Oxygen *K*-edge X-ray Raman spectroscopy for solid oxygen up to 140 GPa with hard X-rays

Oxygen is one of the most familiar materials to us as it is essential to sustain life. In the ground state, one O_2 molecule has two unpaired electrons, making this molecule a magnet. The magnetic and van der Waals interactions between O_2 molecules cause four solid phases with different structures up to ~10 GPa. Above this pressure, in contrast, four O_2 molecules form an O_8 cluster. The two unpaired electrons are thought to play a role in combining the four O_2 molecules. The epsilon phase of oxygen, which has O_8 clusters as structural units, has been reported to have no long-range magnetic order but stable up to ~96 GPa. At this pressure, oxygen exhibits a structural phase transformation and metallic electrical conductivity [1]. Note that the crystal structure of metallic oxygen has not yet been solved completely. Although the epsilon phase is considered to be stable between 10 and 96 GPa, some experimental studies have reported anomalies at 20–40 GPa. The phase transitions and anomalies are expected to involve changes in the electronic structure.

X-ray spectroscopy is a tool for studying the electronic structures of matter. Soft X-rays are usually used to measure the electronic structure of oxygen, e.g., in X-ray absorption spectroscopy. However, it is extremely difficult to collect oxygen *K*-edge absorption spectra of dense solid oxygens under high-pressure conditions even with the present synchrotron sources. The oxygen *K*-edge is located at around 530 eV. Soft X-rays of approximately this energy are absorbed by the surrounding materials compressing the sample oxygen, and hardly penetrate to or pass through the materials. Inelastic X-ray scattering enables us to collect such spectra using hard X-rays as a probe and signals. X-ray Raman scattering (XRS) is one form of the inelastic X-ray scattering related to the core-electron excitation. XRS spectra, similar to those of X-ray absorption spectroscopy, can be obtained only by tuning the energy difference of the incident and scattered X rays to the absorption edge energy, even if the absorption edge energy is in the soft X-ray region. A study in which this technique was applied to oxygen has revealed the change in the electronic structure when the structural unit changes from O_2 to O_8 [2]. We have applied this technique to dense solid oxygen having O_8 structural units over the range of pressures at which it is insulator (17 GPa) to metal (137 GPa) and have interpreted these spectra based on theoretical calculations [3].

XRS spectra of solid oxygen were measured at SPring-8 **BL12XU**. The incident X-ray energy and the typical energy resolution were 9.9 keV and 1.4 eV, respectively, using the spectrometer with the Si(111) double-crystal monochromator and the Si(555) analyzers. At several pressures, the generated pressure and the crystal structure of the existing phase were confirmed by X-ray diffraction at SPring-8 **BL10XU**. An XRS spectrum contains two components: a sharp π^* band and a broad σ^* band (Fig. 1). The π^* band corresponds to the lowest unoccupied orbital of an O_2 molecule and the σ^* band corresponds to an antibonding orbital along the molecular axis. Their positions are shifted to higher energies and the widths become broader with increasing pressure. At 67 GPa, the π^* band has a side band on the higher energy side.

The positions of these two bands generally shift to higher energies with increasing pressure. However, the positions shifted to lower energies in the pressure region where oxygen becomes a

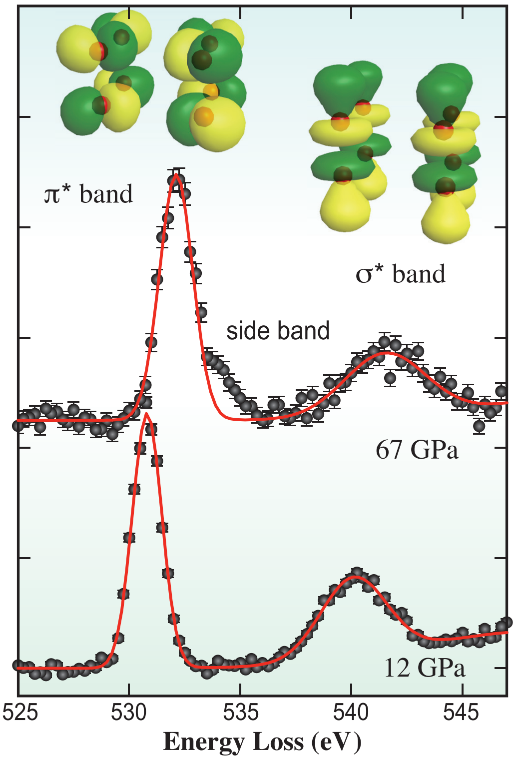

Fig. 1. Typical X-ray Raman scattering spectra of solid oxygen. Red lines indicate fitting of two Gaussians and one linear line to the spectra. (Inset) O_8 cluster with examples of π^* and σ^* orbitals. Red balls indicate oxygen atoms.

metal (between 94 and 115 GPa), and then shifted to higher energies after metallization (Fig. 2). Electrons belonging to the σ^* and π^* bands are considered to be distributed along and off the O_2 molecular axis, respectively (Fig. 1). Therefore, the change in σ^* and π^* is related to the change in bonding between the two oxygens in an O_2 molecule and between the four O_2 molecules in an O_8 cluster, respectively. The negative shift of the π^* band position was qualitatively reproduced in the calculation, indicating closure of the direct bandgap during metallization and delocalization of electrons in a plane perpendicular to the O_2 molecular axes. In contrast, the negative shift of the σ^* band, which was not reproduced in the calculation, indicates weakening of O_2 intramolecular bonding. This is consistent with the softening of the Raman active O_2 vibron mode [4].

Another notable point is the appearance of the π^* side band (Fig. 1). By comparison with the theoretical calculation, it is concluded that this is most probably because of semi-metallization of epsilon oxygen [3] and may be related to the reported anomalies at around 30 GPa. The pressure dependences of the σ^* and π^* band positions also seem to change at this pressure (Fig. 2). Microphotographs of the sample chamber exhibit three different conditions of the dense solid oxygen, i.e., insulator, semimetal, and metal (Fig. 2). Further detailed comparisons with theoretical studies would be helpful in understanding what occurs in the electronic structure at around 30 GPa. Measurements with higher energy resolution are imperative.

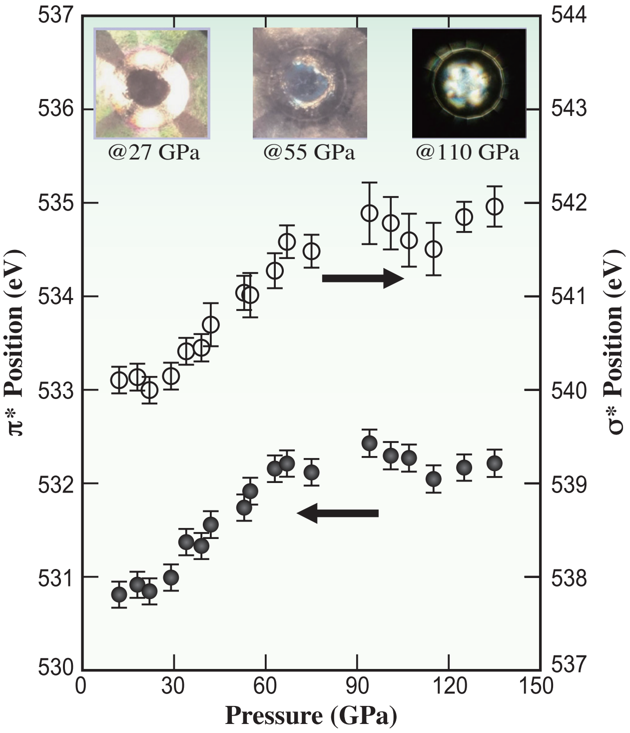

Fig. 2. Pressure dependence of the π^* and σ^* band positions shown by closed and open circles, respectively. (Inset) Microphotographs of the sample chamber at the pressures indicated.

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