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High Energy-Resolution EELS and SXES Studies on Characteristic Chemical Shifts and Charge Transfer in Al-Si-Mn and Zn-Mg-Zr Alloys

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In recent years, Hume-Rothery mechanism, which predicts a existence of a pseudogap around the Fermi level E_F, is accepted as a major reason for the stabilization of quasicrystals. The presences of pseudogap in quasicrystals were confirmed by X-ray photoemission spectroscopy and electron energy-loss spectroscopy (EELS). EELS experiments also pointed out characteristic chemical shifts in Al L-shell excitation spectra of Al-based quasicrystals [1], which suggested a decrease of valence electron charge at Al sites. Recently, a covalent bonding nature in quasicrystals was reported by MEM/Rietveld analysis [2]. Thus, it is interesting to investigate the relation between a chemical shift and bonding nature of the quasicrystals.

In this study, the chemical shift of $Al_{53}Si_{27}Mn_{20}$ alloys [3] and Zn-Mg-Zr alloys [4] were investigated by using EELS and soft-X-ray emission spectroscopy (SXES). For EELS and SXES measurements, a high energy-resolution EELS-TEM [5] and an SXES-TEM [6] were used. Those results of the amount of chemical shifts are compared with those of pure materials or their oxides.

Figure 1(a) shows Al L-shell excitation (EELS) spectra of amorphous (Am), quasicrystalline (QC) and crystalline (Cryst) phases of $Al_{53}Si_{27}Mn_{20}$ alloys. Only the QC phase shows an apparent shift to the larger binding energy side by 0.4 eV compared with that of Al single crystal. This result should be due to a shift of Al L-level of QC phase to the larger binding energy side (chemical shift). Figure 1(b) show SXES spectra of Al-K_α and Si-K_α of Am, QC and Cryst phases. A peak position of each spectrum is assigned as the top of intensity maximum indicated by a vertical line. Al-K_α emission of QC phase clearly shows a shift to the larger energy side by 4 eV. This tendency is consistent with that of EELS measurements. Si-K_α of QC phase also shows a clear shift. However, there was not a chemical shift for Mn-L_α. This suggests that the amount of valence electron of Al and Si atomic sites decreased, expect Mn sites, in the QC phase [7].

Figure 2(a) shows Zn M-shell excitation (EELS) spectra of Zn-Mg-Zr alloys of primitive icosahedral quasicrystal (P-QC), face-centered icosahedral quasicrystal (F-QC) and a 1/1-approximant (1/1-AP) of F-QC phases. Only P-QC and F-QC alloys show an apparent shift to larger binding energy side compared with pure Zn. The apparent chemical shifts in QC alloys were also observed in Mg L-shell excitation spectra (not shown here). Figure 2(b) shows Zn-L_α emission spectra of the alloys. The Zn-L_α emission of pure Zn and ZnO are also shown for comparison. P-QC and F-QC alloys clearly show a shift to the larger binding energy side by about 2 eV compared with pure Zn. These shifts are comparable to that of ZnO.1/1-AP does not show any shift within experimental accuracy.

Those results show a presence of characteristic chemical shift not only in Al-based quasicrystalline alloy but also in Zn-based quasicrystalline phase. Therefore, a chemical shift to the larger binding energy side (decrease of valence charges on atomic sites) can be a common characteristic in quasicrystalline states. It strongly suggest that an increase of covalency in quasicrystal states.

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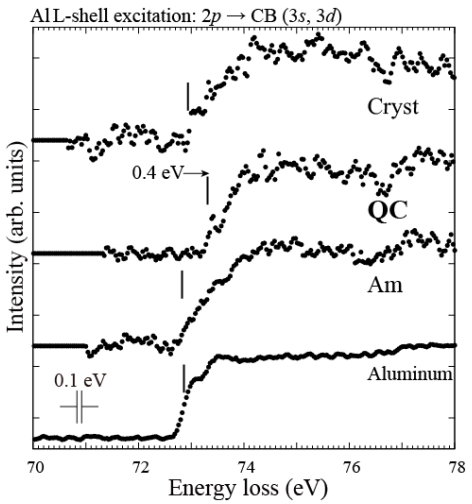

FIG 1(a). Al L-shell excitation (EELS) spectra of Am, QC and Cryst phases of Al-Si-Mn alloy and pure Al.

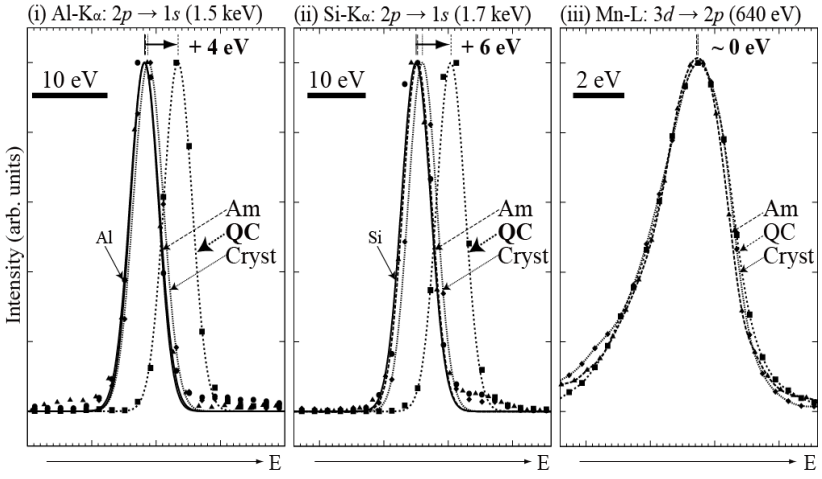

FIG 1(b). Al-K_α, Si-K_α and Mn-L emission (SXES) spectra of Am, QC and Cryst phases of Al-Si-Mn alloy.

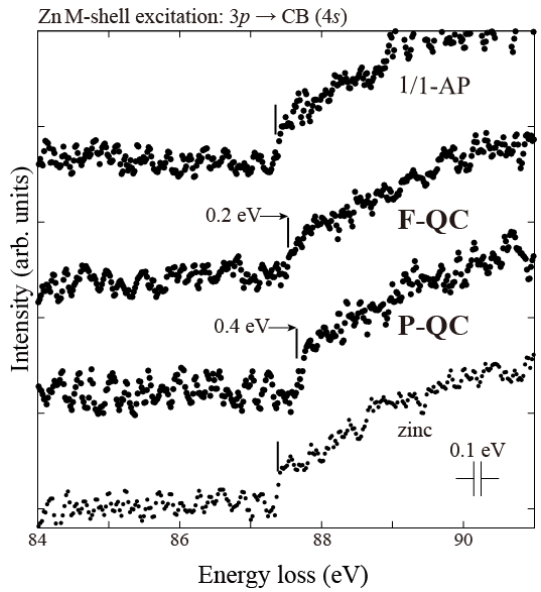

FIG 2(a). Zn M-shell excitation spectra of P-QC, F-QC and 1/1-AP of Zn-Mg-Zr alloy and pure Zn.

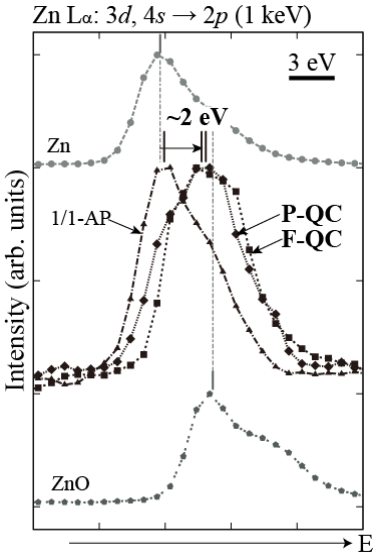

FIG 2(b). Zn L_α-emission spectra of P-QC, F-QC and 1/1-AP alloys of Zn-Mg-Zr, pure Zn and ZnO.

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