Interchain Valence Correlation in Quasi-One-Dimensional Pt Complex Having 3D-Ligand Network

New class of quasi-one-dimensional ···Pt^{2+}···I^--Pt^{4+}-I^-··· chain complex is synthesized; ligand molecules connecting the quasi-one-dimensional chains form a three-dimensional network. In order to reveal the interchain correlation of the Pt valence arrangement, X-ray diffraction measurements were performed using newly furnished area detector at BL-8B. Clear diffuse scattering forming flat planes in the reciprocal space, which reflects a valence alternation within a chain, was observed. Minute intensity undulation within the plane shows weak negative correlation between the first neighbor chains.

Dimensionality is one of the key parameters to characterize materials. It is well known that Peierls instability makes one-dimensional metal unstable, and the system turns into an insulator with finite structural modulation. To control the dimensionality, ladder system and its variation have attracted much attention. Here, we examine the interchain valence correlation in quasi-one-dimensional Pt complex to study the dimensionality control based on the structural linking among the chains through the shared ligand molecules. **Figure 1** shows a conceptual diagram of the dimensionality control using a ladder derivative system. The white vertical rods in **Fig. 1** show ···M^{2+}···X^--M^{4+}-X^-··· chains (M and X denote metal and halogen, respectively), both are connected by ligand molecules shown by the red rung. Panel **(a)** shows a simple ladder, and **(b)** shows 2-dimensional sheet structure, which are previously synthesized and analyzed the valence arrangements [1-3]. Newly synthesized $[Pt(en)(dpye)I]_2(NO_3)_4$•$2H_2O$ (en = ethylenediamine; dpye = 1,2-di(4-pyridyl)ethane) exhibits the three-dimensionally expanded ladder structure [4]; Pt-I chains are connected by dpye ligand molecules to form the three-dimensional (3D) network exhibited in **Fig. 1 (c)**.

The *c* lattice parameter contains 4 Pt ions within a chain, which causes strong $l = 4n$ Bragg reflections. The Pt valence arrangement on a chain is either (A) 2+4+2+4+ or (B) 4+2+4+2+; such a valence alternation in a chain produces X-ray scattering on $l = 4n + 2$ planes (*n*: integer) through the displacements of iodine ions. Let us express the phase of the *i*-th chain by $\sigma_i = \pm 1$, where +1 and −1 correspond to the A and B phases, respectively. The correlation between *m*-th neighbor chains is defined by the average of the product $\sigma_i\sigma_j$, where *i* and *j*-th chains are the *m*-th neighbor. Interchain valence correlation is reflected in the intensity distribution of $l = 4n + 2$ plane. If the Pt valence has three-dimensional correlation, the scattering amplitude on a $l = 4n + 2$ plane from each chain interferes with each other to produce superlattice reflections, and no diffuse scattering appears. To examine the interchain correlation, X-ray diffraction measurements were conducted.

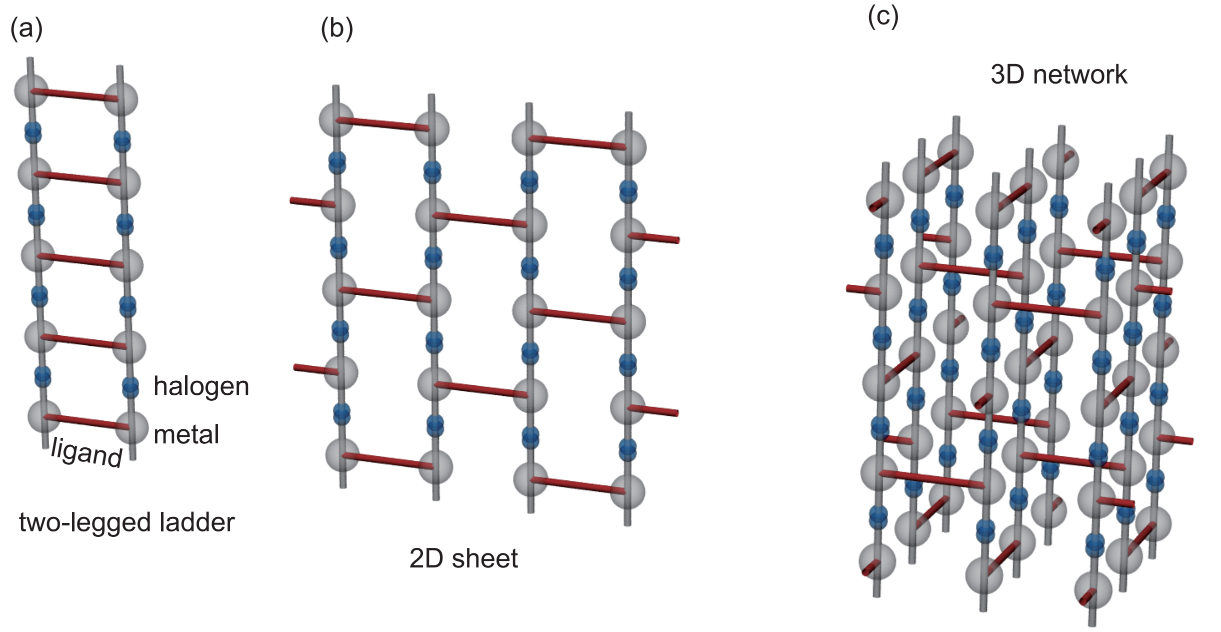

Figure 1: Dimensionality control using a ladder-related system. White and blue spheres denote metal and halogen ions, and red rungs denote ligand molecules. White vertical rods show the quasi-one- dimensional MX chains.

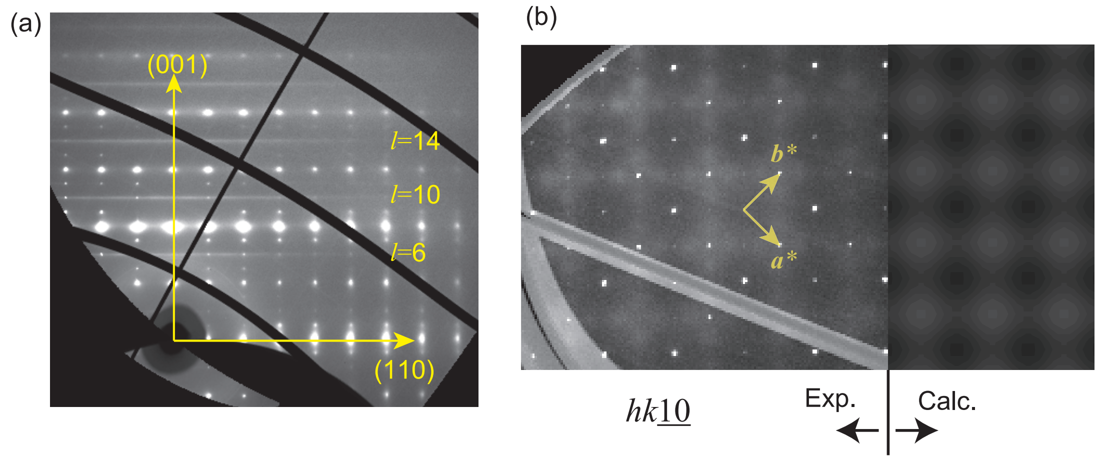

Figure 2: Scattered X-ray intensity distribution on **(a)** (*hhl*)-plane and **(b)** (*hk*10)-plane. Right-hand-side of panel **(b)** shows the calculated diffuse intensity map for the structure of 8% negative correlation between the nearest neighbor chains.

The X-ray diffraction measurements were performed at BL-8B. We have constructed a new X-ray diffraction measurement system using the large pixel array detector, PILATUS S 1M, based on the diffractometer originally installed. X-ray photographs were recorded with exposure time of 6 second during the omega-rotation with the angular velocity of 1 degree per minute. The recorded diffraction images were converted to reciprocal space maps. **Figure 2 (a)** shows the scattered X-ray intensity distribution on the (*hhl*) plane. In addition to the Bragg reflections, clear diffuse streaks are observed at l = 6, 10, and 14. It shows that, despite the 3D network of ligand molecule is formed, 3D interchain valence correlation is not established. The intensity distribution on (*hk*10) plane is presented in **Fig. 2 (b)**. In addition to weak Bragg reflections, diffuse intensity having clear modulation was observed. The diffuse intensity exhibits maxima at $h+k = 2n+1$ positions, which indicates a negative correlation of the Pt valence between the neighboring chains.

The diffuse intensity distribution was simulated assuming the values of $\langle\sigma_i\sigma_j\rangle$; $\langle\sigma_i\sigma_j\rangle = 0$ means no correlation, positive $\langle\sigma_i\sigma_j\rangle$ means in-phase valence arrangement, and negative $\langle\sigma_i\sigma_j\rangle$ means out-of-phase valence arrangement between *i*-th and *j*-th chains. The calculated diffuse intensity distribution shown in **Fig. 2 (b)** was derived from $\langle\sigma_i\sigma_j\rangle = -0.08$ for the 1st neighbor, and 0 for further chains. The similarity between the measured and calculated diffuse intensity distributions shows that the weak interchain interactions lead to an out-of-phase Pt^{2+}/Pt^{4+} valence arrangement in the 3D network-type ladder system.

Observed diffuse intensity distribution reveals weak anti-phase correlation of the Pt valence arrangement. The newly installed pixel array detector was fully utilized to measure the diffuse X-ray scattering intensity distribution in a minimum X-ray irradiation. It should be noted that the weak correlation disappeared within an hour of X-ray irradiation, showing the value of quick measurements enabled by the new measurement system.

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Y. Wakabayashi[1], H. Sagayama[2], K. Otsubo[3] and H. Kitagawa[4] ([1]Tohoku Univ., [2]KEK-IMSS-PF, [3]Tokyo Univ. of Science, [4]Kyoto Univ.)