

Tunneling Evidence of Half Metallicity in Epitaxial Films of Ferromagnetic Perovskite Manganites and Ferromagnetic Magnetite.

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Direct evidence of half-metallic density of states is observed by scanning tunneling spectroscopy of ferromagnetic $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.3, 0.33$) epitaxial films which exhibit colossal magnetoresistance (CMR). At 77 K, well below the Curie temperatures, the normalized tunneling conductance $(dI/dV)/(I/V)$ for all samples exhibits similar pronounced peak structures, consistent with the spin-split density of states spectra for the itinerant bands in the ferromagnetic state. The exchange energy split of the majority and minority spins, and the energy gap in the minority bands, show variations with the chemical composition and the temperature. For comparison, the tunneling spectrum of a half-metallic ferrimagnet Fe_3O_4 is also studied. The characteristic spin-split density of states spectrum is observed, and the similarities and differences of Fe_3O_4 compared with the perovskite manganites are discussed.

Half-metallic ferromagnetic materials, characterized by the presence of an energy gap for one of the spin polarizations at the Fermi level and continuous bands for the other, have been a subject of interest for more than a decade[1-4]. An important consequence of the half-metallicity is the complete spin polarization in the ferromagnetic state of these materials [1,2], giving rise to novel physical properties, such as very large magneto-optical Kerr effects[5] in the Heusler alloys (e.g., PtMnSb)[6]. Recently, the intensively studied phenomenon of negative colossal magnetoresistance (CMR) in the perovskite manganites, $\text{Ln}_{1-x}\text{M}_x\text{MnO}_3$ (Ln: trivalent rare earth ions, M = divalent alkaline earth ions), has been attributed to the half-metallic characteristics of these materials based on electronic band structure calculations [7] and on various supportive and yet indirect experiments [8,9]. In this work, we provide temperature-dependent tunneling spectroscopy data as the direct experimental evidence for the half metallicity of various perovskite manganites. In addition, we compare these results with the tunneling spectroscopy of a ferromagnetic system, Fe_3O_4 , which has not been shown direct tunneling evidence for half-metallicity [10-12] prior to this work. The similarities and differences in the tunneling spectroscopy of these half-metallic ferromagnets and ferrimagnets (HMF) are also discussed.

The perovskite manganites studied in this work are 200 rim-thick epitaxial films of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ on single crystalline LaAlO_3 substrates[13-16], and 150 rim-thick $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ on single crystalline SrTiO_3 substrates, using pulsed laser deposition[17]. The Curie temperatures (T_C) for these samples are 260 K, 320 K and 360K, respectively. Details of the deposition procedure and the characterizations of the structural and physical properties (including the electronic, electrical transport, magnetic and optical properties) of the manganite epitaxial films have been reported elsewhere [13- 17]. The Fe_3O_4 sample is an epitaxial film grown on a (001)-oriented MgO substrate, also using the pulsed laser deposition technique[12].

To investigate the HMF characteristics of these ferromagnetic films, we employ tunneling spectroscopy on these samples using a variable-temperature scanning tunneling microscope (STM). The tunneling spectroscopy is known to be a sensitive probe for studying the density of states of material[18], particularly if the tunneling is into a many-body system

characterized by a renormalized quasi-particle dispersion[19]. In this work, we study the tunneling spectroscopy of the magnetic epitaxial films by measuring the tunneling current as a function of the sample bias voltage. All measured spectra are highly reproducible, and the characteristics are essentially independent of the junction impedance, ranging from high impedance $\sim 100\text{M}\Omega$ to low impedance $\sim 1\text{M}\Omega$. We use paramagnetic Pt for the tunneling tip to prevent possible complications in revealing the magnetic properties of the samples.

The main panels of Figs.1–3 illustrate the differential conductance, $(dI/dV)/\langle I/V \rangle$, normalized with the standard formalism given in Ref. [18], as a function of the bias voltage (V) for $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (LCMO), $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO), and Fe_3O_4 films at $T = 77$ K, respectively. The insets depict the corresponding data taken at $T = 300$ K. Similar measurements have also been conducted on the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ sample, and the results are qualitatively similar to those obtained on the $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ sample, although small quantitative differences exist. These quantitative variations are given in Table I.

Several important features of the data are noteworthy: First, two large peaks, which correspond to the density of states of the majority and minority carriers energetically separated by the on-site exchange energy, are clearly visible in each sample at 77 K. These features disappear at room temperature. Second, near zero bias voltage, the normalized differential conductivity appears to be zero for each sample at 77 K, suggesting the existence of a small energy gap ΔE_G near the Fermi level, characteristic of the half-metallic behavior[4]. Furthermore, AE_c is the largest in LCMO and the smallest in Fe_3O_4 . Third, in the case of perovskite manganites, the exchange energy splitting ΔE_{ex} for the same alkaline earth doping level $x = 0.3$ is larger in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ than in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, (see Table I). For the Sr-doped manganites, on the other hand, the exchange energy splitting is larger in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ than that in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. Fourth, we note that the bandwidths of the majority and minority bands are significantly narrower in the LCMO system than those in the LSMO system. Finally, the exchange energies ΔE_{ex} in the perovskite manganites are significantly larger than that in magnetite Fe_3O_4 , as summarized in Table 1.

Next, we consider the physical implications of our tunneling data taken on these HMF epitaxial films. On the issue of increasing AE_{ex} with the increasing alkaline doping level in

the ferromagnetic state of perovskite manganites, we note that the ratio of Mn^{4+} ions ($e_g^0 t_{2g}^3$) to Mn^{3+} ions ($e_g^1 t_{2g}^3$) increases with increasing x , and that the energy difference between the e_g - and t_{2g} -orbitals results in a larger on-site exchange energy for the Mn^{4+} ions than for the Mn^{3+} ions. Hence, ΔE_{ex} increases with increasing x , which is also consistent with the increase of T_C .

Regarding the enhanced ΔE_{ex} and reduced AE_c from the Ca-doped manganites to the Sr-doped manganites, we note that the smaller ionic size of Ca^{2+} results in a larger degree of lattice distortion from the ideal cubic structure[20]. There are two important consequences of the larger degree of lattice distortion. First, stronger electron localization occurs near the Ca^{2+} site, thereby increasing the density of localized minority carriers and reducing the density of mobile majority carriers. Hence, the conductivity of LCMO is smaller relative to that of LSMO, and the double exchange interaction between the neighboring Mn^{3+} and Mn^{4+} ions[21,22], which is responsible for the ferromagnetism of these doped manganites[20-22], is also weakened in the case of LCMO. Both the Curie temperature T_C and the exchange energy ΔE_{ex} therefore decreases with the decreasing alkaline earth ion size, consistent with our experimental observation. Second, a larger deviation from the cubic structure also results in stronger hybridization of the Mn t_{2g} -orbital and the oxygen p -orbital. The stronger p - d hybridization is believed to enhance the half-metallicity of the manganites[4,6], yielding a larger energy gap in the minority bands. This argument is consistent with our observation of a larger energy gap AE_c in the minority bands of LCMO relative to that in LSMO.

Comparing the exchange energy splitting of the perovskite manganites with that of magnetite Fe_3O_4 , we note that the ferromagnetic exchange interaction for Fe^{2+} ($e_g^2 t_{2g}^4$) and Fe^{3+} ($e_g^2 t_{2g}^3$) at the B-site of the spinel lattice[5] is compensated by the antiferromagnetic exchange interaction between the A-site and B-site Fe^{3+} ions[5]. Hence, the resulting exchange energy split between the minority (associated with the A-site ions) and majority (at the B-site) carriers is significantly reduced, consistent with our experimental observation of a much smaller ΔE_{ex} in Fe_3O_4 than in the manganites.

The above discussion suggests that the tunneling spectra in Figs. 1-3 can be well understood in the context of ferro- and ferrimagnetic half-metallicity. Next, we consider the

temperature dependence of the tunneling spectra. In the case of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, it is easily understood that the energy splitting between the majority and minority bands disappear in the paramagnetic state at room temperature, because $T_c \approx 260$ K. Regarding the absence of room temperature half-metallicity in Fe_3O_4 , we note that magnetite Fe_3O_4 is known to exhibit a sharp Verwey order-disorder transition involving Fe^{3+} and Fe^{2+} ions [10] below the ferromagnetic-to-paramagnetic transition at $T_C = 850$ K. An energy gap ~ 0.76 eV in the minority bands has been predicted from the band structure calculations [3,5]. However, the presence of disorder above the Verwey transition temperature $T_V \sim 120$ K may result in smearing of the energy gap in the minority subbands, and hence the loss of half-metallic characteristics. This scenario is consistent with the NMR measurements of the longitudinal spin relaxation rate $(1/T_1)$ [11], where anomalous temperature dependence of $(1/T_1) \sim T^{5/2}$ for the HMF disappears and a typical metallic dependence of $(1/T_1) \sim T$ is recovered at $T_V < T \ll T_c$. Recent magnetization and magnetoresistance measurements of Fe_3O_4 epitaxial films also indicate the occurrence of the Verwey transition T_V at about 120 K [12].

On the other hand, the disappearance of room-temperature (below T_c) energy splitting between the majority and minority bands in both Sr-doped manganites is not easily comprehensible. This observation is nonetheless consistent with a recent finding of temperature-dependent spin-resolved photoemission spectroscopy on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ [23], where the difference between the spin density of states of the majority and minority bands decreases linearly with increasing temperature, even at temperatures well below T_c . The rapidly vanishing half-metallic ferromagnetism with increasing temperature from the surface-sensitive photoemission measurements has been attributed to the existence of surface magnetization in LSMO, which may be significantly different from the bulk magnetization. Since STM measurements are also surface-sensitive, our results may also be representative of the surface magnetization, and therefore not inconsistent with the bulk half-metallic properties. This issue awaits further quantitative investigation.

In summary, we have investigated the spin-dependent density of states of various half-metallic ferromagnets and ferrimagnets using scanning tunneling spectroscopy. The tunneling spectroscopy of all samples at low temperatures ($T = 77$ K) can be quantitatively

described in the context of half metallicity due to strongly spin-dependent energy bands and the density of states. The room temperature tunneling spectroscopy in the ferromagnetic state of Sr-doped manganites suggests the existence of surface magnetic states which differ from the bulk states.

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- [1] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, *Phys. Rev. Lett.* 50, 2024 (1983).
- [2] P. G. van Engen, K. H. J. Buschow, R. Jongebreur, and M. Erman, *Appl. Phys. Lett.* 42, 202 (1983).
- [3] R. A. de Groot and K. H. J. Buschow, *J. Magn. Magn. Mater.* 54-57, 1377 (1986).
- [4] V. Yu. Irkhin and M. I. Katsnel'son, *Physics-Uspekhi* 37,659 (1994).
- [5] A. Yanase and K. Siratori, *J. Phys. Soc. Jpn.* 53,312 (1984).
- [6] W. E. Pickett and D. J. Singh, *Phys. Rev.* B53, 1146 (1996).
- [7] F. Heusler, *Verb. Dtsch. Phys. Ges.* 5,219 (1903).
- [8] H. Y. Hwang, S.-W. Cheong, N. P. Ong, and B. Batlogg, *Phys. Rev. Lett.* 77, 2041 (1996).
- [9] J. Z. Sun, W. J. Gallagher, P. R. Duncombe, L. I{rusin-Elbaum, R. A. Altman et al., *Appl. Phys. Lett.* 69, 3266 (1996).
- [10] E. J. Verywey, P. W. Haayman and F. C. Romeijn, *J. Chem. Phys.* 15,458 (1947).
- [11] T. Mizoguchi and M. Inoue, *J. Phys. Sot. Jpn.* 21,310 (1966).
- [12] G. Q. Gong, A. Gupta, G. Xiao, W. Qian and V. P. Dravid, *Phys. Rev.* B56, 5096 (1997).
- [13] N.-C. Yeh, R. P. Vasquez, D. A. Beam, C. C. Fu, J. Huynh and G. Beach, *J. Phys.:* *Condens. Matter*9, 3713 (1997); N.-C. Yeh et al., *J. Appl. Phys.* 81, 5499 (1997); *Epitaxial Oxide Thin Films – III*, *Mat. Res. Sot. Sym. Proc.* 474,145(1997).
- [14] J. Y. T. Wei, N.-C. Yeh and R. P. Vasquez, submitted to *Phys. Rev. Lett.* (1997).
- [15] R. P. Vasquez, *Phys. Rev.* B54, 14938 (1996).
- [16] A. V. Boris, N. N. Kovaleva, A. V. Bazhenov, A. V. Samoilov, N.-C. Yeh, and R. P. Vasquez, *J. Appl. Phys.* 81,5756(1997).
- [17] A. Gupta, G. Q. Gong, G. Xiao, P. R. Duncombe, P. Lecoeur, P. Trouilloud, Y. Y. Wang, V. P. Dravid, and J. Z. Sun, *Phys. Rev.* B54, R15629 (1997); *Appl. Phys. Lett.* 67, 3494 (1995).
- [18] For a review, see, for example, R.M. Feenstra, *Surf. Sci.* 299/300,965 (1994); R. J. Harems, *Ann. Rev. Phys. Chem.* 40, 531 (1989).

- [19] G. D. Mahan, *Many Particle Physics*, Plenum, New York (1990); E. L. Wolf, *Principles of Electron Tunnel Spectroscopy*, Oxford Univ. Press (1985).
- [20] J. B. Goodenough, A. Weld, R. J. Arnott, and N. Menyuk, *Phys. Rev.* **124**, 373 (1961); J. B. Goodenough, *Progress in Solid State Chemistry*, vol.5, ed. by H. Reiss, Oxford: Pergamon, (1971).
- [21] G. H. Jonker and J. H. van Santen, *Physics* 16, 337 (1950); J. H. van Santen and G. H. Jonker, *Physics* 16, 599 (1950).
- [22] C. Zener, *Phys. Rev.* 82, 403 (1951); E. O. Wollan and W. C. Koehler, *Phys. Rev.* **100**, 545 (1955).
- [23] J. H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, submitted to *Phys. Rev. Lett.* (1997).

Fig.1 The normalized differential conductance, $(dI/dV)/(I/V)$, of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ as a function of the bias voltage (V) at $T = 77$ K. The inset shows the corresponding tunneling spectroscopy at 300 K. The exchange energy splitting is $\Delta E_{ex} = 3.3 \pm 0.2$ eV, and the energy gap in the minority states is $AE_c = 0.9 \pm 0.1$ eV.

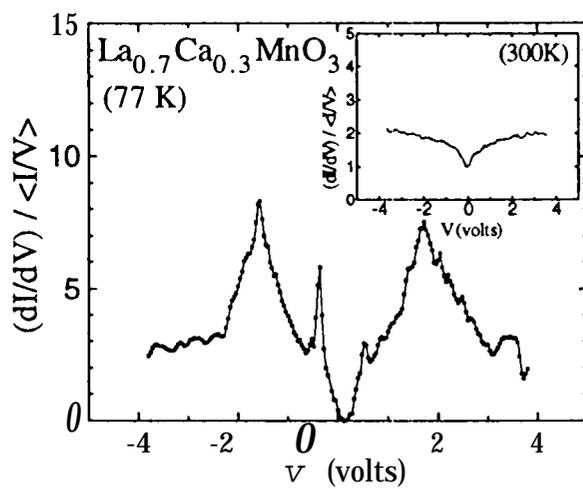
Fig.2 The normalized differential conductance, $(dI/dV)/(I/V)$, of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ as a function of the bias voltage (V) at $T = 77$ K. The inset shows the corresponding tunneling spectroscopy at 300 K. The exchange energy splitting is $\Delta E_{ex} = 5.0 \pm 0.2$ eV, and the energy gap in the minority states is $AE_c = 0.6 \pm 0.1$ eV.

Fig.3 The normalized differential conductance, $(dI/dV)/(I/V)$, of Fe_3O_4 as a function of the bias voltage (V) at $T = 77$ K. The inset shows the corresponding tunneling spectroscopy at 300 K. The exchange energy splitting is $\Delta E_{ex} = 0.8 \pm 0.2$ eV, and the energy gap in the minority states is $AE_c = 0.2 \pm 0.1$ eV.

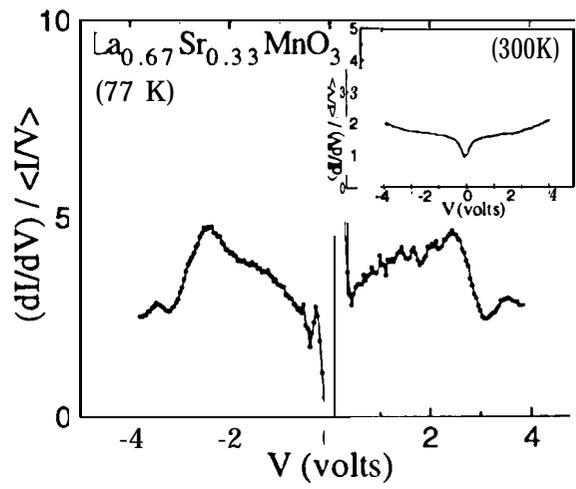
Table 1. Summary of the tunneling spectroscopy measurements on the manganite and magnetite **epitaxial** films. The uncertainties in the energies come from spectral variations, and T_V is the Verwey temperature for Fe_3O_4 .

Material	T_c [K]	ΔE_{xx} [eV]	ΔE_G [eV]
$\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$	260	3.3 \pm 0.2	0.9 \pm 0.1
$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$	320	4.0 \pm 0.2	0.7 \pm 0.1
$\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$	360	5.0 \pm 0.2	0.6 \pm 0.1
Fe_3O_4	850 ($T_V=120\text{K}$)	0.8 \pm 0.2	0.2 \pm 0.1

HC-10
Fig. 1
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Fig. 2
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HC-10
Fig. 3
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