Electronic Structure of the Organic Conductor (DMe-DCNQI)$_2$Cu Studied by Photoemission Spectroscopy

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An x-ray photoemission study of (DMe-DCNQI)$_2$Cu is reported. The line-shape analysis reveals the mixed valency of Cu$^+$ and Cu$^{2+}$, and the Cu$^+$ : Cu$^{2+}$ ratio is found to be $\sim 2 : 1$. This suggest that Cu is in a valence fluctuating state in the metallic state and, in other (DCNQI)$_2$Cu compounds, a Cu$^+$-Cu$^{2+}$ charge-ordering takes place below the metal-insulator transition temperature.

1. INTRODUCTION

The (DCNQI)$_2$Cu salts show many intriguing properties and have attracted interest especially from the viewpoints of the synthesis of a new type of organic superconductors and the possibility of organic dense-Kondo systems. It has been suggested that these anomalous properties may stem from the mixed valency of the Cu atoms. If the Cu atoms are in a mixed-valent state, the x-ray photoemission spectroscopy (XPS) spectra of the Cu 2p core level of these salts should show satellite structures characteristic of the Cu$^{2+}$ state. But there have been two different reports on the Cu 2p XPS spectra of these salts, which aroused a controversy. In the present work, we have studied the photoemission spectra of (DMe-DCNQI)$_2$Cu (DMe=dimethyl) in order to clarify this point.

2. EXPERIMENTAL

This experiment was performed using a spectrometer having a base pressure of $\sim 10^{-10}$ Torr equipped with a Mg x-ray source for XPS. Needle-like crystals were glued side by side like a raft on an Al sample holder with conducting epoxy and the surface layers were removed by scraping with a diamond file in the ultra-high vacuum chamber.

3. RESULTS AND DISCUSSION

As-received samples show pronounced satellite structures at $\sim 945\,\text{eV}$ as reported by Kobayashi et al.\textsuperscript{1}; these satellite could be removed by scraping the surfaces in the present study. The spectrum for the scraped surfaces (Fig.1 top) is highly reproducible; its line-shape resembles that reported by Schmeißer et al.\textsuperscript{2} and seems that only Cu$^+$ exists. However, there is a weak feature at $\sim 945\,\text{eV}$, and the shape of the main peak is evidently asymmetric. Therefore, the decomposition of the Cu 2p spectrum into
In order to explain the nature of the MI transition, from this standpoint, the bulkiness of the substituents is considered as a controlling parameter. When the bulkiness of the substituents are large, such as CH₃ or CH₃O, the CuN₄ cluster cannot be distorted so much, then it is close to the T₅ symmetry and stabilizes the Ψ₉(Cu⁺) state through the bond formation between the ligand ρₜ orbital and the 4s4p₃ hybrids of Cu. In these salts, an ionization level of Cu is not high enough to fill the ρ₁ conduction band to the third. On the other hand, when its bulkiness is small, such as halogens, the CuN₄ cluster is distorted towards the square-planer configuration through the increase in the ρ₁-d covalency to stabilize the Ψ₉(Cu²⁺) state; hence the ionization level of Cu⁺ is raised. Accordingly the number of the electron in the conduction band is increased to be enough to fill the conduction band to the third. In addition, if the Cu⁺ : Cu²⁺ ratio is incommensurate, it will be energetically unfavorable for the MI transition to occur, because a Cu ion itself cannot take an intermediate valence in the insulating, charge-ordered state.

Thus, the degeneracy of the Ψ₉(Cu²⁺) and Ψ₁(Cu⁺) accompanied by the accidental commensuration of the Cu⁺ : Cu²⁺ ratio drives the MI transition, and these are controlled by the bulkiness of the substituents.

REFERENCES


3. I.H. Inoue et al., to be published.