Revealing the pressure-induced layer-sliding transition in Ta_2NiSe_5 by X-ray diffraction under high pressure

Many exotic phenomena such as insulator-metal transitions and high-temperature superconductivity are found in various compounds. To understand the electronic state behind them correctly, precise crystal structural analysis is essential. In condensed matter physics, despite pressure being one of the most fundamental tuning parameters for controlling the electronic state, structural analysis using diffraction data under pressure is extremely difficult.

Powder X-ray diffraction (XRD) using a diamond anvil cell (DAC) to apply pressure to the sample is the standard method of revealing the crystal structure under pressure. For elucidating the pressure-induced phase transition mechanism, precise integration of the scattering intensity of the sample is the most important issue for precise crystal structure analysis. However, in the case of powder XRD, it is very difficult to precisely obtain the intensity, since the powder XRD data under pressure generally has a weak signal and, furthermore, is often affected by a preferred orientation effect, which causes a significant change in the scattering intensity ratio. Therefore, there was limited scope to discuss the change in the lattice constant and symmetry on the basis of powder XRD analysis. On the other hand, in the case of single-crystal XRD, a much stronger signal than that in powder XRD is expected and the preferred orientation effect is not a problem. Therefore, it is greatly desired to establish experimental and analytical methods for single-crystal XRD under high-pressure conditions.

We performed single-crystal XRD measurement under high-pressure conditions to precisely determine the crystal structure of the layered chalcogenide Ta_2NiSe_5. Interestingly, this compound shows an insulator-metal transition at 3 GPa and superconductivity at 8 GPa and 1.2 K. However, since the crystal structure above 3 GPa has not yet been precisely determined, the electronic state has also not been revealed.

We employed SPring-8 **BL22XU** beamline, which is equipped with high-pressure XRD facilities such as a goniometer with a closed-cycle helium refrigerator, a helium gas compression system for DAC and a pressure determination system employing ruby luminescence (Fig. 1). Because of these many attachments around the sample, an incident X-ray is scattered from not only the target sample but also such attachments. Therefore, we developed our in-house analytical software so as to obtain the scattering intensity individually from different scatterers and succeeded in precise integration only from the target sample and structural analysis based on it. XRD patterns were measured within the pressure range from 0 to 8 GPa and the temperature range from 10 to 300 K.

Figure 2 shows a comparison of the crystal structure in the low- and high-pressure phases. Ta_2NiSe_5 crystallizes as a layered structure and each layer consists of $TaSe_6$ octahedra and $NiSe_4$ tetrahedra (Fig. 2(a)). In the low-pressure phase there are two layers in a unit cell (Figs. 2(b) and 2(c)) since the upper and lower layers are related by *C*-centered lattice symmetry and shifted relative to each other by 1/2 ***a***.

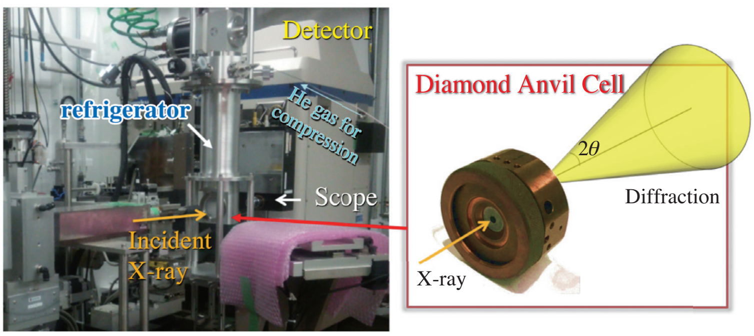

Fig. 1. High-pressure X-ray diffraction facilities in the beamline BL22XU.

On the other hand, there is only one layer in the unit cell in the high-pressure phase (Figs. 2(d) and 2(e)). This means the entire layer "slides" by 1/2 ***a*** at 3 GPa as shown schematically in Fig. 2(f). Furthermore, we revealed that the positional relationship of interlayer Se ions plays an important role in this structural phase transition. There are no other compounds that show the layer-sliding transition at a relatively low pressure comparable to 3 GPa while maintain sufficient crystallinity to enable single-crystal structural analysis. Thus, we conclude that the pressure-induced layer-sliding transition is a unique phenomenon derived from the special layered structure of Ta_2NiSe_5. In recent years, Ta_2NiSe_5 has attracted great interest as a promising exotic insulator state called an "excitonic insulator" caused by the Bose-Einstein condensation of excitons. Our structural analysis will provide important information for discussing the relationship between the excitonic insulator state and superconductivity under pressure.

In this work, we showed that crystal structure analysis with sufficient precision is possible even for relatively complex substances by single-crystal XRD under high pressure. In the near future, it will be possible to elucidate the electronic state of various substances with novel physical properties under high pressure by using our developed analysis method.

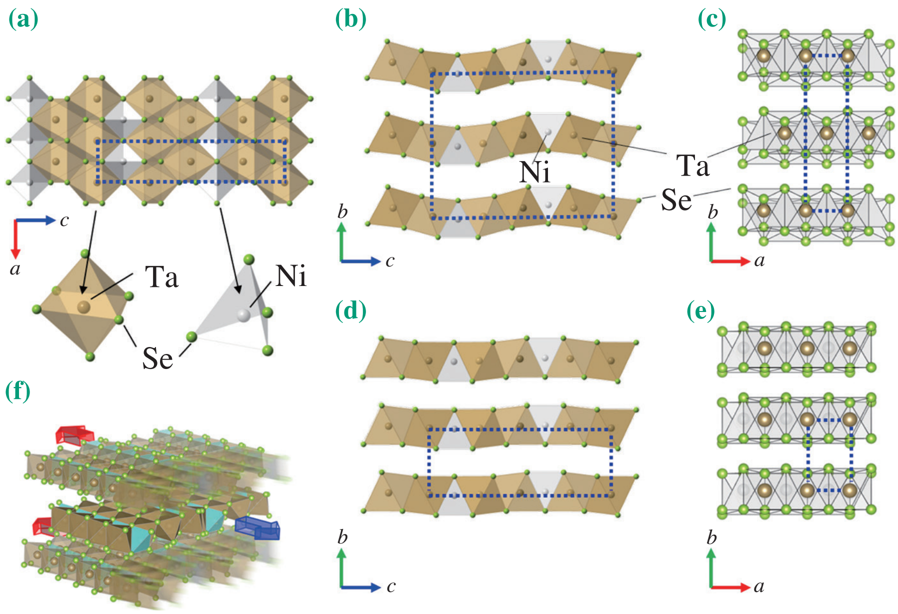

Fig. 2. **(a)** In-plane crystal structure viewed from the *b*-axis (common to phases below and above 3 GPa). **(b)** and **(c)** Crystal structures of phases below 3 GPa viewed from the (b) *a*- and (c) *c*-axes. **(d)** and **(e)** Crystal structure obtained above 3 GPa viewed from the *a*- and *c*-axes, respectively. The dotted blue line indicates the unit cell for each structure at the given pressure. **(f)** Schematic picture of layer sliding.

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