



**Experiment title:** Pressure Dependence of the  
Crystal Structure of  $\text{Sr}_3\text{Fe}_2\text{O}_7$

**Experiment  
number:**

CH356

<b>Beamline:</b> ID9	<b>Date of Experiment:</b> from: Oct. 30                      to: Nov. 3, 1997	<b>Date of Report:</b> Feb. 19, 1998
<b>Shifts:</b> 12	<b>Local contact(s):</b> M. Hanfland	<i>Received at ESRF:</i> <b>04 MAR. 1998</b>

**Names and affiliations of applicants** (\*indicates experimentalists):

P. Adler\*, U. Schwarz\*, K. Syassen\*,  
MPI fuer Festkoerperforschung  
Heisenbergstr. 1  
D-70569 Stuttgart

M. Pasternak  
School of Physics and Astronomy  
Tel Aviv University  
69978 Tel Aviv, ISRAEL

**Report:**

At ID 9 we have performed high pressure monochromatic powder diffraction experiments on the iron oxide  $\text{Sr}_3\text{Fe}_2\text{O}_7$  using gasketed diamond anvil cells and an image plate detection system. The compound  $\text{Sr}_3\text{Fe}_2\text{O}_7$  crystallizes in a tetragonal  $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type crystal structure (space group  $I4/mmm$ ) with double layers of corner-sharing  $\text{FeO}_6$  octahedra. Within each layer every Fe atom is connected to four other Fe atoms by 01 atoms, two octahedra of a double sheet share the 03 atom. The terminal 02 atom completes the  $\text{FeO}_6$  octahedra. The crystal structure contains one perovskite-like Sr1 atom with a coordination number of 12 and a further  $\text{K}_2\text{NiF}_4$ -type Sr2 atom with a coordination number of 9. It was the aim of our study to investigate whether anomalies in room temperature Moessbauer spectra between 6 and 10 GPa and previously detected electronic and magnetic phase transitions (disappearance of the charge disproportionation of Fe(IV) above 20 GPa, increase in near-infrared reflectivity above 10 GPa) are accompanied by structural changes. All data were analysed with the Rietveld method using the programs FULLPROF and CSD. This way lattice parameters as well as the four variable atomic coordinates ( $\text{Sr}2z$ ,  $\text{Fe}z$ ,  $\text{O}1z$ ,  $\text{O}2z$ ) were refined.

We obtained the following results from our studies:

- 1) Up to the highest pressure of 43 GPa reached in our study there is no crystallographic phase transition. All data could be refined assuming the ambient pressure structure.
- 2) At pressures above 15 GPa changes in relative intensities were observed which are due to texture effects. These are presumably due to nonhydrostatic pressure components associated with the nitrogen matrix. The lattice parameters of the sample obtained at ambient pressure before pressurizing and after release of pressure were in good agreement. The texture effects were, however, not reversible.

3) The pressure dependence of the volume  $V$  and particularly of the lattice parameter  $a$  does not reveal any discontinuities up to 28 GPa. Data near 40 GPa may indicate an excess decrease of  $V$  and  $a$  at higher pressures. However, we did not study the behavior of  $\text{Sr}_3\text{Fe}_2\text{O}_7$  above 28 GPa in detail so far. Both, the  $a$  and the  $c$  axis are shortened by about 5 % at 28 GPa, but the curvatures of the  $a(p)$  and  $c(p)$  plots are different. This gives rise to a subtle anomaly in the pressure dependence of  $c/a$  (see figure 1).

4) The atomic  $z$ -parameters of the Sr2 and Fe atoms can be well refined from the data. There is some ambiguity in the positions of the light oxygen atoms, in particular of the O2 atom. This introduces errors into the iron-oxygen distances which are the important ones for correlation with electronic properties. The most reliable distance is the Fe-O1 distance which is mainly determined by the  $u$ -lattice parameter (see figure 2). This distance decreases by about 0.09 Å (ca. 5 %) between 0 and 28 GPa. There are no anomalies in the pressure dependence of this distance, but the refinement of the data indicates a small decrease of the Fe-O1-Fe angle with increasing pressure. The Fe-O3 distance is obtained quite reliably as it depends only on the  $z_{\text{Fe}}$  parameter. It decreases by about 0.05 Å between 0 and 28 GPa. Most uncertain are the results for the Fe-O2 distances at pressures above 20 GPa which depend to some extent on refinement strategies. However, all refinements indicate that the Fe-O2 distance does not decrease with pressure. Accordingly, the iron-oxygen octahedra appear to be more rigid in the  $c$ - than in the  $u$ -direction. The larger compressibility of the structure in the  $c$ - direction at pressures above 15 GPa arises largely from a reduction of the space between the double sheets of iron-oxygen octahedra. This is reflected in a decrease of the Sr2-O2-Fe distance by about 10 %. This result depends only on the  $\text{Sr}2z$  and  $z_{\text{Fe}}$  atomic coordinates.

From our structural studies on  $\text{Sr}_3\text{Fe}_2\text{O}_7$  we conclude that the pressure-induced electronic and magnetic phase transitions are neither driven by structural changes nor accompanied by major structural reorganisations. We believe that the main effect of pressure is to decrease the iron-oxygen bond lengths and, as a consequence, to increase the width  $w_\sigma$  of the  $\sigma^*$  conduction band. Within a Mott-Hubbard-type picture of the electronic structure the ratio  $w_\sigma/U$  increases under pressure, where  $U$  is the effective electron-electron interaction energy. Pressure leads to a stronger itinerancy of the electronic system which results in a disappearance of the charge disproportionation and, possibly in an insulator-metal transition.

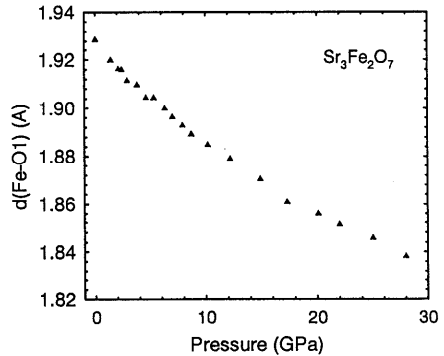
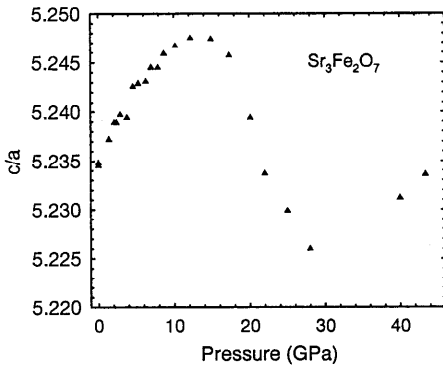


Fig. 1: Ratio  $c/a$  of the lattice parameters of  $\text{Sr}_3\text{Fe}_2\text{O}_7$  as a function of pressure.

Fig. 2: Fe-O1 distance of  $\text{Sr}_3\text{Fe}_2\text{O}_7$  as a function of pressure

3) The pressure dependence of the volume  $V$  and particularly of the lattice parameter  $a$  does not reveal any discontinuities up to 28 GPa. Data near 40 GPa may indicate an excess decrease of  $V$  and  $a$  at higher pressures. However, we did not study the behavior of  $\text{Sr}_3\text{Fe}_2\text{O}_7$  above 28 GPa in detail so far. Both, the  $a$  and the  $c$  axis are shortened by about 5 % at 28 GPa, but the curvatures of the  $a(p)$  and  $c(p)$  plots are different. This gives rise to a subtle anomaly in the pressure dependence of  $c/a$  (see figure 1).

4) The atomic  $z$ -parameters of the Sr2 and Fe atoms can be well refined from the data. There is some ambiguity in the positions of the light oxygen atoms, in particular of the O2 atom. This introduces errors into the iron-oxygen distances which are the important ones for correlation with electronic properties. The most reliable distance is the Fe-01 distance which is mainly determined by the  $a$ -lattice parameter (see figure 2). This distance decreases by about 0.09 Å (ca. 5 %) between 0 and 28 GPa. There are no anomalies in the pressure dependence of this distance, but the refinement of the data indicates a small decrease of the Fe-01-Fe angle with increasing pressure. The Fe-03 distance is obtained quite reliably as it depends only on the  $z_{\text{Fe}}$  parameter. It decreases by about 0.05 Å between 0 and 28 GPa. Most uncertain are the results for the Fe-02 distances at pressures above 20 GPa which depend to some extent on refinement strategies. However, all refinements indicate that the Fe-02 distance does not decrease with pressure. Accordingly, the iron-oxygen octahedra appear to be more rigid in the  $c$ - than in the  $u$ -direction. The larger compressibility of the structure in the  $c$ - direction at pressures above 15 GPa arises largely from a reduction of the space between the double sheets of iron-oxygen octahedra. This is reflected in a decrease of the Sr2-O2-Fe distance by about 10 %. This result depends only on the  $z_{\text{Sr2}}$  and  $z_{\text{Fe}}$  atomic coordinates.

From our structural studies on  $\text{Sr}_3\text{Fe}_2\text{O}_7$  we conclude that the pressure-induced electronic and magnetic phase transitions are neither driven by structural changes nor accompanied by major structural reorganisations. We believe that the main effect of pressure is to decrease the iron-oxygen bond lengths and, as a consequence, to increase the width  $w_\sigma$  of the  $\sigma^*$  conduction band. Within a Mott-Hubbard-type picture of the electronic structure the ratio  $w_\sigma/U$  increases under pressure, where  $U$  is the effective electron-electron interaction energy. Pressure leads to a stronger itinerancy of the electronic system which results in a disappearance of the charge disproportionation and, possibly in an insulator-metal transition.

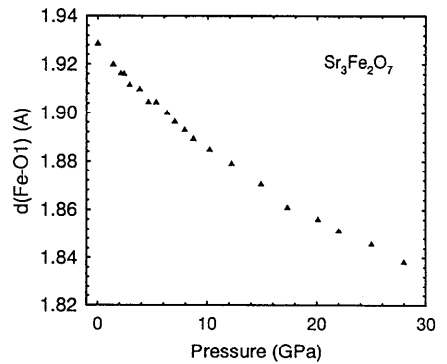
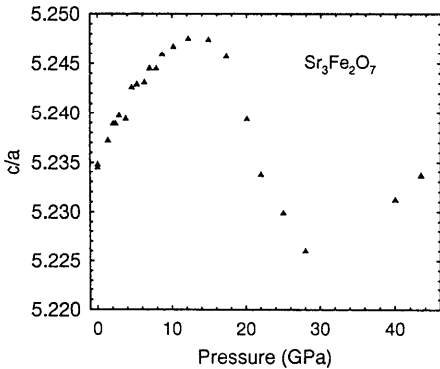


Fig. 1: Ratio  $c/a$  of the lattice parameters of  $\text{Sr}_3\text{Fe}_2\text{O}_7$  as a function of pressure. Fig. 2: Fe-O1 distance of  $\text{Sr}_3\text{Fe}_2\text{O}_7$  as a function of pressure