The Appearance of Jahn-Teller Distortion in the Spinel Structure with Compression

The Jahn-Teller effect of Cu^{2+} in cuprospinel ($CuFe_2O_4$) was investigated by the high-pressure single-crystal X-ray diffraction technique. With increasing pressure, the CuO_6 octahedron in the spinel structure is isotropically compressed and approaches a regular configuration up to 3.8 GPa. This leads to an increase of electrostatic repulsion between the $3d_{z^2}$ orbital of Cu^{2+} and the surrounding oxygen ions. At 4.6 GPa, a phase transition from cubic to tetragonal occurs due to the appearance of Jahn-Teller distortion in which the two Cu-O bonds are stretched parallel to the *c*-axis compared with the four Cu-O bonds parallel to the *ab*-plane.

The mantle transition zone in the Earth is an anomalous region between about 400 and 750 km depth in which density and seismic velocity increase much more steeply than in the surrounding mantle, with particularly sharp changes noted near depths of 410, 520, and 660 km. The 660 km seismic discontinuity divides the upper and lower mantle, and is usually attributed to the spinel to post-spinel transition boundary where ringwoodite with the spinel structure decomposes to bridgmanite and ferropericlase in a peridotite mantle composition. Seismological studies, however, suggest that its depth varies considerably in different regions [1-6]. One of the effects proposed to explain these seismic observations is chemical heterogeneity within the mantle [7-10]. Spinels can crystallize over a wide range of conditions from mafic and ultramafic magma, and also exhibit a wide range of solid solution. The spinel structure with a cubic close-packed arrangement of atoms with two tetrahedral and one octahedral sites can maintain the cubic symmetry even when transition metal cations with Jahn-Teller effect are incorporated into the structure. In this study, we investigated the pressure-induced phase transition due to the appearance of Jahn-Teller distortion [11].

To investigate the Jahn-Teller effect on the spinel structure, synthetic cuprospinel ($CuFe_2O_4$) with cubic structure was used in the study. A single crystal of cuprospinel synthesized from a mixture of Fe_2O_3 and Cu was polished carefully to a thickness of 35 μm, and then mounted in a diamond anvil cell. A high-pressure single-crystal synchrotron X-ray diffraction study was carried out using a high-resolution, vertical-type four-circle diffractometer and scintillation counter. A total of 6 high-pressure data collections were carried out. To clarify the structural changes before and after the phase transition caused by Jahn-Teller distortion, intensity data were collected and used for the structure refinement at 0.0, 1.8, 2.7, and 4.6 GPa. *Ab initio* quantum chemical calculation was also performed for the electronic structure of the cuprospinel.

The variations in volume and unit cell parameters with pressure are shown in **Fig. 1**. In order to provide a convenient reference between cubic and tetragonal structures, the volume of the tetragonal lattice is doubled in **Fig. 1a**. The *a* unit cell parameter in the tetragonal lattice is multiplied by $\sqrt{2}$ in **Fig. 1b**. At 4.6 GPa, the *a* lattice parameter of 8.325(5) Å was obtained by least squares refinement of the observed peak positions. The measured pressure-volume curve shows a slight discontinuity at this pressure. Miller indices for the cubic *F*-lattice are reassigned to those corresponding to a tetragonal *I*-lattice. Unit cell parameters for the tetragonal lattice were *a* = 5.882(1) Å (the pseudo-cubic *a*-axis length multiplied by $\sqrt{2}$ was 8.318 Å), *c* = 8.337(1) Å,

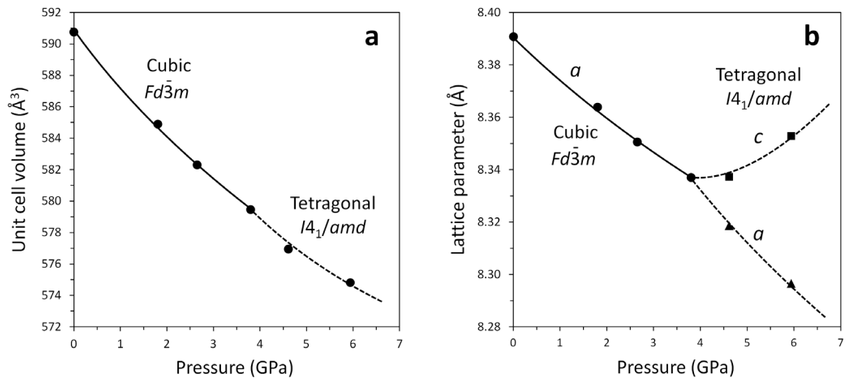

Figure 1: Variations of **(a)** the unit cell volume and **(b)** the unit cell parameters with pressure. The errors are smaller than the symbols used in the figure.

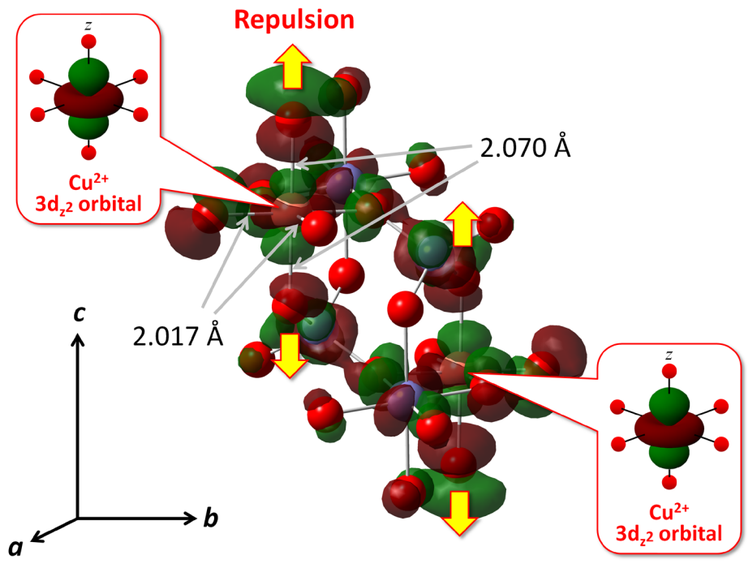

Figure 2: Electronic orbitals in the tetragonally distorted cuprospinel at 4.6 GPa calculated by the *ab initio* method. The red, pink, and purple spheres represent oxygen, copper, and ferrous iron atoms, respectively. The brown and green colors indicate positive and negative phases in the wave function.

and *V* = 288.5(1) $Å^3$. The unit cell parameter of 8.337(4) Å at 3.8 GPa was also recalculated by the Miller indices of the tetragonal *I*-lattice. However, the obtained unit cell parameters *a* = 5.895(1) Å (the pseudo-cubic *a*-axis length, $a' = \sqrt{2}a$, was 8.337 Å) and *c* = 8.340(1) Å were approximately equal to the unit cell parameter of the cubic lattice, 8.337(4) Å, within the standard deviation. Accordingly, it can be concluded that the phase transition from cubic to tetragonal occurs between 3.8 and 4.6 GPa.

With compression, both tetrahedral and octahedral sites in the cuprospinel are isotropically compressed and approach a regular configuration up to 3.8 GPa. This leads to an increase of electrostatic repulsion between the $3d_{z^2}$ orbital of Cu^{2+} and the surrounding oxygen ions. At 4.6 GPa, the appearance of the Jahn-Teller distortion of Cu^{2+} leads to distorted tetrahedral and octahedral coordinations. In the octahedral site, the two Cu-O bonds parallel to the *c*-axis are stretched to 2.070(9) Å compared with the four Cu-O bonds of 2.017(1) Å parallel to the *ab*-plane. **Figure 2** gives the results of the *ab initio* calculation, showing the electronic orbitals in the distorted coordination environment around Cu^{2+} at 4.6 GPa. In tetragonally distorted cuprospinel, the electronic orbitals are much more localized on the octahedral environment of the Cu^{2+} than the tetrahedral environment of the Fe^{3+}. It is important to mention that there is a strong orbital interaction between the $3d_{z^2}$ orbitals of Cu^{2+} and 2*p* orbitals of O^{2-}, which has a completely antibonding orbital character. Hence, the elongated octahedral geometry observed by the X-ray diffraction measurement is ascribed to the repulsive interaction between the large positive and negative phases of the wave functions of Cu^{2+} and O^{2-}, respectively.

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A. Kyono[1], S. Gramsch[2], Y. Nakamoto[3], M. Sakata[3] and T. Yamanaka[2] ([1]Univ. of Tsukuba, [2]Carnegie Inst. of Washington, [3]Osaka Univ.)