XAS and XMCD study of Mn and Co nanoclusters on Si (111)-(7x7)

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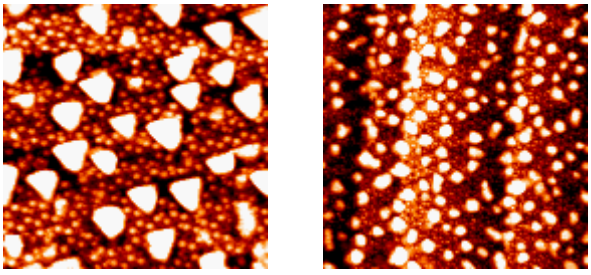
Magnetic nanoclusters attract growing interest because of the great potential applications in the fields of high-density data storage, sensors and spin electronic devices. Recently, Jia et al. found that a high quality ordered Al nanocluster array could be prepared on Si (111)-(7x7) surface and the array exhibit a remarkable thermal stability that it is an ideal template for growing magnetic nanostructures [1]. In this work, Co and Mn nanoclusters were deposited on the template. Fig 1 shows the observed STM images. In both images, the homogeneous small white dots are Al nanoclusters and the larger white spots are Co and Mn ones. Subsequently, Au film with 2 nm thickness and Ag film with 5 nm thickness were capped on the Co and Mn clusters respectively to prevent them from oxidation.



(a) (b)

Fig.1. (a) STM image (40 nm x 40 nm) of Co nanoclusters at a Co coverage of 1 ML. (b) STM image (80 nm x 80 nm) of Mn nanoclusters at a Mn coverage of 1.5ML.

X-ray absorption spectroscopy (XAS) combined with x-ray magnetic circular dichroism (XMCD) is probably the most powerful technique to study magnetic clusters. The line shape of the XAS spectra is a fingerprint for the d-state configuration, whereas XMCD yields the spin and orbital magnetic moment via well-known sum rules [2,3] in an element specific manner. We performed *ex-situ* XAS and XMCD measurements for Mn and Co nanoclusters by means of a total photoelectron yield method at the temperature of about 50 K. The spectra were taken at a fixed applied magnetic field and XMCD was obtained by switching the helicity of light at each data point.

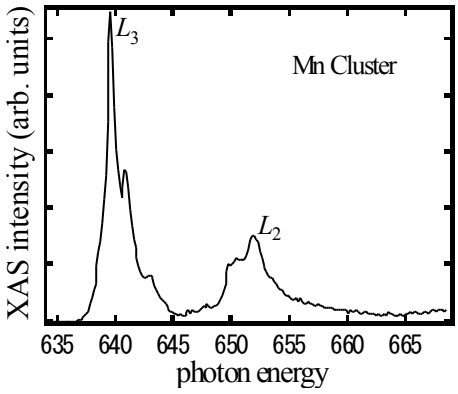


Fig.2. $L_{2,3}$ edge XAS spectra of Mn nanocluster

Fig.2 (a) shows Mn $L_{2,3}$ XAS spectrum of Mn nanocluster. Several fine structures on both L_3 and L_2 absorption edges were found. For L_3 edge, a distinct peak and shoulders at photon energies 1.2 eV and 3.5 eV higher than the L_3 edge (hv=639.7 eV) can been observed. On the L_2 edge, the peak at hv=

652.0 eV and some structures on the lower hν side can be observed.

It is well known that the L_3-L_2 branching ratio (R_0=I(L_3)/I(L_2)) and multiplet structures are quite sensitive to the electronic configuration and hence the charge state of the transition metal cation especially for Mn and Cr as pointed out by F. de Groot et al [4]. And the variation of the ratio could be distinguishable even for relatively low concentrations of an element [5]. The small XAS L_3-L_2 branching ratio (2.1) and rich fine structures in the lineshape of the Mn nanoclusters show that Mn^{3+} electronic configuration should be taken into account, which indicates that Mn3*d*-Al3*p* hybridization is important.

Fig.3 (a) shows Co 2*p* XAS spectrum of the Co nanoclusters, where a linear background has been subtracted. We observe L_2 and L_3 core absorption edges at the incident photon energies (hν's) of 778.4 eV and 793.7 eV, respectively. The superpositions of peaks in the L_3 edge are very clear and marked by arrows (a) and (b). These multiplet fine structures superimposed on the metallic background can be attributed to Co^{3+} in an octahedral environment with different magnitudes of crystal field parameter $10D_q$[4]. We assume that this kind of Co^{3+} character comes from the Co-Al covalence bonding at the Co-Al interface. The R_0 was estimated to be 3.1, which is much larger than the statistical value of 2.0. Such a high intensity ratio indicates that the 3*d* ground state of Co nanoclusters is a high spin state [6].

Fig.3 shows XMCD spectrum for the Co nanoclusters. One finds the clear XMCD ($\mu_+ - \mu_-$) with negative sign at hν=778.4 eV, and there is a much smaller satellite at 780.6 eV. Compared with the strong peak at L_3 edge, the peak at L_2 edge is very weak.

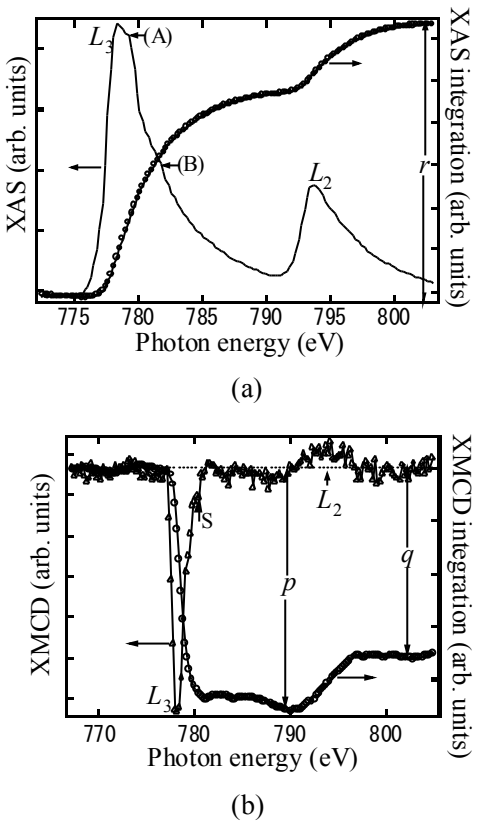


Fig.3. (a) Co $L_{2,3}$ XAS spectrum (arrows A and B indicate the multiplet structures) and its integration. *r* is the integral needed in the sum-rule analysis. (b) XMCD spectrum (arrow S indicates the satellite structure) and its integration. *p* and *q* are the integrals needed in the sum-rule analysis.

The satellite structure appeared in the XMCD spectrum indicates a localized atomiclike character of the Co 3*d* electrons. Estimation based on the sum rules gives out a very large value of m_L / m_S =0.37. This remarkable property combined with the advantage of Si substrate make the present system an attractable candidate for the future high-density magnetic recording.

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