

Advanced Research Center for Beam Science – Electron Microscopy and Crystal Chemistry –

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Scope of Research

We study crystallographic and electronic structures of materials and their transformations through direct imaging of atoms or molecules by high-resolution electron spectromicroscopy, which realizes energy-filtered imaging and electron energy-loss spectroscopy as well as high-resolution imaging. By combining this with scanning probe microscopy, we cover the following subjects: 1) direct structure analysis, electron crystallographic analysis, 2) elemental analysis and electronic states analysis, 3) structure formation in solutions, and 4) epitaxial growth of molecules.



KEYWORDS

STEM EELS ELNES Core-Hole First-Principle Calculation

Recent Selected Publications

Haruta, H.; Nii, A.; Hosaka, Y.; Ichikawa, N.; Saito, T.; Shimakawa, Y.; Kurata, H., Extraction of the Local Coordination and Electronic Structures of FeO₆ Octahedra Using Crystal Field Multiplet Calculations Combined with STEM-EELS, *Appl. Phys. Lett.*, **117**, [132902-1]-[132902-5] (2020).

Yamaguchi, A.; Nemoto, T.; Kurata, H., Study of C K-Edge High Energy Resolution Energy-Loss Near-Edge Structures of Copper Phthalocyanine and Its Chlorinated Molecular Crystals by First-Principles Band Structure Calculations, *J. Phys. Chem. A*, **124**, 1735-1743 (2020).

Haruta, M.; Fujiyoshi, Y.; Nemoto, T.; Ishizuka, A.; Ishizuka, K.; Kurata, H., Extremely Low Count Detection for EELS Spectrum Imaging by Reducing CCD Read-out Noise, *Ultramicroscopy*, **207**, [112827-1]-[112827-6] (2019).

Yamaguchi, A.; Haruta, M.; Nemoto, T.; Kurata, H., Probing Directionality of Local Electronic Structure by Momentum-Selected STEM-EELS, *Appl. Phys. Lett.*, **113**, [053101-1]-[053101-4] (2018).

Haruta, M.; Fujiyoshi, Y.; Nemoto, T.; Ishizuka, A.; Ishizuka, K.; Kurata, H., Atomic-Resolution Two-Dimensional Mapping of Holes in the Cuprate Superconductor La_{2-x}Sr_xCuO_{4±δ}, *Physical Review B*, **97**, [205139-1]-[205139-5] (2018).

Study of C K-Edge High Energy Resolution Energy-Loss Near-Edge Structures of Copper Phthalocyanine by First-Principles Band Structure Calculations

While electron energy-loss spectroscopy combined with scanning transmission electron microscopy (STEM-EELS) is powerful tool for high spatial resolution elemental and state analyses, it has not been used very often for organic crystals because of problems with radiation damage to the specimen and poor energy resolution. However, these problems can be partly overcome by a reduction of the acceleration voltage and the incorporation of a monochromator into the electron gun. On the other hand, energy-loss near-edge structure (ELNES) spectrum for organic crystals is often interpreted by using molecular orbital (MO) method. However, first-principles band structure calculation is necessary to include the effect of core-hole. In the present study, we aim to interpret C K-edge ELNES measured from copper phthalocyanine (CuPc) crystals using monochromated STEM-EELS by first-principles band structure calculation including a core-hole.

There are four nonequivalent carbon atoms in the molecule; therefore, it is necessary to calculate the spectrum by the introduction of a core-hole at each nonequivalent carbon site (C1, C2, C3, C4). Figure 1 shows the C K-edge ELNES spectra measured for CuPc. The calculated spectra based on the ground state (GS), half core-hole state, and full core-hole state calculations are also presented in this figure. The half core-hole calculation result is most consistent with the experimental result in terms of the spectral shape and the relative intensity of each peak. This suggests that the core-hole potential in conjugate molecules is relatively well screened due to the delocalized π -electrons. Figure 2 shows the PDOSs with p-symmetry of each nonequivalent carbon site in the GS and the half core-hole states to assign each peak in the ELNES spectrum. It is noted that the PDOSs consist of isolated narrow distributions with widths of ca. 0.5 eV, which means that the band dispersion is small and the intermolecular interaction is weak and is consistent with MO method. The introduction of half a core-hole causes the PDOS to be shifted uniformly to the low energy side by ca. 0.6 eV, except for the peaks marked with an asterisk, which indicates the stabilization of electronic states by the potential of the core-hole. Figure 3 shows spatial distributions of the isolated states within a specific energy range in the PDOS of the half core-hole state. The distribution is susceptible to the core-hole effect. Although such site-dependent core-hole effects have already been pointed out in the previous study by MO calculations, we can confirm a similar core-hole effect in terms of the PDOS and the spatial distribution of unoccupied states with half a core-hole obtained from the all-electron first-principles band structure calculation.

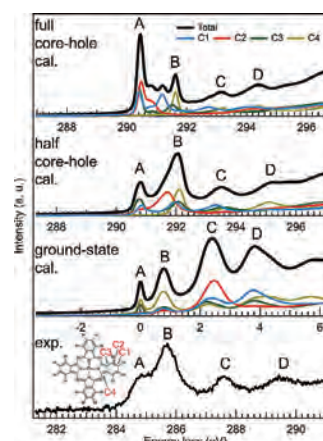


Figure 1. Experimental C K-edge ELNES spectrum of CuPc compared with the calculated spectra of the ground state, half core-hole state, and full core-hole state. The contributions of each carbon site are superimposed in the calculated spectra.

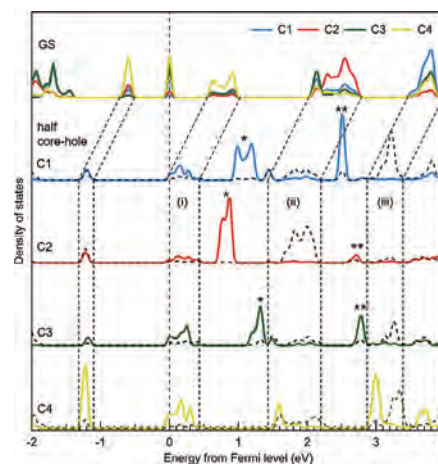


Figure 2. PDOSs with p-symmetry at four nonequivalent carbon sites of CuPc in the GS and the half core-hole state. The PDOSs of the half core-hole state at core-hole sites and its equivalent sites without a core-hole are shown by solid and dashed lines, respectively.

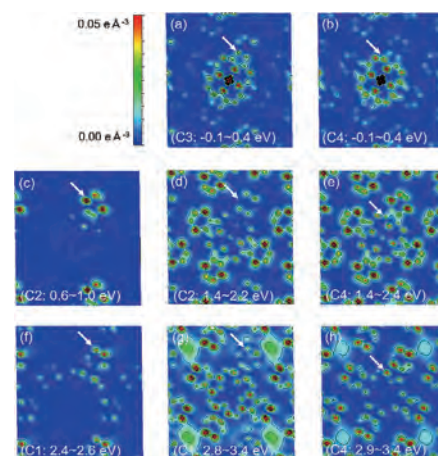


Figure 3. Spatial distributions of the isolated states within a specific energy range in the PDOS of the half core-hole state of CuPc. The arrow indicates the carbon site introducing half a core-hole.