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Mn 3s-2p x-ray emission spectra for $La_{1-x}Sr_xMnO_3$

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Introduction

Perovskite-type Mn oxides attract a great deal of interest from both fundamental and applicational viewpoints because of their interesting properties such as the CMR effect. The Mn 3d electrons in the compounds are closely related to those properties. The number of the 3d electrons in a given Mn compound can be evaluated by measuring the Mn 3s photoemission spectroscopy (PES) spectrum. The spectrum exhibits a double-peak structure, the so-called exchange splitting resulting from the exchange interaction between the Mn 3s hole and the Mn 3d electrons. The splitting energy depends on the number of the 3d electron or Mn valency. Galakhov et al. have illustrated the fair correlation between the splitting energy and the Mn valency of Mn oxide [1]. We also found the Mn 3s PES spectrum for $Pr_{0.5}Ca_{0.5}MnO_3$ reflecting change in the Mn valency across the charge-order transition [2].

The PES spectrum is, however, more or less surface-sensitive and sometimes gives misleading information on the inherent bulk nature of the material. In addition the spectrum for the insulating material suffers the charging effect by photoirradiation. On the other hand x-ray emission spectroscopy (XES) is much less surface-sensitive and is not affected by the charging effect. The 3s-2p radiative transition leaves the 3s hole. Thus the Lη and Ll, i.e. 3s-2$p_{1/2}$ and 3s-2$p_{3/2}$, respectively, XES spectra for Mn compounds also exhibit the exchange splitting. It has been found that the Lη spectrum for Mn oxides does exhibit the double-peak structure reminiscent of the Mn 3s PES spectrum, whereas it is hard to evaluate undoubtedly the splitting energy in the Ll spectrum [3]. We have measured the Lη spectrum for a series of $La_{1-x}Sr_xMnO_3$ from x=0 to 1 and investigate the correlation between the exchange-splitting energy and the Mn valency of $La_{1-x}Sr_xMnO_3$.

Results

Sintered polycrystalline $La_{1-x}Sr_xMnO_3$ samples were fractured in situ before the XES measurements. The excitation energy was set at the Mn 2$p_{1/2}$ absorption peak position, ca. 655 eV to enhance the Lη emission. Measurements were carried out at RT.

Fig. 1 shows the Mn 3s-2p XES spectrum for $LaMnO_3$ measured in the depolarized configuration. The FWHM of the incident photons was about 1.5 eV. The overall shape of the present spectrum is almost identical to the one shown in Fig. 9 in Ref. 3. The 3s-2$p_{3/2}$ emission has a peak at 560.5 eV and the counterpart of the exchange splitting for the peak is located around 557 eV. Two peaks are seen at 568.6±0.2 and 572.7±0.2 eV for the 3s-2$p_{1/2}$ emission. The apparent splitting energy is 4.1 eV, which is smaller than 5.3 eV for the Mn 3s PES spectrum of $LaMnO_3$ [2] as was reported in the previous study [3].

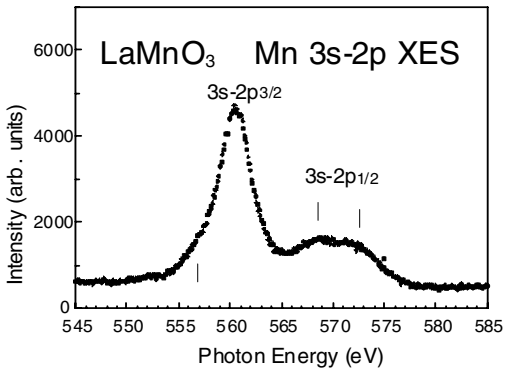

Fig. 1. Mn 3s-2p x-ray emission spectrum for $LaMnO_3$. The excitation photon energy was 654.6 eV.

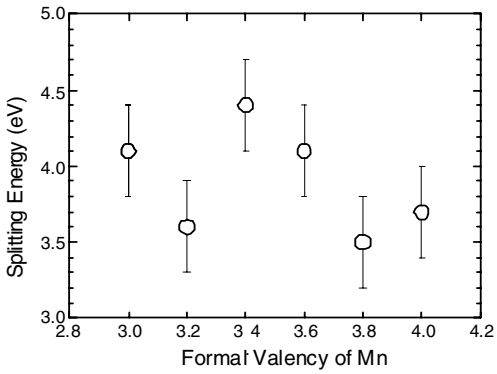

Fig. 2. Splitting energy of Mn 3s-2$p_{1/2}$ emission as function of formal Mn valency of $La_{1-x}Sr_xMnO_3$.

In Fig. 2 the splitting energy of the Mn 3s-2$p_{1/2}$ emission for $La_{1-x}Sr_xMnO_3$ is plotted as the function of nominal Mn valency. The splitting energy tends to decrease with increasing the Mn formal valency of $La_{1-x}Sr_xMnO_3$ as is the case fo0r Mn 3s PES.

References

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