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Evidence of charge ordering of Fe^{2+} and Fe^{3+} in magnetite observed by synchrotron X-ray anomalous scattering

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ABSTRACT

Synchrotron anomalous scattering experiments with X-ray wavelengths at the Fe *K* absorption edge have made it possible to distinguish between ions having different valence states in magnetite at low temperatures. Using a large difference in anomalous scattering factors between Fe^{2+} and Fe^{3+}, the valence-difference contrast method was applied for the intensity measurements of fundamental and superlattice reflections of magnetite at low temperature. Reflections with half-integer indices, such as 0 4 $\frac{7}{2}$ and 4 4 $\frac{9}{2}$, were observed at 102 K, showing that magnetite transformed to a lower symmetry form. The energy dependence in the diffracted intensity was clearly observed at the Fe *K*-edge for the 0 4 $\frac{7}{2}$ superlattice reflection at 102 K. A sharp minimum of the normalized intensity at E = 7.122 keV was explained by the valence contrast between Fe ions occupied in the respective upper and lower parts of the double cell. Thus, our results strongly suggest the existence of charge ordering between ferrous and ferric ions in magnetite at low temperatures.