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High-pressure behavior of cuprospinel $CuFe_2O_4$: Influence of the Jahn-Teller effect on the spinel structure

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1 Introduction

Understanding the crystal structures of spinels under non-ambient conditions is an important step in the effort to correlate geophysical phenomena. Upon compression, the Jahn-Teller effect becomes active and yields a tetrahedral angular distortion, which induces the cubic-to-tetragonal transition of spinels. [1, 2] Here, we report a high-pressure single-crystal synchrotron X-ray diffraction study of synthetic cuprospinel, which exhibits a strong Jahn-Teller effect at octahedrally coordinated Cu^{2+} in the spinel structure. In the present study, the structural features of pressure-induced Jahn-Teller distortion in cuprospinel are described.

2 Experiment

Pure cuprospinel powder $CuFe_2O_4$ was synthesized from a mixture of Fe_2O_3 and Cu, which was first heated in an open quartz tube with a flowing oxygen gas stream at 1000°C for 24 h. The powder sample was then taken out of the furnace and sealed under vacuum in a quartz vessel. It was subsequently placed back into the furnace and heated again at 1300°C for 36 h, resulting in euhedral single crystals with size up to 300 μm.

The high-pressure single-crystal synchrotron X-ray diffraction study was carried out using a high-resolution, vertical-type four-circle diffractometer and scintillation counter installed at BL-10A at the Photon Factory, High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. Unit cell parameters of the sample were determined by a least-squares refinement of the setting angles of 15–25 centered reflections with $20° < 2\theta < 30°$. A total of 7 high-pressure data collections (P = 0.0, 1.8, 2.7, 3.8, 4.6, 5.9, and 6.8 GPa) were carried out.

3 Results and Discussion

The unit cell volume of cuprospinel decreases continuously from 590.8(6) Å^3 to 579.5(8) Å^3 up to 3.8 GPa. Least-squares fitting to a third-order Birch-Murnaghan equation of state yields the zero-pressure volume V_0 = 590.7(1) Å^3 and bulk modulus K_0 = 188.1(4.4) GPa with K' fixed at 4.0. The structural formula determined by electron microprobe analysis and site occupancy refinement is represented as $^{T}(Fe^{3+}_{0.90}Cu^{2+}_{0.10})^{M}(Fe^{3+}_{1.10}Fe^{2+}_{0.40}Cu^{2+}_{0.50})O_4$. Most of the Cu^{2+} are preferentially distributed onto the octahedrally coordinated (*M*) site of the spinel structure. With pressure, the arrangement of the oxygen atoms around the *M* cation approaches a regular octahedron. This leads to an increase in the electrostatic repulsion between the coordinating oxygen ions and the $3d_z^2$ orbital of $^{M}Cu^{2+}$. At 4.6 GPa, a cubic-tetragonal phase transition is indicated by a splitting of the *a* axis of the cubic structure into a smaller *a* axis and a longer *c* axis, with unit cell parameters *a* = 5.882(1) Å and *c* = 8.337(1) Å. The tetragonal structure with space group $I4_1/amd$ was refined to *R1* = 0.0332 and *wR2* = 0.0703 using 38 observed reflections. At the *M* site, the two *M*-O bonds parallel to the *c*-axis direction of the unit cell are stretched with respect to the four *M*-O bonds parallel to the *ab*-plane, which leads to an elongated octahedron along the *c*-axis. The cubic-to-tetragonal transition induced by the Jahn-Teller effect at Cu^{2+} is attributable to this distortion of the CuO_6 octahedron and involves Cu $3d_z^2$ orbital, *ab initio* quantum chemical calculations support the observation (Fig. 1). At the tetrahedrally coordinated (*T*) site, on the other hand, the tetrahedral O-*T*-O bond angle increases from 109.47 ° to 111.7(7) °, which generates a compressed tetrahedral geometry along the *c*-axis. As a result of the competing distortions between the elongated octahedron and the compressed tetrahedron, the *a* unit cell parameter is shortened with respect to the *c* unit cell parameter, giving a *c*/*a*' ratio ($a' = \sqrt{2}\,a$) slightly greater than unity as referred to cubic lattice (*c*/*a*' = 1.002). The *c*/*a*' value increases to 1.007 with pressure, suggesting further distortions of the elongated octahedron and compressed tetrahedron.

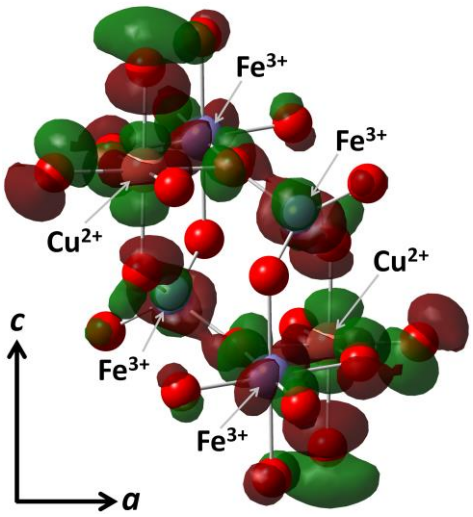

Fig. 1: Electronic orbitals in the tetragonally distorted cuprospinel at 4.6 GPa, calculated by *ab initio* method.

References

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