Prominent 5d-orbital contribution to the conduction electrons in gold probed by polarization-dependent hard X-ray photoemission

Single-element materials in the same column in the periodic table often show mutually similar features, as seen in alkaline-(earth) metals and halogens. On the other hand, it is known that among noble metals, gold has considerably different chemical stability from that of silver even though their electronic structure near the Fermi level, as well as Fermi surface topology, is thought to be almost equivalent. For instance, it is well known that solid gold is very stable under many circumstances, whereas solid silver is gradually oxidized in air. The valence-band electronic configurations of these solids per atom have so far been recognized to be composed of fully occupied nd states (nd\(^{10}\)) plus one conduction electron occupying an \((n+1)s\) state \((n = 4 \text{ for silver and } n = 5 \text{ for gold})\), but it has not been experimentally verified whether these configurations are correct or not.

Hard X-ray photoemission spectroscopy (HAXPES) shows, in addition to high bulk sensitivity, such characteristic features as (1) comparable s and ip \((i > 3)\) photoionization cross sections to those for the d and f orbitals and (2) orbital-dependent photoelectron angular distribution with respect to the polarization of excitation photons [1]. Figure 1 shows the photoelectron angular distribution for the Ag 4d, 5s, and In 5p (nearly equivalent to the Ag 5p) orbitals in the HAXPES region as a function of take-off angle \(\delta\), which is defined as the angle between the direction of the electric field (polarization) of photons and the horizontal plane in which the momentum direction of the photoelectrons to be detected is involved. Here, \(\delta = 0^\circ\) \((90^\circ)\) corresponds to the p-polarization (s-polarization) configuration. One can recognize from the figure, that the Ag 4d photoelectron intensity is not very suppressed in the s-polarization configuration compared with that in the p-polarization configuration, whereas the Ag 5s and 5p photoelectron intensities are strongly suppressed in the s-polarization configuration. As an overall tendency, the theoretical calculation [1] predicts that the photoelectron intensity at the s-polarization configuration relative to that at the p-polarization configuration is as low as \(< 0.1 – 0.2\) for the s and ip \((i > 4)\) states compared with that for the d and f states at the photoelectron kinetic energy of \(~10\) keV, which has been experimentally verified for several inner-core orbitals [2]. Therefore, the orbital contribution in the valence bands in solids could be revealed by linear polarization-dependent HAXPES.

In order to realize the linear polarization-dependent HAXPES, we have switched the linear polarization of the excitation light using a single-crystalline (100) diamond phase retarder with the 220 reflection [2,3] with a thickness of \(0.7\) mm, placed downstream of the post-monochromator (channel-cut Si crystal). The transmittance of the X-ray at \(~8\) keV for the diamond was confirmed to be \(~35\%). The polarization-dependent HAXPES was performed at BL19LXU using an MBS A1-HE photoelectron spectrometer. Polycrystalline gold and silver prepared by \textit{in situ} evaporation were measured at 12–15 K. The energy resolution was set as \(~280 \sim 400\) meV for the measurement of silver (gold). The spectral weights were normalized by the photon flux. It should be noted that this technique is useful even for polycrystalline samples, as we demonstrate here.

Figure 2 shows the polarization dependence of the valence-band spectra for polycrystalline silver and gold. For silver, the relative spectral weight from the Fermi level \((E_F)\) to the binding energy of

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3 eV is markedly suppressed in the s-polarization configuration compared with that in the p-polarization configuration, where both spectra are roughly normalized at the intensity at the binding energy of 4–5 eV. This polarization dependence as a function of the binding energy reveals that the 4d bands are located far below $E_F$ and are well separated from the conduction 5s band in the energy region from $E_F$ to ~3 eV. It is thus experimentally confirmed that the 4d orbitals are nearly fully occupied whereas the conduction electrons are, to some extent, free-electron-like with a negligible 4d contribution in the solid silver, as has long been expected. On the other hand, the polarization dependence of the valence-band spectra near $E_F$ for bulk gold is not only quantitatively but also qualitatively different from that for silver. When the spectra are normalized by the intensity in the binding energy region of 2–5 eV, where the Au 5d bands are located, the spectral weight near $E_F$ is negligibly suppressed even in the s-polarization configuration. Our detailed analysis has shown the prominent (about 50%) 5d-orbital contribution to the conduction electrons in gold.

The revealed qualitative difference in the mixing of d-orbitals in the conduction bands crossing $E_F$ between silver and gold, which is schematically shown in Fig. 3, originates from the different strengths of the electron correlation. In the case of silver, the Ag 4d electron correlation effects cannot be neglected when discussing its electronic structure, whereas the Au 5d correlation effects are much weaker. Considering our finding and the fact that platinum with a band structure almost equivalent to that of gold is also very stable in air, where the 5d contribution to the conduction electrons is undoubtedly predominant, we can conclude that the prominent 5d contribution to the conduction electrons has a role in protecting gold from oxidization in air.

Our result has also revealed the presence of intrinsic 5d holes in gold. It is expected that there are 5d holes even in the previously investigated gold nanoparticles that show magnetism at beamline BL39XU [4]. The number of 5d holes will increase if the conduction electrons are transferred from the nanoparticles to neighboring molecules as discussed in Ref. [4]. In this context, it is natural to consider a role of 5d holes in the magnetism of gold nanoparticles, although our result does not give direct evidence of such a situation.

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### References


