EUROPEAN SYNCHROTRON RADIATION FACILITY

ESRF User Office

BP 220, F-38043 GRENOBLE CEDEX, France

Delivery address: 6 rue Jules Horowitz, 38043 GRENOBLE, France

Tel: +33 (0)4 7688 2552; fax: +33 (0)4 7688 2020; email: useroff@esrf.fr; web: http://www.esrf.fr

Iron – Oxygen interaction at High Pressure - High Temperature

This document should consist of a maximum of two A4 pages with a minimal font size of 12 pt.

A novel iron oxide with surprising composition of FeO_2 was synthesized just recently (Hu *et al.*, 2016). The material was interpreted as pyrite-structured ferrous iron peroxide. Nowadays it attracts great attention of scientific community because it may have drastic effect on chemistry of Fe–O system at high pressure, chemical processes in the Earth's mantle and core-mantle boundary, oxygen fugacity in deep interiors, past and present of oxygen and hydrogen cycles, and even on our understanding of life appearance and evolution on our planet (Nishi *et al.*, 2017; Hu *et al.*, 2017; Liu *et al.*, 2017).

The chemical nature of FeO_2 is yet to be clarified. Indeed, theory considers different possible forms of the compound, from dioxide (no direct chemical bonds between O^{2-} oxygens) to peroxide (covalent bonds between oxygen atoms forming O_2^{2-} anions) (Streltsov *et al.*, 2017; Garcia-Sosa & Castro, 2000). For peroxides (in molecular or crystalline forms) the distances between closest oxygen atoms at ambient pressure are very characteristic and vary from about 1.2 to 1.5 Å (Li *et al.*, 2008), while with the compression such distances are not expected to increase. The shortest O…O contact for pyrite-type FeO_2 was reported to be ~1.9 Å (Hu *et al.*, 2016). It is too long for peroxides, but too short for cubic dioxides with high-pressure PdF_2-type structure (*HP*-PdF_2). For the latter the shortest O–O distance is ~2.5 Å at ambient conditions, while all distances are characterized by low compressibility (see for details (Haines & Léger, 1993; Haines *et al.*, 1996, 1997; Tse *et al.*, 2000)). In fact, osmium and ruthenium, iron's neighbors in VIII*b* group in periodic table, form typical dioxides OsO_2 and RuO_2 with *HP*-PdF_2-type structure (Haines *et al.*, 1998; Shirako *et al.*, 2014). According to well-established "rule of a thumb" compounds (particularly oxides) of an element behave at high-pressure like compounds of the elements located below in the same group of periodic table at lower pressures. Thus, one could expect that FeO_2 would also form dioxide, not peroxide.

In the present experiment at ID27 we demonstrated that upon heating of pure iron in oxygen at pressures of about 55 GPa and 1200 K reaction products indeed contain cubic FeO_2 phase. However, refinement of crystal structure based on single-crystal XRD data (Fig. 1) unambiguously shows that FeO_2 crystallizes in *HP*-PdF_2-type structure and thus iron has formal oxidation state +4.

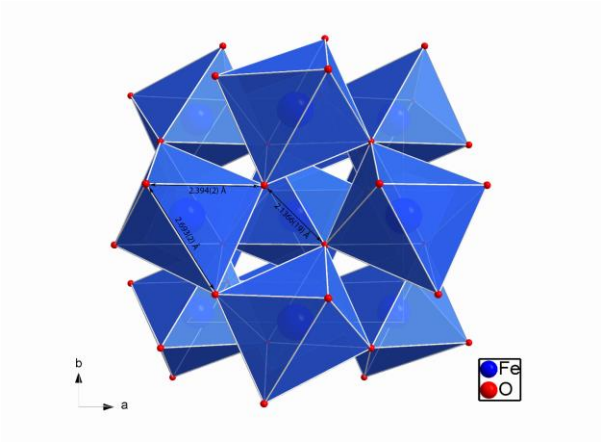

Fig. 1. Crystal structure of cubic FeO_2 as refined from single-crystal diffraction data collected at 58(1) GPa. Shortest O-O distance is 2.137(2) Å characteristic for HP-PdF_2-type structure.