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Photoluminescence probed minority processes in $La_{2/3}Sr_{1/3}MnO_3$ thin films

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ABSTRACT

$La_{2/3}Sr_{1/3}MnO_3$ thin films are studied with temperature variable photoluminescence (PL) spectroscopy. Two emission peaks are assigned to the minority carriers related transition processes. The temperature independent 2.526 eV peak is attributed to the charge transfer type inter-band transition, while the redshifted doublet peak around 1.686 eV to the spin flip process. Band structures are obtained within the density functional theory, which show the consistent band gaps with the PL data. The temperature dependence of the intensity of PL emission suggests that these minority carrier processes are relevant to polaron formation.

1. Introduction

Spintronics exploit the spin related properties by distinguishing and manipulating the spin up and spin down currents as well as the associated spin information [1]. A group of transition metal oxide with strong correlated electrons such as $La_{1-x}Ca_xMnO_3$ (LCMO) and $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) [2,3] has the property of spin polarization, which makes them interesting and a possible candidate for spintronics applications. The underlining physics of the spin polarization in these materials is indispensible from their electronic band structure. At temperature higher than the Curie temperature T_c, the majority carriers of e_g band have equal density of states (DOS) to those of the minority ones. With decreasing temperature, the DOS of majority spin up (minority spin down) increases (decreases) until it reaches a fully polarized state. In such a state, it becomes metallic in majority band with one spin channel and insulating in minority band with a semiconducting gap, i.e. a state of half-metal which spins can be manipulated for the spintronic applications. Understanding of electronic states, especially of minority carriers, is important from both fundamental and technical points of view. While $La_{1-x}Ca_xMnO_3$ (LCMO) is the first system to be claimed with colossal magnetoresistance (CMR) and most thoroughly investigated CMR material $La_{2/3}Sr_{1/3}MnO_3$ (LSMO), though in many ways alike LCMO, is different from LCMO in two aspects: firstly, the optimally doped composition of LSMO has a T_c above room temperature and 100% of spin polarization [4]. Secondly, in LSMO, the ferromagnetic transition is of conventional second order and no polaron order has been observed associated with the ferromagnetic transition [5,6]. Up to now the electronic states of doped manganites have been studied mostly by using optical conductivity [7], photoemission [8], and pump-and-probe method as well as[9,10], elastic and inelastic neutron diffraction [11]. Most of the above-mentioned electronic-structure studies are on LCMO. On the other hand, photoluminescence (PL) spectroscopy is a powerful tool to detect the electronic structure by measuring the emissions from the transitions between various electronic states, and has not been widely employed on CMR materials. In this work, the temperature dependent PL measurements are carried out on good quality LSMO thin films in order to investigate the less studied, yet important electronic structure of this material. In the temperature range of this study (80–310 K), the LSMO thin film is in the metallic ferromagnetic state. In principle, no PL emission is expected for a normal metal. However, due to the half metallic nature, there is a band gap for minority carriers which can be detected via PL measurements. The goal of this study is to understand the minority band structure in LSMO and the origin of the related excitation process, which is important for the future spintronics applications.

2. Experimental

LSMO thin films 30 nm thick are deposited on the $LaAlO_3$ (0 0 1) substrate using a commercial pulsed laser deposition system. The crystalline structure of LSMO film is characterized by X-ray powder diffraction. To demonstrate the diffractions from LSMO, a log scale is used (Fig. 1). Only (0 0 l) peaks of LSMO and

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$LaAlO_3$ show up, indicating a single-phase pattern with *c*-orientation. The temperature dependence of magnetization under zero-field-cool condition is measured with a superconducting quantum-interference device (SQUID)-vibration sample magnetometer (VSM), indicating a Curie temperature of around 320 K. The PL measurements are carried out with a Horiba Jobin Yvon HR-800 UV micro-PL-Raman system. A 325 nm He–Cd laser is used as the excitation source. The PL spectra are collected with a 2400 grooves mm^{-1} grating in a backscattering geometry.

3. Results and discussion

Fig. 2 plots the PL spectra of LSMO thin film with temperature increasing from 80 K to 310 K (bottom up) with 10 K increment. At room temperature, two emission peaks are found around 1.7 eV and 2.5 eV as seen in (a) and (b) respectively. Different from the 2.5 eV peak, the 1.7 eV peak shifts to high energy and decomposes into two peaks at low temperature with a separation of 0.7 meV at 80 K, indicating the nature of a doublet peak.

To analyze the experimental PL results, we calculate the band structures of bulk $La_{2/3}Sr_{1/3}MnO_3$ within density functional theory with the generalized gradient approximation (GGA) plus the modified Becke and Johnson (mBJ) potential by using the WIEN2k package [12–14]. We adopt the experimental values for lattice constant of $a=3.89$ Å [15]. As shown in Fig. 3, our results are qualitatively similar to the calculated results based on SIESTA method as reported by Ferrari et al. [16], but the WIEK2k method is more accurate, since it uses a nearly complete basis.

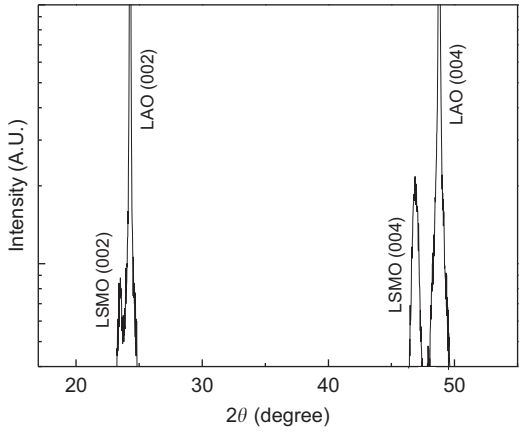

Fig. 1. X-ray diffraction spectrum of *c*-orientation LSMO thin film.

As shown in the left panel of Fig. 3, the band gap between the conduction band minimum (CBM) at Γ point and the valence maximum (VBM) at the M point for minority is 2.752 eV, which is close to experimental gap of 2.526 eV as suggested by Fig. 2. Without adding the mBJ potential, the band gap calculated by WIEN2k method reduces to 1.415 eV. The difference of ~1.3 eV is attributed to the many-body self-energy correction [17]. The energy difference between the minority-carrier VBM and the Fermi level (determined by majority carriers) is around 2.06 eV with the mBJ potential and 1.6 eV without the mBJ potential. Since the inclusion of the mBJ potential overestimated the band gap by ~0.23 eV, it is conceivable that the energy difference of the VBM and Fermi level in actual system could be close to 1.7 eV, which explains the 1.7 eV PL peak in Fig. 2(b). A dipole allowed spin-flip process involving spin up Mn^{3+} and spin down Mn^{4+} was proposed to result in a ~1.7 eV emission in previous reports [18,19]. This transition energy is close to the energy difference between VBM and the Fermi level as calculated here. Based on the calculated band structures shown in Fig. 3(a), there is a flat band near VBM for wave vectors spanning from the M to R point and from M to X point with energy dispersion <0.05 eV. When the system is under photoexcitation, we expect that minority-spin holes to be accumulated near the VBM (distributed along the M–X and M–R directions). These holes can recombine with the majority-spin electrons near the Fermi level via the dipole-allowed spin-flip processes. Although, in principle, all majority-spin electrons below the Fermi level can recombine with the holes via this process, the emission peak should be dominated by electrons near the Fermi level as a consequence of the Fermi-edge singularity effect, sometimes referred to as the Mahan exciton [20,21]. As seen in Fig. 3(b), there are two bands crossing the Fermi level as indicated by circles in the figure. Each Mahan exciton should be a linear combination of electronic states of different k-pts near the Fermi level (i.e. M-X and M-R branches are mixed together). Since there are two bands, we have two Mahan excitons after solving the two band problem, and the two exciton resonances have a small splitting. These two Mahan excitons correspond to the two peaks observed experimentally near 1.7 eV. It should be pointed out that even holes are responsible for the electrical transportation in LSMO; under the laser excitation the majority (spin-up) carriers involved in the optical PL emission of 1.7 eV are electrons.

The exact position and intensity of the PL peaks can be obtained by fitting with Lorentz functions. Fig. 4 (a)–(d) shows the temperature dependent data of position and intensity for

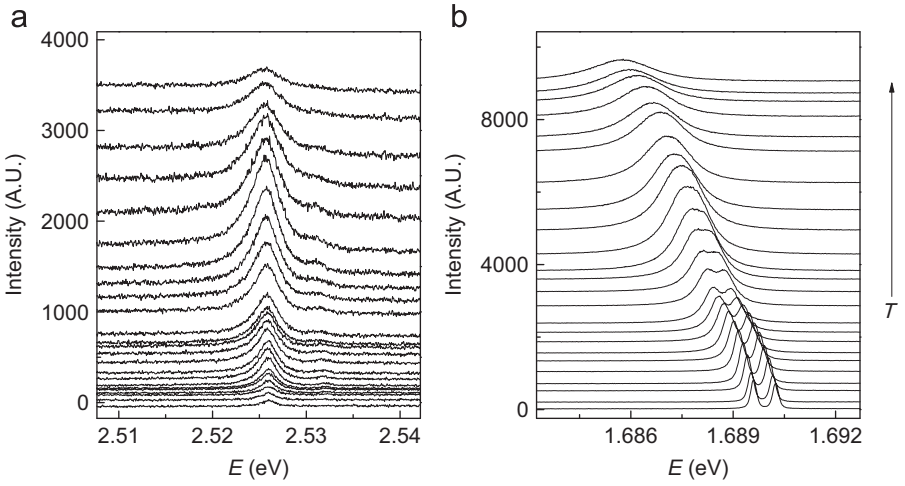

Fig. 2. PL spectra of LSMO thin film in the temperature range of 80–310 K: (a) 2.5 eV emission and (b) 1.7 eV emission.