Thermal equation of state of Fe$_3$O$_4$ magnetite up to 16 GPa and 1100 K

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**ABSTRACT**

Fe$_3$O$_4$ magnetite is an important mineral commonly found in various geological settings, including the planet Mars, whose thermoelastic properties at high pressure and temperature are still poorly constrained. We performed X-ray diffraction measurements on natural magnetite using resistive-heated diamond-anvil cells up to 16 GPa and 1100 K. We fitted a thermal equation of state (EoS) to the collected data resulting in $K_0 = 182(1)$ GPa, $K_0'' = 4$, $\beta_0 = 660$ K, $\gamma = 1.8(1)$, and $q = 2.7$. Moreover, it was possible to explore the structural evolution of magnetite in detail using single-crystal measurements. Over the studied pressure and temperature range, we found no evidence of a transformation from an inverse to a normal spinel structure. The EoS parameters obtained in this study will be implemented into currently available databases for self-consistent thermodynamic modeling. In particular, our results are used to model and compare the sound wave velocities of a magnetite-bearing and magnetite-free martian upper mantle assemblage. We observe that the incorporation of magnetite reduces the sound wave velocities; however, the magnitude of the effect is below the current seismic detection limit of the InSight mission on Mars at the low abundance of magnetite expected in the martian mantle.

**Keywords:** Magnetite, thermal equation of state, X-ray diffraction, high-pressure, high-temperature

**INTRODUCTION**

Magnetite (α-Fe$_3$O$_4$) is an important mineral commonly found in igneous, sedimentary, and metamorphic rocks of the Earth and in meteorites, which also finds industrial applications, ranging from being a traditional recording medium to potentially being a traditional recording medium. Magnetite was also recently suggested to be potentially stable in the most oxidized regions of the upper mantle of Mars (Xu et al. 2021). Magnetite crystallizes at ambient pressure in a cubic structure above the Verwey temperature of $T_V \approx 120$ K (Verwey 1939), in the space group $Fd\bar{3}m$ with $Z = 8$. It has an inverse spinel structure with the tetrahedrally coordinated sites being fully occupied by Fe$^{3+}$, whereas the remaining Fe$^{2+}$ and Fe$^{3+}$ are randomly distributed between the octahedrally coordinated sites ([Fe$^{3+}$]$,[Fe^{2+}\text{Fe}^{3+}]_0$O$_4$). This is in contrast to a normal spinel structure where the tetrahedrally coordinated sites are occupied by the divalent cation and the octahedrally coordinated sites are filled with the trivalent cation. With increasing pressure, magnetite was found to undergo a gradual phase transformation to the so-called β-Fe$_3$O$_4$ (Mao et al. 1974; Huang and Bassett 1986; Fei et al. 1999; Haavik et al. 2000; Lazor et al. 2004) or, following a newer nomenclature, β-Fe$_3$O$_4$ (Khandarkhaeva et al. 2022). Mao et al. (1974) were the first to report the transformation from magnetite to β-Fe$_3$O$_4$ above 25 GPa as reported by powder X-ray diffraction in a diamond-anvil cell (DAC). The transformation was described to be sluggish, especially at ambient temperature, with the completion of the phase transformation being faster at 600 K. These findings were confirmed by the study of Huang and Bassett (1986), which reported a large two-phase hysteresis upon compression and decompression. The structure of β-Fe$_3$O$_4$ was initially suggested to be monoclinic (Mao et al. 1974), but subsequent Rietveld refinements performed on powdered magnetite in a resistively heated DAC proposed β-Fe$_3$O$_4$ to have the orthorhombic CaMn$_2$O$_4$ type structure in the space group $Pbcm$ (Fei et al. 1999). A more recent study by Haavik et al. (2000) confirmed β-Fe$_3$O$_4$ to be orthorhombic, but having the CaTi$_3$O$_4$ type structure in the space group $Cmcm$. This structure was further confirmed by Lazor et al. (2004) who also performed Rietveld refinements on polycrystalline magnetite and a recent study by Khandarkhaeva et al. (2022), who performed single-crystal X-ray diffraction experiments in laser-heated DACs. The latter also reported two new Fe$_3$O$_4$ polymorphs, namely γ-Fe$_3$O$_4$ having the Yb$_3$S$_4$-type structure in space group $Pnma$ stable at 64–73 GPa upon heating at 1500–2000 K, and δ-Fe$_3$O$_4$ having the Th$_3$P$_4$-type structure in space group $I\bar{4}2d$ stable at 78(1) GPa and 4800(300) K (Khandarkhaeva et al. 2022).

In the stability field of α-Fe$_3$O$_4$ at pressures below the structural transformation into β-Fe$_3$O$_4$, the material retains the cubic structure. However, within this pressure range, the electronic state of magnetite is quite controversial. Several studies using Mössbauer spectroscopy and powder X-ray diffraction introduced the notion of a possible coordination crossover in the...