would be consistent with models for CMR involving polaron conduction [13]. Band structure calculations for LMO indicate a direct gap of ~0.7eV [14], which is close to the optical gap of ~1eV measured by **Arima** *et al.* [30]. Our own transport measurements on the LCMO sample used in this experiment suggest a **polaron** binding energy (relative to the Fermi level) of ~0.35eV [27], which compares well with the calculated **Jahn-Teller** coupling energy [13]. These theoretical and experimental results are in general agreement with the energy gaps we observed by tunneling: ~0.7eV in AFM LMO and ~1eV in FM LCMO.

It is interesting to note that the room temperature tunneling spectra for LCMO and LMO (**fig.3(a)** and **fig.3(b)**) show only a weak gap-like behavior, with $(d/W)/(\overline{I/V})$ dipping to its minimum value of unity near zero bias [31]. This behavior could be interpreted in terms of the band-structure cancellation effect first described by Harrison [32]. In the PM state, the electronic dispersion ξ_k (ξ is the energy and **k** is the **wavevector**) is not **renormalized** by any many-body correlations, thus making the DOS ($\sim \partial k/\partial \xi$ in one dimension) prone to cancellation by the group velocity ($\sim \partial \xi/\partial k$) inherent in the tunneling matrix element [23]. In contrast, the DOS in a magnetically ordered state is **renormalized** by the exchange interaction, thus circumventing the group-velocity cancellation which would prevent any gap structures in the DOS from clearly showing up in the tunneling spectra. Therefore, the dip features present in our room temperature data

are not inconsistent with the existence of an energy gap seen in both LCMO and LMO at 77K. On the other hand, the spin-split peak structure seen in LCMO at 77K is clearly absent in the room temperature spectra, consistent with it being unique to the FM state of LCMO and a distinct signature of half-metallic FM.

In summary, we have observed direct evidence, for the first time, of half-metallic density of states in ferromagnetic $La_{0.7}Ca_{0.3}MnO_3$ by scanning tunneling spectroscopy. The normalized tunneling conductance data show pronounced spectral peaks which can be identified as the exchange-split spin-polarized density-of-states peaks for the itinerant band electrons. These half-metallic spectral characteristics are absent at room temperature in the paramagnetic state, as well as in the undoped antiferromagnetic compound $LaMnO_3$. Our results directly implicate the half-metallic ferromagnetism, as a combined effect of double-exchange and lattice distortion in the doped manganites, in the phenomenon of colossal magnetoresistance.

ACKNOWLEDGEMENTS

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sufficiently smooth as not to require any weighted averaging of the denominator,

i.e. $\Delta V \rightarrow 0$. According to the definition by Feenstra *et al.* in Ref.29, the

dimensionless quantity $(dI \, / \, dV) \, / \, \overline{(I \, / \, V)}$ thus reduces to $d \ln I \, / \, d \ln V$, which

has a minimum of unity as $V \rightarrow 0$. This minimum is indicated by the dotted

baselines in fig.3(a) and fig.3(b).

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FIGURE CAPTIONS

Fig.1 STM topography of the LCMO epitaxial film grown on LAO substrate, taken at room temperature. The image is 150x $150nm^2$ in size and 5nm in greyscale, showing atomically smooth "rice-paddy" terraces with unit-cell step heights.

Fig.2 STM spectroscopy data taken at 77K, plotted as the normalized conductance $(dI/dV)/(\overline{I/V})$ *vs.* the sample bias voltage *V*. **(a) is** for the LCMO film in the FM state, showing pronounced peaks at ~±1.75V and a gap structure with edges at ~±0.5V. (b) is for the LMO film in the AFM state, showing no peaks but similar gap features at ~±0.35V.

Fig.3 STM spectroscopy data taken at 300K, plotted as the normalized conductance $(dI/W)/(\overline{I/V})$ *vs.* the sample bias voltage *V*. **(a) is** for the LCMO film in the PM state, and (b) is for the LMO film in the PM state. Both spectra show a weak gap-like behavior, dipping to its minimum value of unity (indicated by dotted baseline) near zero bias [see Ref.3 1].

Fig. 1
Wei et al.

30 nm

Fig. 2
Wei et al.

(a) LCMO at 77K (FM)

(b) LMO at 77K (AFM)

$(dI/dV) / (I/V)$

$(dI/dV) \cdot \overline{(I/V)}$

v (volts)

Fig. 3
Wei et al.