

## Low-temperature phase transitions in Fe<sub>4</sub>O<sub>5</sub> under high pressure

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Iron oxides are common and fundamentally important materials for natural sciences. The ‘metal-insulator-type transition discovered in magnetic mineral magnetite (Fe<sub>3</sub>O<sub>4</sub>) near 120 K (so-called Verwey transition) was attributed to a charge ordering at the octahedral sites of its spinel cubic structure [1]. This finding demonstrated that a new class of low-temperature phase transitions is possible in mixed-valent iron oxides, and these charge-ordering-related phase transitions are important both from fundamental perspectives, and because of a high potential for industrial applications. A single-crystal X-ray diffraction study of the Verwey transition in Fe<sub>3</sub>O<sub>4</sub> identified the formation of highly unusual iron trimer units below the transition point [2]. Recent high-pressure high-temperature (HP-HT) studies discovered a number of novel iron oxides, such as: Fe<sub>4</sub>O<sub>5</sub> [3], Fe<sub>5</sub>O<sub>6</sub> [4], Fe<sub>7</sub>O<sub>9</sub> [5], Fe<sub>5</sub>O<sub>7</sub> [6], Fe<sub>9</sub>O<sub>11</sub> [7], FeO<sub>2</sub> [8], and others. One can expect that these mixed-valent oxides can also demonstrate bizarre charge-ordering phenomena, leading to unusual charge-ordered pattern. An example of one of them, Fe<sub>4</sub>O<sub>5</sub> revealed that a low-temperature charge-ordered phase can be composed of both trimers and dimer units [9], thereby suggesting that the charge-ordering phenomena are ruled by a competition of several factors. Applied high pressure can gradually increase the density of materials, and hence, it should affect the completion between different sorts of interactions in materials.

In this presentation, we will present the results of combined single-crystal X-ray diffraction, Mossbauer spectroscopy and magnetization measurements, performed on Fe<sub>4</sub>O<sub>5</sub> samples under high pressure at low temperature [10]. We will show how the applied pressure that tunes the distances between the neighbouring iron atoms can switch the charge-ordering type between the trimers and dimers. We will show that the charge-ordering processes in iron oxides are predetermined not only by spin and charge interactions, but also by ‘‘chemical’’ interactions between the neighbouring iron

atoms. We synthesized large single crystals of Fe<sub>4</sub>O<sub>5</sub> using multi-anvil high-pressure high-temperature synthesis facilities, and the major part of the studies has been done on single crystals. We will report and discuss the first P-T phase diagram of Fe<sub>4</sub>O<sub>5</sub>. We also discuss some preliminary results for the other iron oxides.

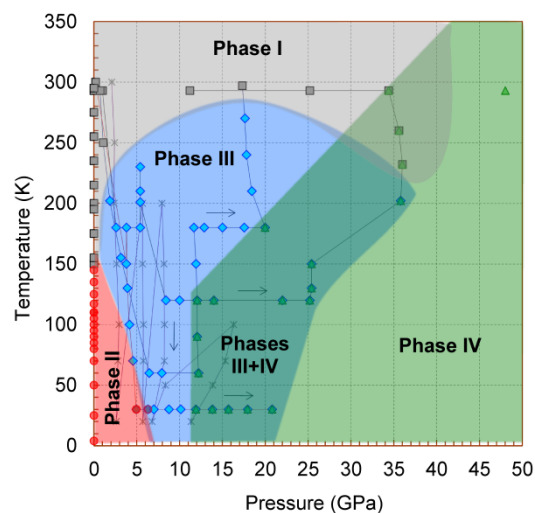


Figure 1. Phase diagram of Fe<sub>4</sub>O<sub>5</sub>

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