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SPINELS RENAISSANCE—PAST, PRESENT, AND FUTURE

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

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Abstract

The Jahn-Teller effect at Cu^{2+} in cuprospinel $CuFe_2O_4$ was investigated using high-pressure single-crystal synchrotron X-ray diffraction techniques at beamline BL10A at the Photon Factory, KEK, Japan. Six data sets were collected in the pressure range from ambient to 5.9 GPa at room temperature. Structural refinements based on the data were performed at 0.0, 1.8, 2.7, and 4.6 GPa. The unit-cell volume of cuprospinel decreases continuously from 590.8(6) 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 *a*-*b* 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. 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.

Keywords: Cuprospinel, $CuFe_2O_4$, high-pressure single-crystal synchrotron X-ray diffraction, Jahn-Teller effect